NBSIR 80-1996 R

Technical Activities 1979

John D. Hoffman, Director
National Measurement Laboratory
National Bureau of Standards
U.S. Department of Commerce

John B. Wachtman, Jr., Director
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Issued March 1980

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U.S. DEPARTMENT OF COMMERCE, **Philip M. Klutznick**, *Secretary*
Luther H. Hodges, Jr., *Deputy Secretary*
Jordan J. Baruch, *Assistant Secretary for Productivity, Technology, and Innovation*
NATIONAL BUREAU OF STANDARDS, **Ernest Ambler**, *Director*

In this volume we summarize the FY79 technical activities of the Center for Materials Science. The purpose of this report is to provide current information to the materials science community about the present directions of the NBS efforts in materials science. Requests for reprints of individual papers cited in this report should be addressed to the authors.

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CENTER FOR MATERIALS SCIENCE

I. Introduction

The Center for Materials Science (CMS) was formed in 1978 as part of a general reorganization of the National Bureau of Standards. The Center is located within the National Measurement Laboratory (NML), one of the two principal laboratories comprising NBS. Figures 1, 2, and 3 give the organizational structure of the CMS, NML, and NBS, respectively. The CMS is one of the largest Centers at NBS. It has approximately 327 staff members; ∿ 72 percent are professionals, of which 68 percent hold Ph.D. degrees. The operating budget of the Center for FY 1979 amounted to ∿ $18.8M.

The long-term goal of the Center for Materials Science is to support the private sector and other Government agencies in the most effective application and utilization of materials -- metals, polymers, and inorganic materials. Center activities currently focus on those aspects of materials research involving processing science, structure/property science, and durability science. More specifically the Center

- Develops and maintains the scientific competences and experimental facilities necessary to provide the nation with a central basis for uniform physical measurements, measurement methodology, and measurement services necessary to define the properties and performance of materials and other essential areas in the materials science discipline.

- Provides government, industry, universities, and consumers with essential standards, measurement methods, data, concepts, and information concerning metals, polymers, and inorganic materials.

- Characterizes the structure of materials, chemical reactions, and physical properties which will lead to the safest, most efficient uses of materials, improve materials technologies, and encourage recycling.

- Obtains accurate experimental data on the behavior and properties of materials over time under service conditions to assure effective utilization of raw materials and manufactured materials.

- Provides technical information in the form of reference data, materials measurement methods, and standards to materials processors, designers, and materials users to enable them to select cost effective combinations of materials, processes, designs, and service conditions.

The Center is organized in six Divisions, each having responsibilities in different areas of materials science. These Divisions vary in their balance between theory and experiments, between direct standards work and research, and in their orientation toward industrial and government needs and the needs of other components of the scientific and technological community. The research activities of the Divisions are structured according to a task system; each task has specific goals.

objectives, and milestones which support the overall goals of the Center. The following listing tabulates the tasks for each Division. Detailed description of FY79 technical activities encompassed by the various tasks is given in section II of this report.

Task Numbers, Titles, and Leaders

Center Office

12101	Materials Measurement Services	J. B. Wachtman, Jr.

Chemical Stability and Corrosion Division

12111	Corrosion and Chemical Stability of Materials in Service Environments	T. D. Coyle
12112	High Temperature Chemical Stability of Materials for Processing and Service	T. D. Coyle

Fracture and Deformation Division

12121	Fracture Mechanisms and Analyses	R. P. Reed
12122	Durability of Ceramics and Composites	S. M. Wiederhorn
12123	Elastic-Plastic Fracture Mechanics	H. I. McHenry

Polymer Science and Standards Division

12132	Polymer Standards for Control and Equity	L. E. Smith
12133	Predictive Models for Polymer Performance	B. M. Fanconi
12134	Chemical Durability of Plastics in Use	L. E. Smith
12135	Manufacture and Durability: Dental Medical Materials	J. M. Cassel
12136	Mechanical Durability of Plastics for Design and Use	B. M. Fanconi
12138	Migration and Durability of Plastics in Use	L. E. Smith
12139	Dielectric Plastics Design and Performance	M. G. Broadhurst

Metal Science and Standards Division

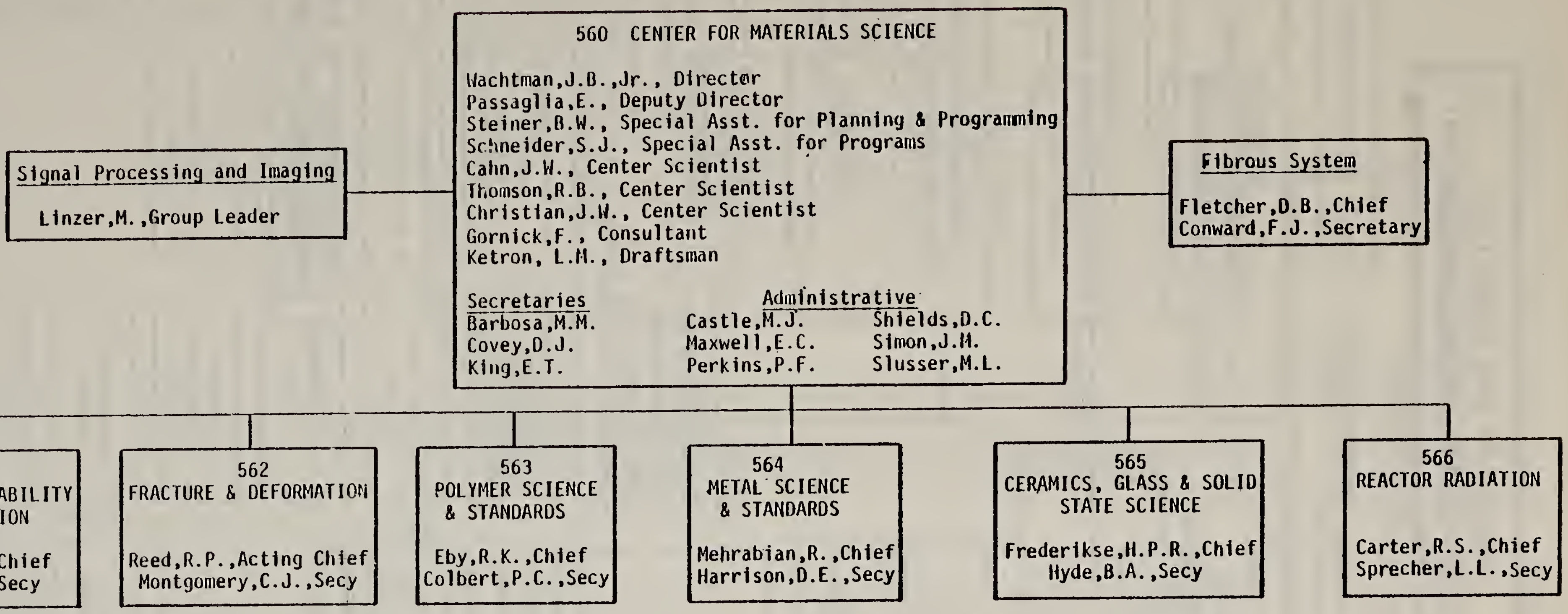
12142	Alloy Structure, Properties, and Standards for Quantitative Characterization	J. A. Simmons
12143	High Temperature Processes for Durability	J. R. Manning
12144	Alloy Durability for Wear and Implant Applications	A. W. Ruff
12145	Metallurgical Chemistry for Durability	L. H. Bennett

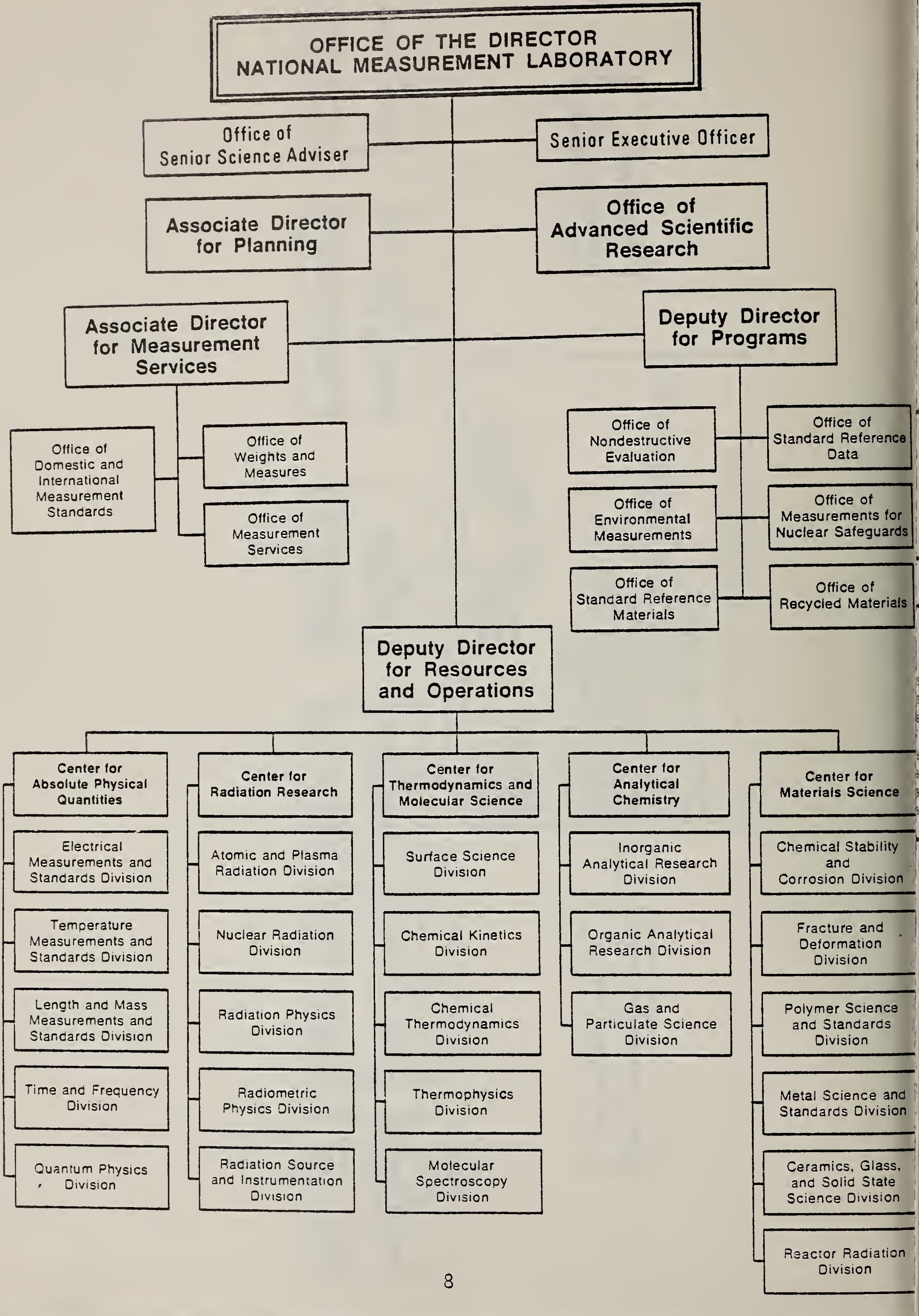
Ceramics, Glass, and Solid State Science Division

12151	Structural Chemistry for Ceramic Processing and Durability	R. S. Roth
12153	Structural Methods for Processing Manufacture and Durability	S. Block
12154	Property, Structure, and Standards for Glass Processing and Manufacture	W. K. Haller
12155	Durability of Ceramics and Glass in Service Environments	H. P. R. Frederikse

Reactor Radiation Division

12161	Reactor Operation and Services	T. M. Raby
12162	Neutron Scattering Characterization of Materials for Advanced Technology	J. J. Rush
12163	Neutron Diffraction and Radiographic Methods for Materials Utility and Durability	J. J. Rush


560 CENTER FOR MATERIALS SCIENCE
Wachtman,J.B.,Jr., Director
Passaglia,E., Deputy Director
Steiner,B.W., Special Asst. for Planning & Programming
Schneider,S.J., Special Asst. for Programs
Cahn,J.W., Center Scientist
Thomson,R.B., Center Scientist
Christian,J.W., Center Scientist
Gornick,F., Consultant
Ketron, L.M., Draftsman
Secretaries
Barbosa,M.M.
Covey,D.J.
King,E.T.
Administrative
Castle,M.J.
Maxwell,E.C.
Perkins,P.F.
Shields,D.C.
Simon,J.M.
Slusser,M.L.
Signal Processing and Imaging
Linzer,M.,Group Leader
Fibrous System
Fletcher,D.B.,Chief
Conward,F.J.,Secretary
561
CHEMICAL STABILITY & CORROSION
Coyle,T.D.,Chief
Lamb,D.J.,Secy
562
FRACTURE & DEFORMATION
Reed,R.P.,Acting Chief
Montgomery,C.J.,Secy
563
POLYMER SCIENCE & STANDARDS
Eby,R.K.,Chief
Colbert,P.C.,Secy
564
METAL SCIENCE & STANDARDS
Mehrabian,R.,Chief
Harrison,D.E.,Secy
565
CERAMICS, GLASS & SOLID STATE SCIENCE
Frederikse,H.P.R.,Chief
Hyde,B.A.,Secy
566
REACTOR RADIATION
Carter,R.S.,Chief
Sprecher,L.L.,Secy


OFFICE OF THE DIRECTOR
NATIONAL MEASUREMENT LABORATORY
Office of Senior Science Adviser
Senior Executive Officer
Associate Director for Planning
Office of Advanced Scientific Research
Associate Director for Measurement Services
Deputy Director for Programs
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Office of Weights and Measures
Office of Measurement Services
Office of Nondestructive Evaluation
Office of Standard Reference Data
Office of Environmental Measurements
Office of Measurements for Nuclear Safeguards
Office of Standard Reference Materials
Office of Recycled Materials
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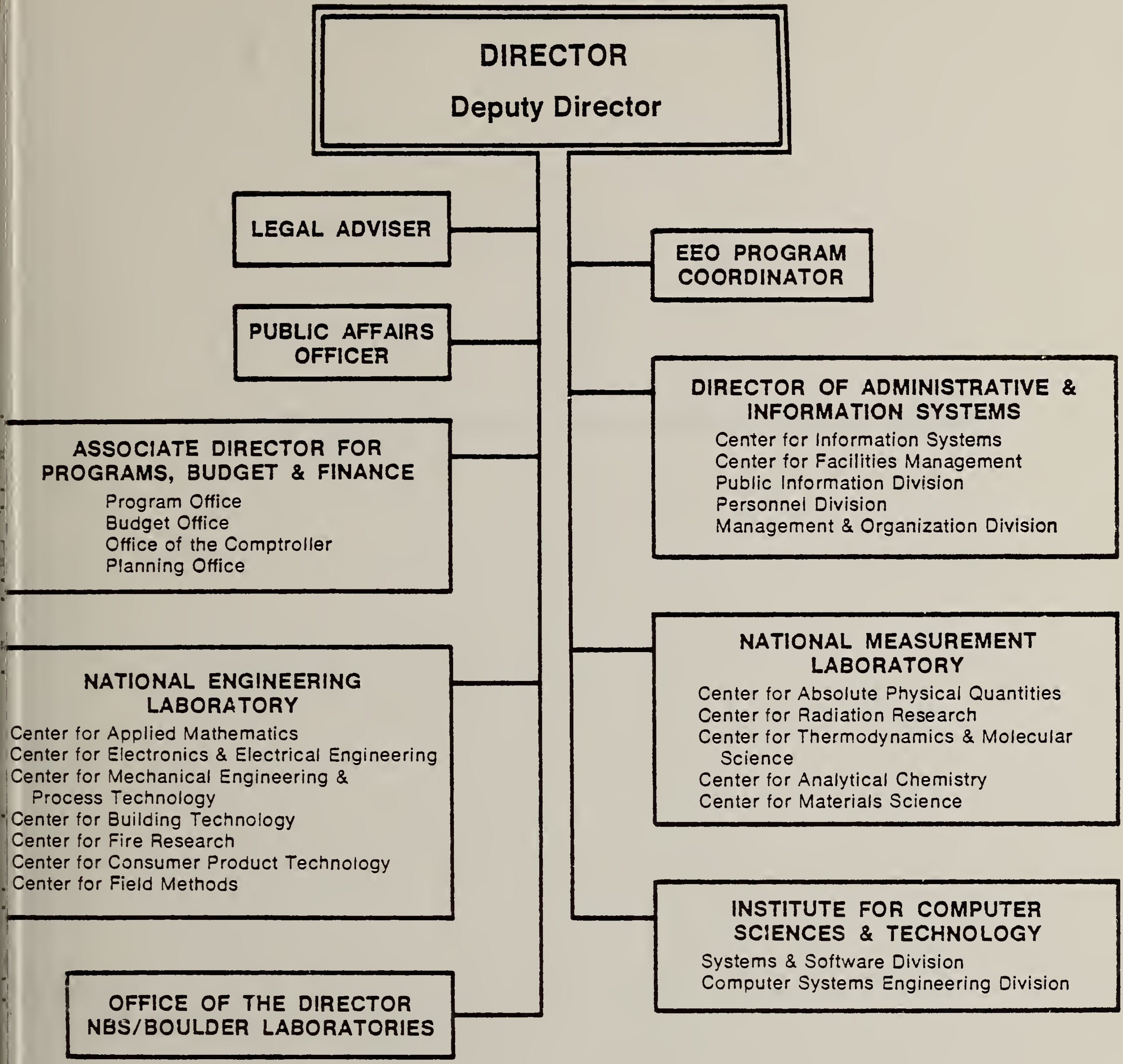
Temperature Measurements and Standards Division
Length and Mass Measurements and Standards Division
Time and Frequency Division
Quantum Physics Division
Center for Radiation Research
Atomic and Plasma Radiation Division
Nuclear Radiation Division
Radiation Physics Division
Radiometric Physics Division
Radiation Source and Instrumentation Division
Center for Thermodynamics and Molecular Science
Surface Science Division
Chemical Kinetics Division
Chemical Thermodynamics Division
Thermophysics Division
Molecular Spectroscopy Division
Center for Analytical Chemistry
Inorganic Analytical Research Division
Organic Analytical Research Division
Gas and Particulate Science Division
Center for Materials Science
Chemical Stability and Corrosion Division
Fracture and Deformation Division
Polymer Science and Standards Division
Metal Science and Standards Division
Ceramics, Glass, and Solid State Science Division
Reactor Radiation Division



DIRECTOR

Deputy Director

LEGAL ADVISER

PUBLIC AFFAIRS OFFICER

ASSOCIATE DIRECTOR FOR PROGRAMS, BUDGET & FINANCE
- Program Office
- Budget Office
- Office of the Comptroller
- Planning Office

NATIONAL ENGINEERING LABORATORY
- Center for Applied Mathematics
- Center for Electronics & Electrical Engineering
- Center for Mechanical Engineering & Process Technology
- Center for Building Technology
- Center for Fire Research
- Center for Consumer Product Technology
- Center for Field Methods

OFFICE OF THE DIRECTOR NBS/BOULDER LABORATORIES

EEO PROGRAM COORDINATOR

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- Center for Information Systems
- Center for Facilities Management
- Public Information Division
- Personnel Division
- Management & Organization Division

NATIONAL MEASUREMENT LABORATORY
- Center for Absolute Physical Quantities
- Center for Radiation Research
- Center for Thermodynamics & Molecular Science
- Center for Analytical Chemistry
- Center for Materials Science

INSTITUTE FOR COMPUTER SCIENCES & TECHNOLOGY
- Systems & Software Division
- Computer Systems Engineering Division

II. TECHNICAL ACTIVITIES OF THE CENTER FOR MATERIALS SCIENCE

OFFICE OF THE CENTER FOR MATERIALS SCIENCE

OFFICE OF THE CENTER FOR MATERIALS SCIENCE

John B. Wachtman, Jr., Director
Elio Passaglia, Deputy Director
Samuel J. Schneider, Special Assistant for Programs
Bruce W. Steiner, Special Assistant for Planning and Programming
Melvin Linzer, Leader, Signal Processing and Imaging Group
Robb M. Thomson, Center Scientist
John W. Cahn, Center Scientist
Marge M. Barbosa, Secretary
Delores J. Covey, Secretary
Ellen T. King, Secretary
M. Jocelyn Castle, Senior Administrative Officer
Ebbie C. Maxwell, Administrative Officer
Jean M. Simon, Administrative Assistant
Marian L. Slusser, Administrative Assistant
Patricia H. Perkins, Administrative Aid

The Center Office has the responsibility for providing the technical and administrative framework for the planning and operation of the technical programs carried out by the six Divisions and the Center Office scientists. Efforts this past year have focused on the development, strengthening, and implementation of programs and plans of the Center. Although the majority of the activities of the Center Office are reflected through accomplishments of the Divisions, several are of particular interest:

- The Center's program on Materials Durability will be significantly enhanced in FY 1980 through increased activities in the areas of corrosion, fracture, and additive migration in polymers.

- The formal long-range plan (five year) was up-dated by the revision of specific elements. Commensurate with this, the Center developed detailed plans for possible programs on 1) the Durability of Structural Composites, and 2) Materials Transformation Science for improved materials processing.

- In an effort to expand Center competences, work was started this past year on the development of facilities and research on small angle neutron scattering (SANS) at the NBS Reactor. Work on the facility is in the Reactor Radiation Division with the first research to be performed by that Division and the Polymers Division. In FY 1980 the Center for Materials Science and the Center for Absolute Physical Quantities will undertake work to utilize the Brookhaven Synchrotron high intensity x-ray source.

Measurement Services

Although most of the program planning and laboratory activity in the Center takes place in the six Divisions, a single task, Measurement Services, in the Center Office takes a general view of American materials science. This task assures adequate attention to major new challenges and opportunities, particularly those that may affect two or more Divisions.

This activity also provides a window on policy studies in the Executive and Legislative Branches. At the same time, through this activity, the Center provides senior consultation to other agencies.

Technical Activity

Center staff have participated in the senior management activity of a number of professional societies, the National Academy of Engineering, the American Ceramic Society, the American Society for Metals, the American Society for Testing and Materials, the Federation of Materials Societies, the National Research Council, the Optical Society of America, and the Society for Photooptical Instrumentation Engineers. The staff also participated in the National Materials Advisory Board Conference on Materials for Energy Conversion, and formal and informal Congressional hearings on materials durability and Federal materials policy.

The staff have worked closely with other agencies to develop specific programs including materials programs for the Department of Transportation and the Department of Energy. Center scientists have worked particularly closely with the American Physical Society including the Solid State Division and a special group studying the prospects and status for photovoltaic, low energy conversion.

Signal Processing, Imaging

M. Linzer, S. I. Parks, S. J. Norton, and J. A. Abbott[1]

[1]Postdoctoral Research Associate

In the past year emphasis was placed on the development of computer-based imaging methodology. Two papers were published on convolution/backprojection methods for producing ultrahigh-resolution reflectivity images using enclosing and partially-enclosing apertures. Both circular arrays for 2-D imaging and spherical (as well as hemispherical) arrays for 3-D imaging were analyzed. Narrowband, wideband, and optimum transmit waveforms were considered and detailed computer simulations were carried out for a variety of potential experimental situations. A method was developed for tomographic reconstruction from restricted projections using iterative revisions in image and transformed spaces. A preliminary investigation was made of methods for correcting velocity, attenuation, and reflectivity images for ray refraction and of algorithms for frequency-dependent time gain compensation. These studies are expected to result in images with greatly improved resolution and accuracy. Construction was initiated on a stepper-motor-controlled scanner for testing the various imaging methods.

The sensitivity of our expanding-aperture annular array system was improved by over 20 dB and the device was successfully demonstrated in a clinical environment. The Sonochromascope, a quantitative ultrasonic device developed by the Signal Processing and Imaging Group and now installed at the NIH Clinical Center, was shown to be capable of diagnosing cystic fibrosis and other diffuse pancreatic diseases. This is the first time that such pathology has been detected by ultrasonic techniques. A wideband analysis of annular array focusing was completed. A paper was completed on the use of an optical interferometer to reconstruct three-dimensional ultrasound fields generated by a wideband transducer.

A new journal, Ultrasonic Imaging (Academic Press) was inaugurated, with Dr. Linzer as its Editor-in-Chief.

Fracture Theory

R. M. Thomson

Dr. Thomson's technical activities are focused on the problems of fracture and in particular on atomic processes occurring at crack tips. Most of this work has been in collaboration with Dr. E. R. Fuller, Jr., in the Fracture and Deformation Division. The mathematical part of this work is based on various analytical treatments of discrete lattices in one and two dimensions in which trapping occurs. A general theory of chemical reactivity at the tips of cracks has been developed which incorporates the chemistry within the purely mechanical aspects of crack growth. This work distinguishes two broad classes of chemical action: 1) that wherein molecular interactions occur directly between gaseous species and the atoms at the tip, and 2) that wherein vacancy formation in the adsorbed layer at the crack tip is required. One feature of this work shows how the thermodynamic limit can be obtained from the statistical mechanical treatment, and leads to the Griffith result in its full thermodynamic generality. Another feature is to point out the strong chemical specificity in chemically assisted fracture. We are led from this to consider what classes of chemical species will assist fracture, and which will strengthen the material. Thermodynamic considerations show that a prime effect is simply the modified surface energy caused by chemical adsorbtion, but kinetic considerations also point to the importance of bridging and other types of chemical reactions.

During the year, work with one-dimensional models has been able to develop predictions for how the activation energy varies with stress, and yields a form for the stress dependence of the velocity. Finally, we can apparently now understand the results of Wiederhorn on crack growth of glass in vacuum in terms of the variation of the radius of the stretching to bending force laws in the atomic bonds.

Our approach to ductile fracture has borne fruit during the past year in terms of a spate of approaches taken by other workers using various aspects of our previous models of ductile fracture. This field now requires experimental effort to disentangle the various theories now extant. If our proposal with Hockey (Fracture and Deformation Division) for studies of fracture in partially ductile materials is approved, we will be able to pursue a joint theoretical and experimental approach to this problem.

Finally, we have given some thought to the problem of fatigue, and the role of crack closure. A model is being developed of how this leads to harmonic generation of ultrasonic waves.

A major concern for the future is to attempt to understand how electrochemical effects modify our results to date on atmospherically assisted fracture; also to pursue (possibly with others at NBS and elsewhere) the question of chemical specificity at crack tips.

Associated activities. During the year, I participated as a member of an American Physical Society study group to evaluate the technical and scientific potential of photovoltaics as a possible major source of electrical power. The major conclusion was that solar photovoltaic power is a long-term possibility, but that for it to be ultimately viable, major scientific developments would be necessary. Scientific opportunities exist in materials aspects of interfaces, in materials synthesis, and in the development of photochemical fuel making processes. Recommendations were made to the President's Office of Science and Technology and to the Department of Energy which were important in the design of the national R&D programs in photovoltaic power development.

Theoretical Materials Stability

John W. Cahn and John W. Christian

This work addressed fundamental factors in the stability of materials. It is carried on with a wide variety of colleagues. This past year they have worked with colleagues in Montpellier, in Cambridge (Massachusetts), and in Malibu. The activity can be divided into two general areas, interface activity and bulk stability.

In addressing interface activity, they have shown first that in any two-phase mixture of fluids near the critical point, one of the phases will wet a third phase so that contact with the other phase is excluded. The surface layer of the wetting phase continues to exist past the onset of instability in the bulk phase. This perfect wetting terminates in a first-order transition which has been found and is being studied. For solids, a satisfactory microscopic theory for antiphase domain wall, motion in ordered structures has been demonstrated. The velocity of motion is predicted to be proportional to mean curvature, but independent of surface-free energy, in contrast to the unsatisfactory predictions of previous models. The behavior of FeAl and Cu_3Au alloys has been demonstrated to be consistent with that predicted.

For the growth of monotectic solid composites from solution, theoretical factors have been reexamined. There are indications that phase growth may be determined by the velocity necessary to overcome disjoining pressure, which will be small. Critical experiments have been proposed to verify the analysis: variation in pressure and ternary additions. Perfect wetting should occur close to the critical temperature.

Equilibrium antiphase and interphase boundaries in the CuAu system have been examined. Near the congruent point antiphase boundaries undergo a second order surface phase transition to an interfacial layer resembling inhomogeneous CuAu. One of the antiphase boundaries is predicted to be perfectly wet by the disordered phase at the disordering temperature.

A two-dimensional lattice-gas model of a grain boundary has been investigated and shown to exhibit a phase transition that can be described as surface melting.

The role of higher order (non-pairwise) energies in FCC alloys has been examined and found to lead to a prediction of either symmetric or asymmetric versions of Cu-Au phase diagrams.

General conditions have also been established for multiphase equilibrium of anisotropically stressed solids in contact with fluids. The equilibrium obtained is sensitive both to the presence of vacancies and the nature of the phase contact. Equilibria at coherent boundaries are insensitive to the existence of vacancies, while vacancies do govern the equilibrium of incoherent phases.

Finally, reports that low temperature diffusion can cause grain boundaries to migrate and thereby provide a mechanism of greatly enhanced (by factors in excess of 10^9) diffusion have been confirmed and investigated in greater detail. The effect exists for at least six different metallic systems and for symmetric as well as unsymmetric boundaries.

* * * * * * *

Other Center Activity

Sponsored Conferences

Interamerican Conference on Materials Technology
Sao Paulo, Brazil
November 1978

International Materials Congress: Materials Aspects of World Energy Needs
Reston, Virginia
March 1979

Diffusion-induced Grain Boundary Migration
NBS
May 1979

Fourth International Symposium on Ultrasonic Imaging and Tissue Characterization
NBS
June 1979

IUPAC Conference on Oxides for Energy Applications
Toronto, Canada
July 1979

Fourth Annual Conference on Materials for Coal Conversion and Utilization
NBS
October 1979

Invited Talks

The Future of Ceramics and the Ceramic Research Program of the National Bureau of Standards
Refractories Division, American Ceramic Society, Bedford Springs, Pennsylvania
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of the National Bureau of Standards
Lehigh Valley Section, American Ceramic Society, Quakertown, Pennsylvania
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of the National Bureau of Standards
Glass Division, American Ceramic Society, Bedford Springs, Pennsylvania
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of
the National Bureau of Standards
Hudson-Mohawk Valley Section, American Ceramic Society, Albany,
New York
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of
the National Bureau of Standards
Pacific Northwest Section, American Ceramic Society, Seattle,
Washington
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of
the National Bureau of Standards
Eastern Washington Section, American Ceramic Society, Richland,
Washington
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of
the National Bureau of Standards
American Ceramic Society, Oakland, California
John B. Wachtman, Jr.
October 1978

The Future of Ceramics and the Ceramic Research Program of
the National Bureau of Standards
Ceramic-Metal Systems Division, American Ceramic Society,
Merritt Island, Florida
John B. Wachtman, Jr.
January 1979

Trends in Ceramic Research and the Program of the National
Bureau of Standards
Symposium on R&D Needs of Canadian Glass, Ceramic, and Allied
Industries in the Eighties, Canada Centre for Mineral and Energy
Technology, Department of Energy, Mines, and Resources, Ottawa,
and Ontario Research Foundation, Ottawa, Ontario, Canada
John B. Wachtman, Jr.
March 1979

An Overview of Materials Science Today in Relation to the Materials
World
Carnegie-Mellon Institute, Washington, D.C.
John B. Wachtman, Jr.
June 1979

Trends in Ceramic Research and the Program of the National
Bureau of Standards
Western New York Section, American Ceramic Society, Buffalo,
New York
John B. Wachtman, Jr.
June 1979

Computerized Ultrasonic Tomography
Symposium on Ultrasonic Tissue Characterization, American Physical Society, New York, New York
Melvin Linzer
February 1979

Improved Sensitivity Ultrasonic Inspection
Seminar on Railroad Nondestructive Evaluation
NBS
Melvin Linzer
May 1979

Tomographic Reconstruction of Reflectivity Images
2nd Meeting of the World Federation for Ultrasound in Medicine and Biology, Miyazaki, Japan
Melvin Linzer
July 1979

Physical Aspects of the Fracture of Materials
Physics Department, Pennsylvania State University
University Park, Pennsylvania
Robb M. Thomson
February 1979

Brittle Fracture in a Partially Ductile Material
Materials Science Center, Pennsylvania State University, University Park, Pennsylvania
Robb M. Thomson
February 1979

Understanding Materials Reliability - The Mechanisms of Fracture
NDE Conference, La Jolla, California
Robb M. Thomson
July 1979

The Economic Effects of Corrosion
Congressional Meeting on Corrosion
Washington, D.C.
E. Passaglia
1979

The Economic Effects of Corrosion
ACS Conference on Corrosion and Wear
Washington, D.C.
E. Passaglia
1979

The National Cost of Corrosion
Conference on Materials Solution to a National Problem
Washington, D.C.
September 1979

The Program of the Center for Materials Science
Department of Energy
Germantown, Maryland
E. Passaglia
September 1979

Long-range Planning at NBS
Committee on Research and Technical Planning
ASTM, Philadelphia, Pennsylvania
E. Passaglia
November 1978

Standards Activities at NBS
Committee on Research and Technical Planning
ASTM, Philadelphia, Pennsylvania
E. Passaglia
July 1979

Publications

An Overview of Materials Science Today in Relation to the Materials World
John B. Wachtman, Jr.
Proceedings of National Symposium on Wear and Corrosion, American Chemical Society, Washington, D.C., June 1979

Wideband Annular Array Response
D. R. Dietz, S. J. Norton, and M. Linzer
1978 IEEE Ultrasonic Symposium, pp. 206-221, IEEE Cat. #78 CH 1344-1 SU (1978)

Expanding-Aperture Annular Array
D. R. Dietz, S. I. Parks, and M. Linzer
Ultrasonic Imaging 1, 56-75 (1979)

A Comprehensive Ultrasonic Tissue Analysis System
M. Linzer, S. I. Parks, S. J. Norton, F. P. Higgins, D. R. Dietz, R. S. Shideler, T. H. Shawker, and J. L. Doppman
Ultrasonic Tissue Characterization II, M. Linzer, Ed., pp. 255-265, NBS Special Publication 525 (1979)

The SonoChromascope
M. Linzer and S. I. Parks
Proceedings of the IFIP TC-4 Working Conference on Computer Aided Tomography and Ultrasonics in Medicine, P. J. Raviv, J. F. Greenleaf, and G. T. Herman, Eds., pp. 73-76, North Holland Publishing Co., Amsterdam, The Netherlands (1979)

Ultrasonic Reflectivity Tomography: Reconstruction with Circular Arrays
S. J. Norton and M. Linzer
Ultrasonic Imaging 1, 154-184 (1979)

Engineering Aspects of Medical Ultrasonic Imaging: A Few New Directions (in Japanese)
T. Sato and M. Linzer
Japanese J. Clin. Med. (special issue on "Body Imaging"), 37, 148 (1979)

Ultrasonic Reflectivity Imaging in Three Dimensions: Reconstruction with Spherical Arrays
S. J. Norton and M. Linzer
Ultrasonic Imaging 1, 210-231 (1979)

Internal Friction and Sodium Transport in Beta Alumina
J. H. Simmons, A. D. Franklin, K. F. Young, and M. Linzer
J. Amer. Ceram. Soc., 62, (December 1979)

Optical Interferometric Visualization and Computerized Reconstruction of Ultrasonic Fields
F. P. Higgins, S. J. Norton, and M. Linzer
J. Acoust. Soc. Amer. (submitted)

Tomographic Image Reconstruction from Restricted Projections Using Iterative Revisions in Image and Transformed Species
T. Sato, M. Linzer, S. J. Norton, O. Ideda, and M. Hirama
Appl. Optics (submitted)

Array Imaging System with Data Selection Processing
T. Sato, M. Linzer, O. Ikeda, and M. Hirama
J. Acoust. Soc. Amer. (submitted)

Further Development and Clinical Evaluation of the Expanding-Aperture Annular Array System
S. I. Parks, M. Linzer, and T. H. Shawker
Ultrasonic Imaging (submitted)

Numerical Analysis of the B-Scan Image: A Clinical Evaluation of the Pancreas
T. H. Shawker, S. I. Parks, M. Linzer, B. Jones, L. A. Kester, and V. S. Hubbard
J. Clin. Ultrasound (submitted)

Ultrasonic Tissue Characterization II
M. Linzer, Ed., NBS Special Publication 525 (1979)

Thermochemical Equilibrium of Multiphase Solids Under Stress
F. Larche and John W. Cahn
Acta Met., 26, 1579 (1978)

Thermodynamics of Solid and Fluid Surfaces
John W. Cahn
Segregation to Interfaces, ASM Seminar Series (1978), p. 3-23

Monotectic Composite Growth
John W. Cahn
Met. Trans. 10A 119 (1979)

A Microscopic Theory for Antiphase Boundary Motion and Its Application to Antiphase Domain Coarsening
S. M. Allen and J. W. Cahn
Acta Met., 27, 1085 (1979)

On Diffusional Mass Transport in Polycrystal Containing Stationary or Migrating Grain Boundaries
J. W. Cahn and R. W. Balluffi
Scripta Met., 13, 499 (1979)

Diffusion Induced Grain Boundary Migration
J. W. Cahn, J. D. Pan, and R. W. Balluffi
Scripta Met., 13, 503 (1979)

Ground State of FCC Alloys with Multiatomic Interactions
J. W. Cahn and R. Kikuchi
Acta Met., 27, 1329 (1979)

Theory of Interphase and Antiphase Boundaries in FCC Alloys
R. Kikuchi and J. W. Cahn
Acta Met., 27, 1337 (1979)

Interpretation of Elastic Wave Scattering by Flaws in Materials
R. M. Thomson, J. A. Krumhansl, and J. E. Gubernatis
J. Appl. Phys., 50, 3338 (1979)

Theory of Chemically Assisted Fracture
R. M. Thomson
International Conference on Mechanical Properties of Materials, IV, Cambridge University (1979)

Solar Photovoltaic Energy Conversion
R. M. Thomson
J. Amer. Phys. Soc. (submitted)

MHD Materials, Topics in Materials Science
S. J. Schneider, H. P. R. Frederikse, T. Negas, and G. Rudins
North Holland Publishing Co. (in press)

Thermodynamics and Kinetics of Martensite
J. W. Christian
Proceedings of ICOMAT Conference, MIT, Cambridge, Massachusetts
June 1979

Martensitic Transformations in Iron-Nickel-Carbon Alloys
J. W. Christian
Proceedings of ICOMAT Conference, MIT, Cambridge, Massachusetts
June 1979

The National Cost of Metallic Corrosion in U.S.
E. Passaglia
Proc. Tri-Services Conference on Corrosion, 1979

The Economic Effects of Corrosion
E. Passaglia
Proc. Congressional Conf. on Corrosion
In press

Corrosion: The Silent Scourge
E. Passaglia
Proc. ACS Conf. on Corrosion and Wear
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In preparation

Technical and Professional Committee Participation and Leadership

American Ceramic Society
John B. Wachtman, Jr.
Past-President, and member of Executive Board

American Physical Society
John B. Wachtman, Jr.
Committee on Applications of Physics

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CHEMICAL STABILITY AND CORROSION DIVISION

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CHEMICAL STABILITY AND CORROSION DIVISION

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The Chemical Stability and Corrosion Division provides a focus, within the NBS Center for Materials Science, for research and measurement activities related to the chemical stability and reactivity of materials in their service environments. The Division carries out field and laboratory research to assess the resistance of materials to chemical and biological degradation under service conditions. It identifies and characterizes the mechanisms underlying corrosion, corrosion inhibition, and molecular level chemical transformations critical to materials stability and processing and to the environmental impact of materials use. As required, it develops measurement methods for quantitative characterization of degradation processes, test methods to predict in-service durability, and appropriate standards.

The Division's accomplishments during fiscal year 1979 are described in the following pages. A number of these are of particular interest:

(1) Experimental studies of electrochemical "corrosion noise" have shown that the amplitude and frequency dependence of these minute fluctuations of potential or current from a corroding metal are a sensitive measure of the presence or absence of pitting corrosion. These observations suggest the possibility of new approaches to detection and measurement of localized corrosion.

(2) At the request of the Dutch and German governments, Division staff members have participated in cooperative studies using NBS-developed methodology for investigations of heavy-metal pollution in the Rhine River.

(3) New techniques have been developed and validated to measure chemical equilibria and concentrations of active species in high-temperature reactions of refractories with aggressive atmospheres. These methods provide both a means for evaluating materials stability in these conditions and an important new measurement tool for high temperature science.

(4) Research on charge transport in high-temperature solid electrolytes has resulted in the development of electrical measurement techniques with potential for probing the nature of grain boundaries in ceramics.

The Division's program is described here in terms of three tasks. One of these emphasizes metallic corrosion and the chemical stability of materials in ambient service environments. The other focuses on chemical processes affecting materials durability and processing at high temperatures. A third area of activity, new in fiscal year 1979, includes work on the chemical properties and performance of lubricants in support of the NBS Recycled Oil Program.

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CORROSION AND CHEMICAL STABILITY OF MATERIALS IN SERVICE ENVIRONMENTS

The objective of the work carried out under this task is to provide data, measurement methodology, test methods, and standards required in processing, design, manufacture, and use; to enhance chemical durability of materials (including corrosion resistance); and to reduce adverse impacts of chemical and biodegradation of materials on health, safety, and the environment.

The technical activities under this task are carried out by two groups, one emphasizing metallic corrosion and protective coatings, and the other focusing on chemical and biological degradation processes affecting several classes of materials:

Technical Activity

Corrosion and Electrodeposition

J. Kruger, U. Bertocci, C. F. Derr, E. Escalante, J. L. Fink, W. F. Gerhold, W. P. Iverson, C. E. Johnson, D. R. Kelley, J. L. Mullen, F. Ogburn, B. T. Sanderson, J. Smit, J. P. Young, S. Ito[1], D. S. Lashmore[1], and S. Wolynec[2]

[1] Research Associate
[2] Guest Worker

Technical activity in this area is carried out in several specific project areas ranging from test method development through field and laboratory studies of corrosion resistance of materials, to more basic investigations of corrosion mechanisms, electrochemistry, and coatings. Activities in the individual projects are summarized below:

Test Methods for Corrosion

J. Kruger, J. J. Ritter, S. Ito, U. Bertocci, E. Escalante, J. L. Mullen, and S. Wolynec

This project seeks to develop, improve, and evaluate test methods which will measure pitting, crevice and stress corrosion, hydrogen embrittlement, gaseous oxidation, underground, marine, and atmospheric corrosion in order to provide industry and government with improved test methods. To accomplish these objectives, the approach is to apply the newest techniques provided by electrochemistry, surface physics, and chemistry to a study of corrosion processes and eventually develop from these studies simpler techniques that can be applied by testing laboratories

(1) A successful test of the validity and usefulness of the electrochemical noise technique was accomplished. It was demonstrated that this measurement technique, which analyzes small fluctuations of potential or current associated with electrochemical or corrosion

processes taking place on a metal in an electrolyte, can detect significant differences between pitting and non-pitting systems. As Fig. 1 shows, noise currents of almost two orders of magnitude and a substantial different spectrum was observed for an aluminum surface exposed to a pitting regime as compared to the same surface exposed to non-pitting conditions. A beginning has been made on applying the electrochemical noise technique to study the electrochemical behavior of amorphous alloys.

(2) A new approach toward making impedance measurements for corrosion studies has been developed. Ordinarily, in making impedance measurements, potentials of the order of a few millivolts have to be applied to a corroding surface. Potentials of this magnitude, which can cause a possible change in the corrosion conditions at a metal surface have had to be applied because the currents that must be determined in impedance measurements, resulting from the application of lower potentials, are so low that they are swamped out by electronic noise. This is especially true for metals with highly protective (passive) films such as aluminum and stainless steels where high potentials have been necessary to make impedance measurements. By coupling a newly developed low noise potentiostat, originally developed for the electrochemical noise measurements described in (1) above, with a frequency spectrum analyser, it is now possible to make impedance measurements by applying potentials as low as 10^{-6} to 10^{-4} volts (depending on frequency) and thereby cause less disturbance of a corrosion process by the measurement of impedance. Such impedance measurements are important in determining the ability of metals and alloys to withstand exposure to environments of practical interest.

In addition to the development of this new approach to impedance measurements, improvements have been introduced that promise to enhance data handling. The ac signals to be processed have been put in digital form and transmitted to a computer for analysis. This method allows the processing of a wider range of frequencies than possible with the equipment used so far extending its application to more corrosion-resistant materials.

(3) In order to provide a basis for the development of measuring techniques for the corrosion processes of steel in concrete, a systematic study has been carried out in aqueous ($(Ca(OH)_2$, and in a sand media with variables of dissolved oxygen, pH, and chlorine content.

A number of important results have been obtained. For example, the onset of corrosion occurs between a pH of 11.5 to 12.5, depending upon chloride content. The amount of dissolved oxygen governs the corrosion rate after initiation. For a better simulation to the steel rebar in concrete, an environment with less than 3 ppm O_2, more than 1 mole/l Cl^- and saturated $Ca(OH)_2$ is being used in this study.

Electrochemical studies have also been initiated using a potentiostatic and a galvanostatic pulse signal applied to a mortar-covered steel electrode in chloride solution. Thus far extremely low

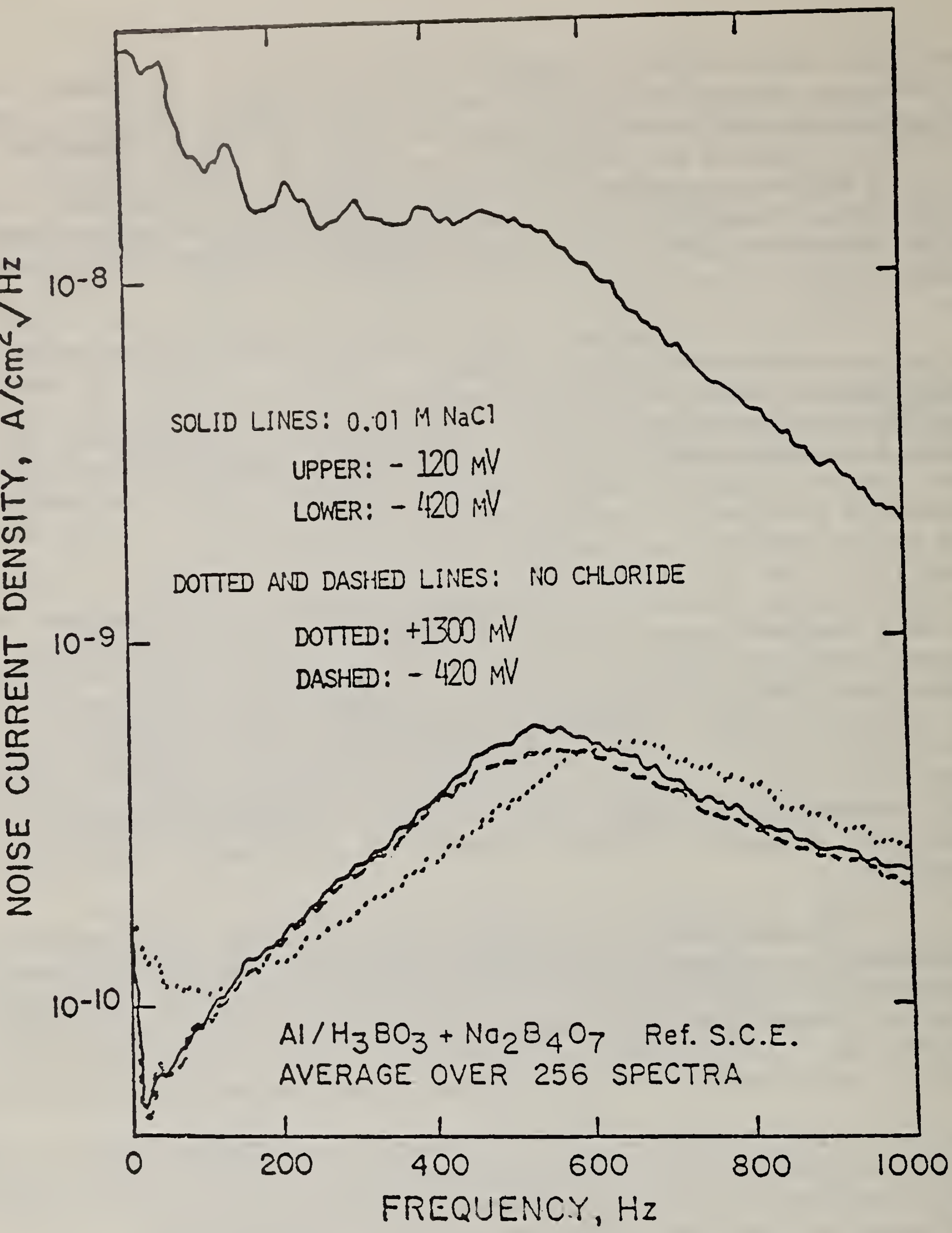

Fig. 1. Electrochemical noise spectra for Al in boric acid-sodium tetraborate solution with and without chloride ion addition. The upper spectrum was obtained for Al under pitting conditions (with chloride present and at a potential above the critical potential for pitting). The lower spectra are those obtained under conditions where pitting does not occur.

corrosion rates have been observed for rebars in mortar containing 0.1-1 moles/l Cl^- for periods of exposure as long as 1.4 months.

(4) Work concerned with studying the factors that effect electrochemical polarization corrosion rate measurements has been completed. This work was carried out in cooperation with Instituto de Pesquisas Tecnologicas of Brazil, which sent a guest worker to NBS (S. Wolynec). A new method for obtaining polarization data was derived from chronoamnerometric investigations. This method is similar to the potentiostatic one with two differences: (i) the polarization potential is switched off for some minutes between two consecutive steps so as to allow the corroding system to recover, at least partially, the conditions observed initially; (ii) the current is determined by extrapolating the data of the current decay curves to infinite time. It was observed that in those curves the current holds a logarithmic relationship to the inverse of the square root of time. The data generated by this method is in good agreement with weight-loss and corrosion potential measurements not only in terms of corrosion rate but also in terms of Tafel slopes. The approach developed promises to improve the accuracy of electrochemical corrosion rate measurements.

Localized Corrosion

J. J. Ritter and J. Kruger

This work, which is partially supported by the Office of Naval Research, is concerned with developing techniques that will determine the susceptibility of alloys to various forms of localized corrosion. The emphasis in this project is on the role repassivation plays in localized corrosion, on corrosion mechanisms under organic coatings, and on how the initial stages of hydrogen entry are affected by alloy structure and composition.

(1) Repassivation rate studies of current vs. time on 304 stainless steel in 1N NaCl were conducted with an improved triboellipsometric apparatus which permits observation of repassivation processes on a time scale of the order of a millisecond. Repassivation rates for unsensitized material were found to be essentially independent of applied potential between -0.124 and -0.025V SCE. With sensitized 304, the repassivation rates became significantly slower as the applied potentials were made more positive within this same range. Repassivation rate for unsensitized 310 stainless steel was similarily found to be independent of potential in 1N NaCl between -0.10 and +0.10V SCE. However, sensitized 310 showed a significantly higher repassivation rate than unsensitized 310 within this potential range. These data indicate that repassivation rate studies may not be generally applicable to the detection of sensitization in stainless steels.

(2) Studies have been initiated for making simultaneous ellipsometric and specific ion measurements on active substrates protected by transparent organic coatings while immersed in adverse media. These studies have as their objective the elucidation of corrosion

mechanisms under paints. Initial experiments designed to evaluate the effects of immersion media on optically clear acrylic and cellulose nitrate coatings were made using gold as an inert substrate. Both coating materials were found to give minimal ellipsometric changes in 0.05N NaCl while in a borate buffer medium they suffered swelling and delamination. Experiments with iron coated with cellulose nitrate and immersed in 0.05N NaCl are characterized by a gradual rise (over one to two days) in pH under the coating accompanied by ellipsometric changes which signify the buildup of a film at the iron-coating interface. This is followed over the next few days by a significant decrease in pH and an ellipsometric response indicating the thinning of the film at the iron-coating interface and possibly the onset of corrosion.

Future experiments will examine the effects of inhibitors (e.g. CrO_4^{-2}) either incorporated into the coatings or placed in the immersion media. Attempts will be made to effectively characterize the sub-coating environment and perform triboellipsometric repassivation rate studies in a simulated sub-coating environment.

(3) In work carried out cooperatively with the Surface Science Division concerned with the mechanism of localized corrosive attack by hydrogen the following results were obtained using field ion microscopy:

(a) Niobium, although suffering surface damage from hydrogen does not seem to undergo crystallographically selective deep damage as found for Ti and Zr subjected to similiar conditions.

(b) Significant but not deep surface defects occur when Al is exposed to hydrogen and tensile stress.

(c) Cathodic polarization of an Fe-24 percent Cr alloy results in a broad array of surface effects including film formation and surface damage.

Metal Corrosion--Slow Strain Rate Test

C. E. Johnson and J. Kruger

In order for the engineers responsible for the design of new coal conversion systems to select alloys resistant to stress corrosion cracking (SCC), a reliable but rapid non-real time test is needed to evaluate susceptibility to this failure mode for the alloys chosen. Therefore, the objective of this task is to develop and evaluate testing techniques that determine susceptibility to SCC in environments of relevance to coal conversion technology. The emphasis of this project sponsored by DoE is on technique development and not on the selection and development of candidate materials. The approach taken to accomplish this task was to adapt and evaluate the slow strain rate test developed by R. N. Parkins of Newcastle upon Tyne University to coal conversion alloys and environments. With the completion of testing seven coal gasification candidate materials and the discovery that four of the seven failed by a brittle cracking mechanism, the slow strain rate test has been shown to be a viable technique for the testing of susceptibility to failure of alloys in simulated coal gasification environments at a temperature of 600 °C.

Owing to a shift in sponsor priorities and reassignment of personnel to other tasks, the project was terminated at the end of FY 78. During the last quarter of FY 78, Type 309 SS (similiar in composition and properties to Type 310 SS) was tested in helium and simulated coal gasification environments at 600 °C at a strain rate of 10^{-6}/s. The Type 309 SS remained ductile with no cracking; whereas, the Type 310 SS was one of the alloys that cracked with loss of ductility when tested at the same conditions. Photomicrographs of the microstructure of Type 309 SS revealed islands of ferrite in the austenitic structure which could contribute to the higher ductility than was seen in Type 310 SS where no ferrite was found. Type 310 SS was obtained from another supplier and was tested at 600 °C in helium at a strain rate of 10^{-6}/s. Specimens of Type 310 SS from this supplier cracked with low ductility much the same as the Type 310 SS specimens did that were obtained from the first supplier. These tests seem to rule out the possibility that the first set of Type 310 SS specimens were from a bad lot. It appears that only the slow strain rate test can detect the cracking in Type 310 SS since other researchers using other techniques, such as creep rupture and standard tensile tests, have not detected cracking, but it must be considered that each of these incorporates a different mechanistic approach and cannot be compared directly.

The final report of this project's work has been completed.

Metal Coatings--Electrodeposition

F. Ogburn, J. P. Young, and C. E. Johnson

(1) Standard Reference Material production--coating thickness calibration standards are produced on a routine basis. This is a continuing project that produces about 3000 items each year which are ultimately sold to the metal finishing industry and its suppliers.

(2) SRM research--Each year some investigations are conducted as a backup for the SRM production. During the past year the development of improved techniques of preparing our primary calibration standards was completed and a number of new calibration standards were prepared for x-ray measurements. A new coating thickness gauge was evaluated and set-up for routine use in the SRM program. Another investigation has led to a reliable method of measuring the thickness of gold coatings by using the Scanning Electron Microscope to measure the cross section of the coating. Plans call for evaluating a new x-ray spectrometer for measuring coating thickness and for investigating the magnetic properties of nickel coatings as they relate to the coating process and to the response of coating thickness gauges.

(3) Penetrant crack panels--This work is concerned with the development of dye penetrant sensitivity crack panels by electrodeposition techniques. Such crack panels are used to evaluate an important NDE crack detection method. A number of crack panels have been produced and measured and turned over to private and government labs for evaluation. A new method of determining crack depth shows that the depth is 30 to 50 times crack width. This depth is beyond the critical point for affecting dye performance according to information received from users of the dye-penetrant systems. Microscopic examinations and measurements show the electroformed crack panels to be quite uniform and reproducible. Several hundred crack panels may be produced from one 9 x 9" nickel-copper layered electroform. Development work is in progress to improve the adhesion of the plastic mounting material to the nickel-copper crack panel to reduce dye indications at the juncture.

(4) Black Coatings--A simple chemical immersion technique has been developed which produces ultra-black surfaces on electroless nickel-phosphorus coatings. The blackness is associated with a unique surface morphology consisting of a dense array of microscopic conical pores perpendicular to the surface. This structure is produced by a selective etch with nitric acid. This extremely high light-absorbing surface can be applied to a variety of substrates, such as metals, ceramics, glass, and plastics.

The unique surface morphology, acting as light traps, is capable of absorbing over 99 percent of the incident light when tested at wavelengths of light from 350 to 2100 nanometers (see Fig. 2). This capability of the ultra-black surface of this coating may offer potential for applications to optical devices, flat plate solar collectors, low temperature calorimetry studies, and because of the large surface area, as a catalyst.

Plating on Aluminum

D. S. Lashmore[1]

[1]Research Associate

The applications for plated aluminum have greatly increased in recent years due to the demand for a material with a high strength to weight ratio to replace steel, not only for decorative applications but also in cases where a material with a low inertial moment and high wear and abrasion resistance is required. Because there is little scientific understanding of the deposition process on aluminum, a Research Associateship was established at NBS (in FY 1977) by private industries interested in aluminum plating. The objective of this program was the investigation of some of the more fundamental aspects of the process.

The research effort during the past year was in the area of anodic and immersion pretreatments for plating onto aluminum. It was found that in all common immersion pretreatments that the dissolution of

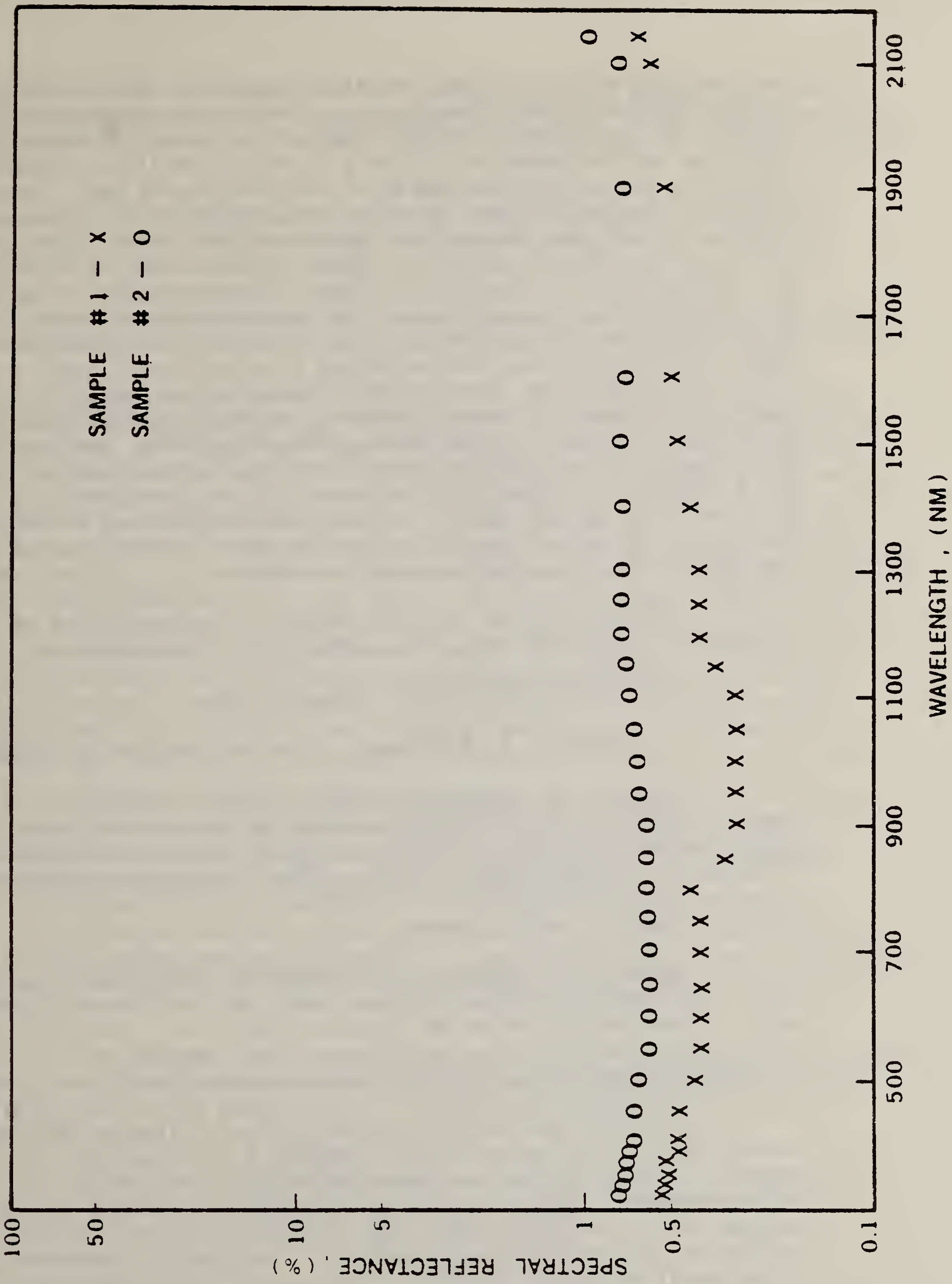

Figure 2. Spectral reflectance vs. wavelength of light for two samples of the ultra-black chemically etched deposits of electroless nickel. Curve referenced to $BaSO_4$.

the substrate was a structure sensitive property, that is, certain crystallographic planes dissolved at a faster rate than others in the presence of the sodium hydroxide common to all these electrolytes. The morphology of the deposits is also a structure sensitive property, indeed in the case of zincated aluminum (perhaps the most common pretreatment) the deposit was found to be epitaxial on all the aluminum principal planes and this epitaxy was characterized as, Zn: (0001) <10$\bar{1}$0> // Al: (0001) <010> Zn: (0001) <1120> // Al: (1$\bar{1}$0) <111> and Zn: (0001) <1120> // Al: (111) <1$\bar{1}$0>. The morphology of the deposits was also found to be sensitive to the alloy type even though the epitaxial relationships were not affected. The aluminum dissolution and zinc deposition reactions were not affected by alloy type. Small additions of ferric chloride and Rochelle salt, however, had a drastic effect on a number of process and deposit property variables such as adhesion, morphology of deposit, enhanced aluminum dissolution, and decreased zinc deposition. The rate of the deposition dissolution reaction, however, was drastically affected by alloy type. It was found that a zinc iron alloy remained on the surface following an immersion of a zinc coated specimen in 50 percent nitric acid. The above information has aided the development of a new aluminum plating process.

Anodic films on two high strength aluminum alloys were characterized with regard to pore size, pore density and adhesion.

Underground Corrosion of Power Lines

U. Bertocci, E. Escalante, J. L. Mullen, and J. Kruger

The use of underground cables for the transmission of electric power has brought new corrosion problems to the electric power industry. One of the more elusive and serious of these is the underground corrosion of concentric neutral wires. This project is aimed at the development of methods for the detection of dangerous corrosion conditions in these buried concentric neutral wires.

Work on the problem of corrosion of underground power transmission lines continued during the past year, both on laboratory samples and on actual cables buried at a special NBS site. The partial sponsorship of this work by DoE ended this year, but the project is continuing in cooperation with the Electric Power Research Institute.

(1) The question of the effect of a.c. leakage from cables to ground, which is believed to be an important contributory factor in enhancing corrosion, has been attacked both at the theoretical and at the experimental level. Last year the equation relating current to voltage for an electrode under charge-transfer control was solved for a modulation of the electrode potential. The solution, expressed in terms of the modified Bessel function, allows one to calculate the rectified current as well as the other harmonic components of the faradaic current. The results show that shifts in the d.c. electrode potential as well as enhanced corrosion might occur as a consequence of the a.c. modulation.

The predictions of the mathematical model have been tested and shown to hold for electrodes under charge-transfer control. Instrumentation for the use of FFT methods to obtain electrochemical data is being implemented.

(2) In our program to develop techniques and equipment to measure the corrosion rate of electric cables in service, four 15 m sections of cable were buried on the corrosion test site on the NBS grounds. An alternating current (60 Hz) was applied to two of these cables to better simulate in service conditions. During this year electrochemical measurements and associated equipment have been developed to the degree that measurements are being made on a regular basis.

These measurements indicated that the cables with an imposed a.c. were corroding at a signficantly higher rate than those without a.c. In addition, an intentional local modification of the soil environment made to increase the corrosion rate on a section of the cable was having little effect on corrosion as indicated by these measurements. Prior to removal of the cables, the imposed a.c. was turned off. Within a few days, the corrosion rate of the cables that had the a.c. began to decrease. After removal, all cables were cleaned and inspected and revealed that, in fact, the cables with a.c. had suffered extensive damage compared to the cables without a.c. and that the section of the cable in the modified soil had undergone little additional corrosion compared to other sections of the same cable as the electrochemical measurements had predicted. Weight loss measurements revealed that the weight loss predicted by the electrochemical polarization measurements were low by less than 30 percent, an acceptable error under the varying conditions in the field.

Preliminary polarization corrosion rate measurements carried out on cables in-service and owned by the Prince William Electric Cooperative, Manassas, Virginia, indicate that the corrosion measurements can be made under operating cable conditions.

Future studies include continued corrosion rate measurements on the new cables with and without a.c., evaluation of current distribution during polarization, and improving the equipment for use on in-service cables.

In an effort to substantiate results and improve the measurement techniques, four new sections of cable 50 m in length have been buried. Initial data in the absence of a.c. show that the corrosion rate of these cables is low and comparable to the first set of cables.

Corrosion Protection of Shielding Materials for Direct-Burial Cable in Underground Soil Environments

W. F. Gerhold

Historically, 5-mil copper has been used as a shield material in non-gopher infested areas with 10-mil copper being used in areas requiring gopher protection for telephone cables. Bi-metallic shields using copper and stainless steel have also been used in lieu of 10-mil copper. Due to an increase in underground telephone cable installation coupled with increasing cost and fluctuating availability of copper, a program was initiated by NBS and REA to develop and investigate metals or combinations of metals and other materials for use as a substitute for copper in buried telephone cables. REA estimates that the NBS work has an impact on 90 percent of the 600 million dollar industry producing and using the telephone cables, whose design is based on the NBS program.

The corrosion behavior of many different shield systems utilizing other metals or alloys and composite metals and plastics has been investigated over a six year period at six NBS soil corrosion test sites. Since initiation of the program, it has been expanded to include additional systems. These systems are representative of advances in technology with respect to manufacturing processes or techniques in addition to the use of new materials.

The results to date show that some of the cable systems utilizing aluminum alloy shields with ethylene/acrylic acid copolymer film coatings provided good protection to the cable core in some of the less aggressive soils. However, when coupled to copper, their performance was poor in one more of these soils. The performance of Type 304 stainless steel was excellent in all of the soils. Good protection was afforded in all of the soils by systems incorporating a Type 304 or Type 430 stainless steel outer shield with an aluminum alloy inner shield separated by a polyethylene jacket.

Systems buried up to six years have been evaluated and a report containing the results obtained from these tests is in preparation.

In 1977, this program was further expanded to include "buried plant housings" which are used in the construction of telephone systems. Representative samples, to be investigated over a six-year period, were exposed at four of the NBS soil corrosion test sites and at two additional sites (one, in northern Pennsylvania and the other along the seacoast in South Carolina). Removal of the first set of "plant housings" exposed for one year has been completed at five of the six soil sites. Exposure of additional samples, representative of advanced technology in materials fabrication has been initiated.

Corrosion Evaluation of Stainless Steel Alloys for Underground Applications

W. F. Gerhold, E. Escalante, and B. T. Sanderson

Stainless steels have been proposed for use in underground applications such as gas, water, telephone and electrical distribution systems, ground rods, culverts, transformer cases, residential sewage disposal, etc. In 1970, an investigation was initated with partial support from the American Iron and Steel Institute at six NBS soil test sites to evaluate the corrosion behavior of stainless steels in underground service. This was expanded in 1972 and 1973 to include materials representative of newer alloys. Aspects being studied include general corrosion behavior, pitting and crevice corrosion, stress-corrosion cracking, and hydrogen embrittlement. To date 1054 specimens have been buried at each site for a total of 6324 at the six test sites. The exposure periods chosen were one, two, four, eight, and X years. A report containing the results obtained from specimens buried up to eight years is currently in preparation.

Corrosion of Piling in the Sea

E. Escalante, B. T. Sanderson, and W. P. Iverson

The increased use of offshore structures in the search for energy from the sea has led to a greater awareness of the corrosion of steel in this environment. In 1976, for example, over a quarter of a million tons of steel were put into use for new offshore structures. The corrosion protection of these structures intended for long-term use is imperative.

Since 1967, the National Bureau of Standards under the sponsorship of the American Iron and Steel Institute has been involved in a study of the effectiveness of corrosion protection of steel in sea water by a variety of systems. These systems consist of metallic and nonmetallic coatings, single system and two system coatings, and cathodic protection of bare and coated steel. The degree of protection afforded by these systems is measured annually using electrochemical techniques in conjunction with visual and photographic records.

Originally there were 93 steel piles in the study. In 1973, 26 piles were removed for physical study. This removal resulted in NBS Monograph 158, a progress report on the information up to that time. This winter, a final removal is being planned which will result in a final report on this long-term corrosion and corrosion protection study of steel in sea water.

Corrosion of Downstream Components in MHD Power Generation Systems

J. Smit

The objectives of this program are: 1) to develop a test method for assessing the relative corrosion resistance of alloys in downstream components of MHD systems such as steam cooled tubes; 2) to screen alloys for corrosion resistance under some simulated downstream conditions; 3) to evaluate the materials subjected to the tests in 2 to determine the conditions under which screened alloys may be suitable candidates for incorporation in the design of downstream components.

Using the simple test rig using a propane burner, specimens of AISI 1015 steel, 310, 316, and 446 stainless steel were evaluated after being exposed to a hot gas stream (1330 °C) containing K_2SO_4 for four hours. The specimens were maintained at 550 °C by internal air cooling. Incipient corrosion was observed in all cases sometimes as quasi-uniform wastage and sometimes as pitting. EDX analysis showed Ni, Cr, Fe, and K in pit.

Following the completion of these studies on the extant simple test rig, extensive changes were made to upgrade the rig. The changes were made to provide more control over test parameters and to extend the testing capabilities of the rig to a longer term (≥ 100 hrs.). To provide this control and to extend operating times, automatic equipment was installed, and a gas handling and storage unit was constructed.

The rebuilt rig is composed of: 1) a gas handling and storage unit for oxygen and propane, 2) an instrument unit containing a two gas blender-controller, a mass flow controller, a thermocouple amplifier unit and digital volt meter, 3) a vertical test chamber which houses in descending order: a salt reservoir, burner, combustion chamber, specimen support, and an exhaust duct.

The hot zone temperature of the rebuilt rig is now controlled by a modified two gas blender-controller located between the gas supply and the burner in the oxygen and propane supply lines. This unit, which permits control of both the total flow rate and the oxygen-propane ratio, is interfaced with a thermocouple output amplifier. The specimen temperature is controlled, again automatically, by a mass flow controller located in the cooling air line between the test specimen and the air source. The gas storage and handling unit has the capacity to hold six 1-a 220 cu. ft. oxygen cylinders and two 100 lb. propane cylinders. At anticipated flow rates, it is expected that this capacity will be sufficient to allow about seventy-two hours of operation. However, provisions have been made that permit runs of unlimited duration. One of the test parameters added to this program is the oxygen partial pressure near the specimen surface. A Nernst probe is being prepared to make these measurements.

In the coming year the evaluation of materials for short (4-hour) and long (100-hour) exposure periods will continue. Test conditions for these periods will be varied and will include oxygen partial pressure, specimen temperature and hot gas stream additives.

Corrosion of Steel in Concrete

E. Escalante and S. Ito

The deterioration of bridge decks as a result of the corrosion of steel rebars in concrete is becoming an increasingly serious problem in those areas of the nation where deicing salts are used. This destructive action is not evident until damage is so extensive that it makes itself visible in the form of cracks and spalls.

The objective of this program is to develop a test method for measuring the corrosion of steel in concrete. By being able to evaluate this corrosion action, new protective systems can be evaluated or corrective measures taken.

During this year, the first task of this study has been completed and a second has been initiated.

The first task involved compiling a bibliography of the literature on the corrosion of steel in concrete (NBS Special Publication 550). The search revealed 394 entries from 1964 through 1978 which are listed by subject index in the first section and alphabetically by author in the second section. The subject index shows those areas of the problem where work has been performed in the past which serves as a guide for future work.

In addition, this task included a critical review of destructive and nondestructive techniques available for measuring the corrosion rate of steel in concrete. On the basis of this effort, several techniques have been chosen as having possible application to corrosion studies in concrete. The first technique is the direct measurement of weight loss which will serve as the standard by which other methods are evaluated. Other techniques are Stern and Geary's linear polarization, Mansfeld's polarization resistance, Barnartt's three point method, Schwerdtfeger's break in the curve, and a.c. impedence. Each has its advantages and disadvantages which are discussed in the review.

The second task is the application of the techniques to measure the corrosion of steel in concrete. In this portion of the study several concrete slabs (60 x 30 x 5 cm) each containing three steel bars have been cast. After curing, one of the slabs was immersed in a 3.5 percent NaCl solution for 36 hours to enhance corrosion. Afterwards, it was placed 10 cm above a pool of the solution with which it is wetted 5 days a week. Because of the high resistivity of concrete, compensation for IR is necessary during polarization measurements. This high resistivity has also made it necessary to modify existing equipment previously used in soil corrosion studies by raising the input impedance of the circuitry. Preliminary polarization measurements indicate that the IR error can be successfully compensated, allowing corrosion rate measurements to be made.

Because d.c. potentials have been used successfully by other laboratories to remove Cl^- ions from concrete, a second concrete slab is being subjected to the opposite effect; that is, a potential that will force the migration of Cl^- into the slab is being applied after the curing process is completed. If successful, it is expected that the corrosion rate observed on this slab will be significantly higher after a shorter period of exposure than that found in other slabs of the same age.

Automation of Field and Laboratory Corrosion Measurements

W. G. Eicke and J. E. Sims (Electrical Measurements and Standards Division, Center for Absolute Physical Quantities)

As a result of reprogramming, W. G. Eicke and J. E. Sims of the Electrical Measurements and Standards Division were assigned full-time to collaborate with the Chemical Stability and Corrosion Division (561) in this new activity. The objectives of the activity are to improve electrical measurements in the field of corrosion through improved instrumentation, measurement techniques, automation, and data reduction via digital computers.

The work currently under way is directed toward assisting the Division 561 program concerned with in situ corrosion rate measuring and corrosion detection techniques for underground power cables. Primarily, polarization and corrosion noise measurements are being employed in the program. It is hoped that this new collaboration will result in a number of long-term benefits such as faster, continuous unattended monitoring, more data to extract short term effects, and more effective corrosion field data handling. This activity in support of this 561 program was initiated in the spring of 1979 and has been directed toward both laboratory and field corrosion measurements.

(1) The activities concerned with laboratory measurements have been directed toward a) interfacing a digital oscilloscope to an Interdata 7/32; b) establishing a communication link between Bldgs. 220 and 223; and c) developing software to reduce measurement data obtained via the scope. User oriented software has been successfully developed to transfer data easily between the oscilloscope and the 7/32. The data reduction problem is well in hand. In this latter area a reasonably general purpose user oriented program to accurately determine the period of waveforms and do a Discrete Fourier Transform is under development and should be complete in the near future. It is expected that the work will also benefit corrosion-noise measurements.

(2) The activities directed toward automated field measurements seek to develop an improved measurement system for taking underground corrosion data in the field. Several possible approaches have been reviewed and are still in the very early stages of evaluation. At this time the most likely approach will be a microprocessor based measurement system. To facilitate this work a model of an underground system is being set up in the laboratory so that various measurement techniques and problems using conventional measurement equipment and the 7/32 can be investigated.

A review of various approaches to making corrosion measurements is planned for the future to determine other areas that might benefit from the new expertise that has been introduced into the corrosion program from the Electrical Measurements and Standards Division.

Chemical and Biodegradation Processes

F. E. Brinckman, W. R. Blair, W. P. Iverson, J. A. Jackson, K. L. Jewett, R. B. Johannesen, E. J. Parks, and J. M. Bellama[1]

[1] Guest Worker

The technical activity of this subtask is directed to measurement and mechanistic characterization of chemical and biological processes involved in the transformation and degradation of materials. Currently, emphasis is on organometallic substances because of the widespread use of organometallic materials in technology as well as the significance of organic derivatives in the degradation, mobilization, and transport of metallic elements in the environment. Methods to detect, identify, and measure individual organometal species at nanogram or picogram levels, urgently needed in order to assess durability, service life, and impact of use of these materials, are being developed and applied in specific problem areas. In cooperation with the Division's new Tribochemistry Group, efforts have also been initiated to apply these measurement techniques to characterize hydrocarbon types present in used and re-refined oils and to follow transformations of additives in oil during oxidation and wear processes. Individual project areas are summarized below.

Speciation of Organometallic Compounds

K. L. Jewett, W. R. Blair, J. A. Jackson, E. J. Parks, and F. E. Brinckman

The primary objectives of this continuing project are to develop techniques for the detection, speciation, and quantitation of organometal species at very low levels approaching or equaling concentrations in the environment. Work during the past year has emphasized organotin materials because of the growing applications of these as biocides and antifoulant materials.

The fouling of ships' hulls by marine organisms results in severe economic loss to the Navy and to the maritime industry. These losses are due mainly to increased fuel consumption to overcome the hydrodynamic drag of fouled hulls and to frequent periods of drydocking required when marine growth becomes excessive. Organotin compounds have become prominent as potential replacements for the conventional copper oxide as the active ingredient in these coatings because of their greater durability and possibly greater environmental compatibility.

The effectiveness of an antifouling coating is dependent upon the rate at which the active antifouling agent leaches out from the coating. Too low a leach rate does not provide adequate inhibition; too high a leach rate is wasteful of material and may exert unnecessary stresses on the life cycles of biota. During the past year, work has been continued in cooperation with the Office of Naval Research and the

Naval Ship Research and Development Center to identify the chemical species released from organotin antifoulants and develop techniques for measuring release kinetics. These methods are based on separation of organotin compounds by high pressure liquid chromatography (HPLC) and the use of coupled atomic absorption detectors for element-specific detection and analysis of tin-containing species.

Using these techniques, measurements of the leach rate of the specific organotin moiety, tributyltin (1+), have been made on commercially available marine paints, and similar measurements are in progress on a number of Navy polymeric coatings. Typical results on the commercial paints are shown in Fig. 1. Although measurements of total tin leached from tin-containing coatings have been made in other laboratories, the present NBS work is the first example of measurement of the leach rate of a particular organotin ion. This provides a powerful mechanistic tool as well as a meaningful basis for significant bioassays.

During the past year, significant improvements have been made in the techniques for the separation of trialkyltin species by liquid chromatography. Using a strong cation exchange column with a graphite-furnace atomic absorption (GFAA) detector, it has been possible to effect clean separations in saline media of compounds of the type R_3SnX, where R = phenyl, n-butyl, n-propyl, ethyl or methyl, and X is any anion dissociated in water (as chloride). Some typical results are illustrated in Fig. 2. Separation of compounds R_2SnX_2 is currently being pursued.

A significant increase in sensitivity of detection of tin species, pushing the limits of detection from nanograms down to picograms, has been achieved by modification of a commercial flame photometric detector. An application of this technique will be discussed below under "Biological Transformations."

Similar techniques have been used to characterize concentrated solutions of polymeric antifoulant materials of interest for marine applications. By using high pressure liquid chromatography (HPLC) with size exclusion and reverse phase bonded chromatographic columns, in conjunction with refractive index, ultraviolet and graphite furnace atomic absorption (GFAA) detection systems, some organotin polymer materials have been separated into at least two tin-containing fractions of widely different molecular weights. This inhomogeneity appears to be real and not an artifact of the experiment. It is preferable to have the organotin residue attached to the higher molecular weight fraction to provide tin dissolution over a long lifetime. Experiments are in progress to attempt to correlate the distribution of tin among fractions of varying molecular weight with conditions of preparation. The ultimate objective of the work is to assist the Navy by providing a molecular level basis for development of procurement specifications for these materials.

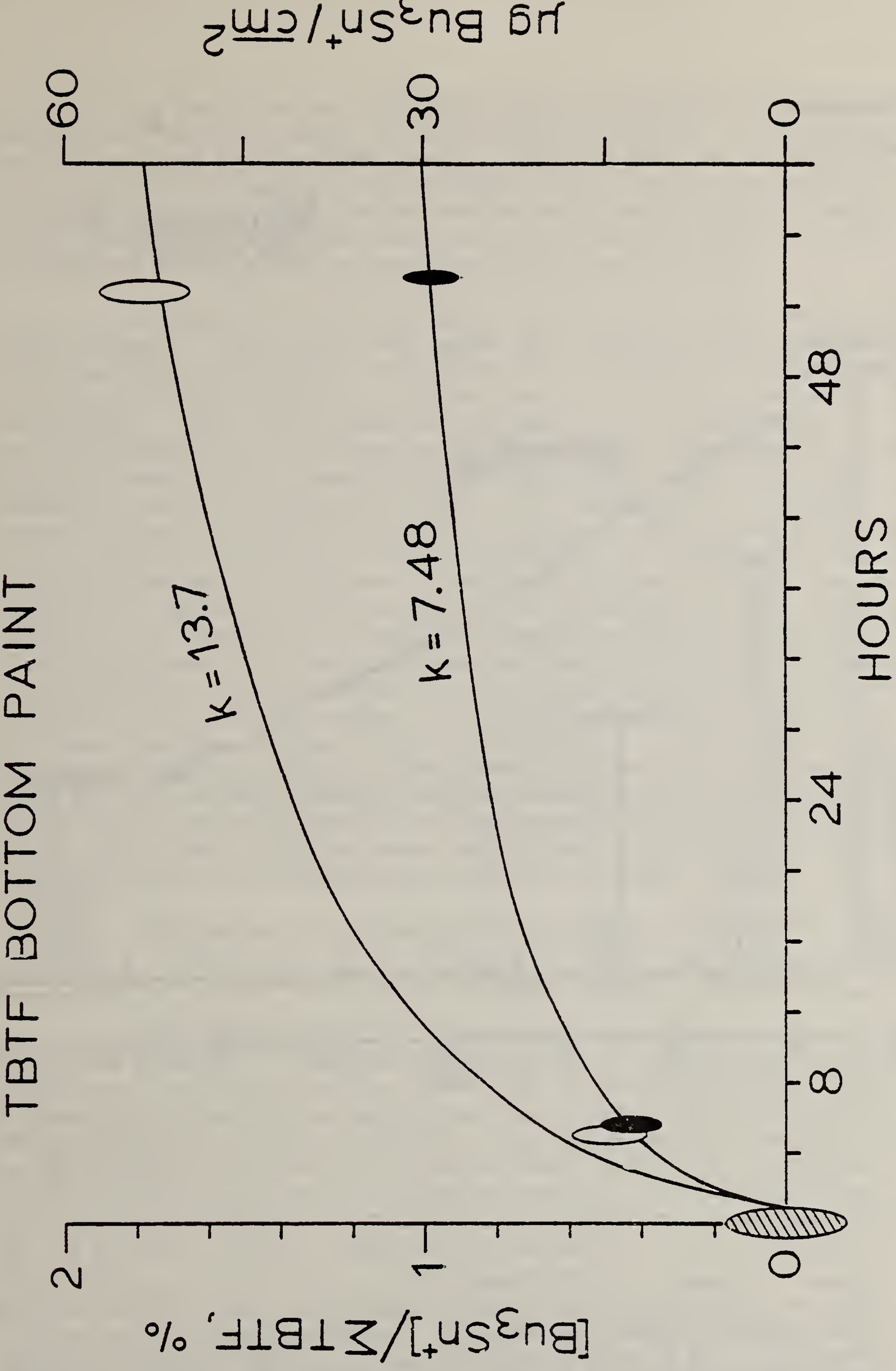

Figure 1. Leaching of Bu_3Sn (1+) from paint samples containing tributyltin fluoride (TBTF). Painted wooden panels are suspended in water and the water is analyzed for Bu_3Sn (1+) at various intervals of time. The observed concentrations of tin have been converted to amount of Bu_3Sn (1+) per cm^2 of paint.

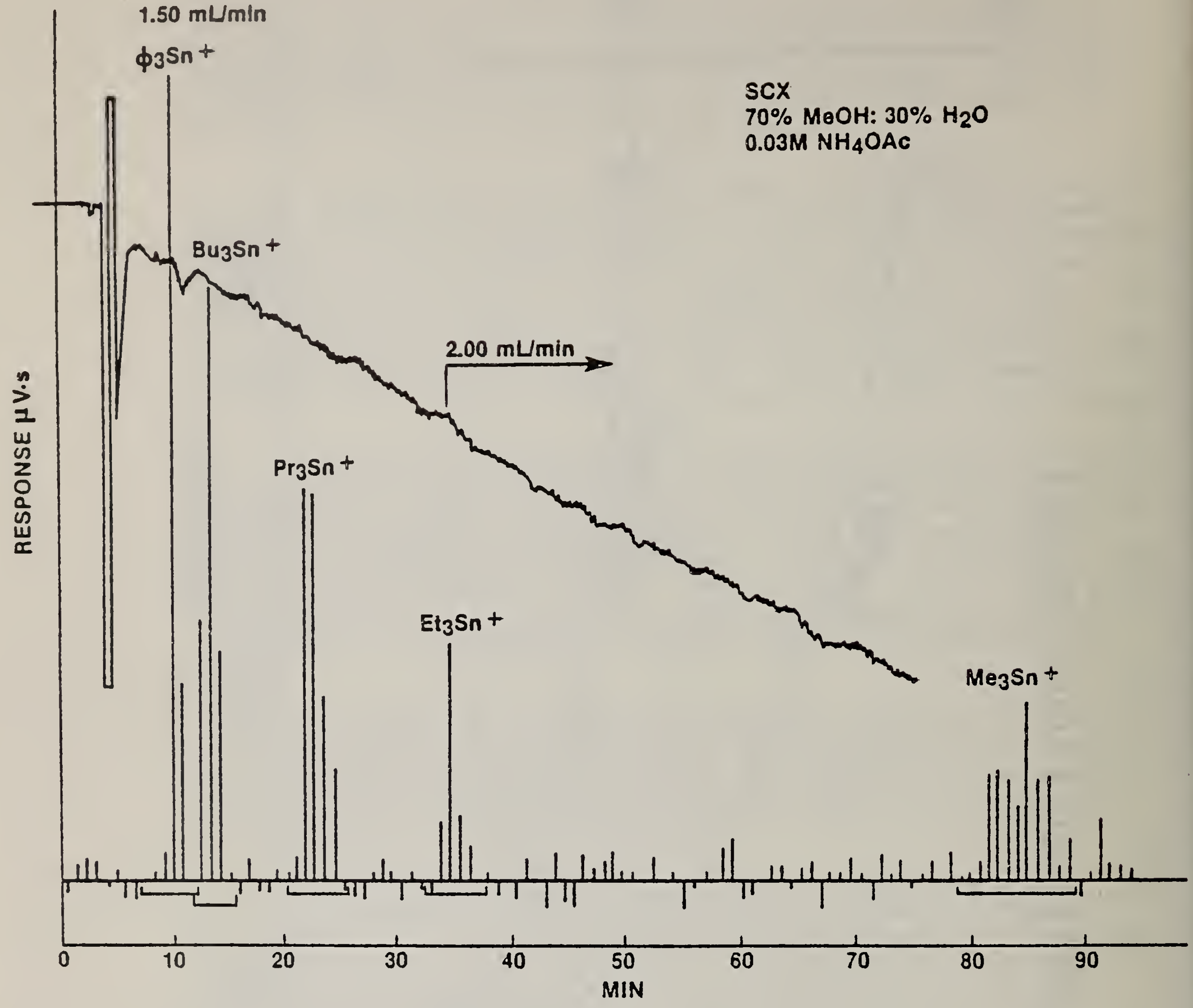

Figure 2. Separation of triphenyltin (1+) and four trialkyltin (1+) ions from one another on a strong cation exchange column. The vertical bars give response of the GFAA detector in arbitrary units at one minute intervals. The mixed tin compounds were injected into the LC system, then eluted with 0.03 M ammonium acetate at a rate of 1.50 mL min^{-1}, changed after 35 minutes to 2.00 mL min^{-1}. The smooth curve gives the response of an ultraviolet detector, offset about one minute. The small dip at 11 minutes arises from $(C_6H_5)_3Sn$ (1+); the alkyltin species do not absorb in the ultraviolet.

The technique of using HPLC-GFAA to speciate organometals has been transferred to a number of other research groups. For example, facilities based on those developed at NBS have been established at the U. S. Navy Ship Research and Development Center and the University of Maryland. This technique for separation and element specific detection (i.e., speciation) developed here avoids the need for derivatization or destructive modification of the materials to be analyzed.

Our speciation methodology program involves work on several other elements. Since 1976 this group has worked collaboratively with the Netherlands government, through the Delft Hydraulics Laboratory and the Soil Fertility Institute, on the speciation of toxic metals in the environment. Particular attention has been given to compounds of mercury, arsenic, and tin because of their actual or potential hazard. With the demonstration, described last year, that metal-containing compounds could be collected in the field (specifically, Rotterdam harbor in the Rhine delta) and concentrated on a pre-column for shipment to the Bureau for analysis, other governments with frontage on the Rhine became interested in the Bureau's work on trace metal speciation. This interest is responsible for an invitation tendered by the University of Mainz to F. E. Brinckman to spend the summer of 1979 at Mainz as a visiting professor to give a lecture and laboratory course in speciation of organometals. The Deutsche Forschungsgemeinschaft has indicated its interest in this work by supporting the chair in Mainz to which Dr. Brinckman has been invited, and by inviting W. P. Iverson as well to act as a consultant on bacterial transformation of metals. A three nation study by Switzerland, Germany, and the Netherlands to measure the introduction and transformations of tin compounds from source to mouth is now being established, with the Bureau acting as a consultant and participant because of its demonstrated expertise in metal speciation.

NMR Studies on Transmethylation between Aquated Metal Ions

J. A. Jackson, R. B. Johannesen, and F. E. Brinckman

Methylmercury (1+) in aqueous solution is far more toxic than inorganic mercury (2+) and has been shown to be responsible for major outbreaks of mercury poisoning, with both crippling and fatal results. Although methylmercury formation has been shown to be bacterially produced as well as being produced by the methylation of mercury (2+) by methylcobalamin (a Vitamin B-12 derivative), these are not the only paths for production of this dangerous material. It has been demonstrated in this laboratory that abiotic methylation of mercury can occur by the action of several other methylated metals, e.g., trimethyltin (1+):

$$(CH_3)_3Sn^+ + Hg^{++} \rightarrow (CH_3)_2Sn^{++} + CH_3Hg^+. \qquad (1)$$

The environmental implications of this type of reaction can be appreciated. Mercury (2+), in quantities which of themselves pose no health hazard, can be converted to the highly poisonous methylmercury (1+) by such relatively innocuous materials as trimethyltin (1+), in aqueous solution at ordinary temperatures by abiotic means. It therefore becomes of great interest to learn how rapidly this transmethylation reaction proceeds, and how it is affected by variables such as pH, pCl, or temperature. Nuclear magnetic resonance (NMR) spectroscopy is ideal for this purpose. The nuclei of interest (H, Sn, Hg) all have magnetically active isotopes. The kinetics of reaction (1) were measured by proton NMR, measuring the disappearance of trimethyltin (1+) and the formation of dimethyltin (2+) and methylmercury (1+). The reaction is second order with a rate of $k_2 = 12.6 \pm 0.58$ L mol^{-1}s^{-1} at 35 °C, $E_a = 22.0 \pm 1.3$ kcal mol^{-1}. It is a particularly fortunate circumstance that the proton signals of interest are all well separated and can be measured independently. The analogous reaction of transalkylation where the alkyl is ethyl or any larger group would be almost hopelessly complex to unravel by proton NMR because of severe overlapping of spectra. Spectra of tin-119 and mercury-199 do not suffer from this problem; the several alkylated species will give distinct lines since the proton signals can be decoupled from the metal spectrum. We have repeated the kinetic study of reaction (1) above, in collaboration with Peter Rinaldi at Florida State University, by following the NMR signal of the tin-119 nucleus. The results were only slightly different than the proton results, viz: $k_2 = 13.4 \pm 0.7 \times 10^{-3}$ L mol^{-1}s^{-1}, $E_a = 22.5$ kcal mol^{-1}. Thus, the principle of the method has been validated and we are prepared to measure transfer of organic groups from one metal to another, regardless of the complexity of the proton spectrum by following the NMR signal of the metal itself. The method is, of course, valid in studying reactions that are free of protons, such as transfer of inorganic radicals from metal to metal (provided the reaction is not too fast to follow).

Biological Transformations of Tin Compounds

W. P. Iverson, J. A. Jackson, and F. E. Brinckman

As a part of our continuing studies on the environmental transformations of toxic metals consequent to the use in the materials cycle, we showed several years ago that a strain of *Pseudomonas* which is common in the Chesapeake Bay was capable of methylating tin, i.e., of converting inorganic tin to an organic (methyl) derivative. This was demonstrated directly by mass spectrometry as well as indirectly by reaction of the biologically produced product with mercury (2+) to form methylmercury (1+) as described previously.

During the past year, new information has been obtained on this process. We have demonstrated, by using a flame photometric detector equipped with a narrow-band interference filter which isolates SnH emission bands, that the organism methylates tin (4+) in its growth medium to a material which has the same retention time as tetramethyltin in a gas chromatograph. Proper adjustment of the hydrogen-rich flame to maximize SnH emission allows a minimum of 10 pg (1×10^{-11} g) (calculated as tin) of tetramethyltin to be detected. This sensitivity will allow either biological or abiotic transformations of metals to be followed at environmental levels. Such transformations are important, as mentioned above, because it is becoming increasingly recognized that inorganic materials which are in themselves innocuous, at the levels which occur, can be changed into more hazardous substances by reactions which are as yet poorly understood.

NMR Studies of Recycled Oil

R. B. Johannesen

The country's growing dependence on imported oil, together with localized shortages of petroleum products, makes it desirable to reuse waste oil materials. Working in cooperation with the Bureau's Recycled Oil Program and the Division's newly formed Tribochemistry Group, we have undertaken a preliminary NMR investigation of used and re-refined oil. One major objective of the investigation is to evaluate the application of NMR to characterize the composition of the oil in terms of hydrocarbon types as a criterion for consistency of used or re-refined oil base stocks. It is also anticipated that the new high field NMR system will allow study of additives in oils, particularly phosphate esters, to define the stability, rate, and products of decomposition of these additives. Preliminary results have been obtained by proton and carbon-13 NMR. These show that used oil contains a considerable amount of paramagnetic material (not further identified) both suspended and in solution. The relative proportions of aromatic/aliphatic carbon and hydrogen can be estimated; when reliable quantitative data have been obtained, these ratios can be analyzed to give the polynuclear/mononuclear aromatic ratio. No NMR spectra of other nuclei have yet been obtained. Phosphorus-31 spectra are expected to be easy to measure with the new NMR system to be installed at NBS late in fiscal year 1979 and will be used to follow reactions of phosphorus-containing additives. Lead-207 spectra may be obtainable if the lead, known to be present in used oil, is in true solution rather than suspension. If obtainable, such spectra will allow us to trace the conversion of lead in the internal combustion engine, and to identify the chemical forms of lead in used oils.

HIGH TEMPERATURE CHEMICAL STABILITY OF MATERIALS FOR PROCESSING AND SERVICE

The objective of the work carried out under this task is to provide measurement methodology, test methods, and data required to enhance chemical durability and related performance of materials in high temperature service environments as well as methodology for prediction of long-term materials performance in those environments.

Technical activities fall into two areas: those in which durability is governed by heterogeneous processes involving interaction of materials with an aggressive (usually gaseous) high temperature environment, and those in which durability is governed by transport processes within the solid.

Technical Activity

High Temperature Processes

J. W. Hastie, D. W. Bonnell, L. H. Grabner, W. S. Horton,
E. R. Plante, P. K. Schenck, A. B. Sessoms, and K. Zmbov[1]

[1] Guest Worker

Technical activities in this area in fiscal year 1979 have emphasized both heterogeneous reaction processes and characterization of high-temperature gaseous environments, including flames.

Vaporization and Chemical Transport Under High Temperature Process Conditions

J. W. Hastie, D. W. Bonnell, W. S. Horton, E. R. Plante,
and K. Zmbov

Objectives of this activity are to develop new or improved measurement techniques and apply them to the characterization of the reactions, performance, and durability of slag and ceramic materials in high-temperature process environments, such as those pertinent to the operation of coal gasifier and MHD plants. Problems of immediate concern include:

(1) Development of improved methods for identification and quantitative measurement of gas and vapor species in heterogeneous systems at high temperatures and pressures.

(2) Defining experimentally and theoretically (through thermodynamic modeling) the degree of alkali seed retention by coal slag under MHD conditions,

(3) Determining the durability of candidate ceramic MHD electrode and coal gasifier components with respect to their possible degradation by vaporization and chemical transport in MHD and coal gasifier atmospheres.

(4) Obtaining molecular data on the rates and mechanisms of the release of alkali and other inorganic impurities from coal minerals and fly ash, pertinent to gas clean up technology in advanced multicycle combustion systems.

Both experimental and theoretical methods are being developed and applied to these questions. The well-established Knudsen effusion mass spectrometric (KMS) method has been adapted to the measurement of slag vaporization thermodynamics at low pressure and in the presence of reactive gases such as H_2O, H_2, and O_2. To deal with slag and ceramic systems in the presence of high pressure reactive gases, a new transpiration mass spectrometric (TMS) technique has been developed and demonstrated. In the NBS-developed TMS apparatus, solids on melts interact in an isothermal high temperature reactor with a flowing stream of mixed reactive gas at high temperature. Downstream of the reaction zone, a portion of the gases containing the products of vaporization and reaction is sampled by expansion through a supersonic nozzle to form a molecular beam. This is mass-analyzed with a quadrupole mass spectrometer coupled to the reactor-sampler. The design of the reactor and sampling system is intended to ensure that the chemical equilibria or relative species concentrations characteristic of the high pressure reaction zone are unperturbed by the sampling process. Thus, quantitative measurements of concentrations and equilibria can be made, with direct observation of the species present in environments approaching in-service conditions. Test application of the method to the vaporization thermodynamics of NaCl yielded monomer and dimer vapor pressures in excellent agreement with conventional techniques (KMS, boiling point, velocity distribution) these measurements extended the range of temperature dependent data from $\sim$ 1000 K to $\sim$ 1500 K and extended by more than three orders of magnitude the pressure range over which vapor species have been directly observed in this system. Subsequent applications of the technique to simple alkali halide, sulfate, oxide, hydroxide, and several complex slag systems at total pressures to ca. one atmosphere and 1700 K have yielded vapor pressures, species concentrations, temperature dependent reaction constants, and substrate composition dependent activities. To relate the laboratory data to actual MHD and coal gasifier conditions, computer based thermodynamic models are being developed. Two computer programs are being used, one being the NASA Gordon and McBride Multicomponent Equilibrium Free Energy Minimization Program (which computes equilibrium heterogeneous system concentrations and thermodynamic properties from data base information under ideal solution assumptions) and the other a more sophisticated recently acquired program SOLGASMIX (Erikkson [Sweden], similar to the Gordon and McBride code, but relaxing the ideal solution constraint) which is applicable to non-ideal solution systems such as slag.

Principal accomplishments during FY 79 include:

(1) Completion of the construction of a new vertical high pressure sampling mass spectrometer system (VHPMS). A schematic of the device is shown in Fig. 1. This system is designed to sample from

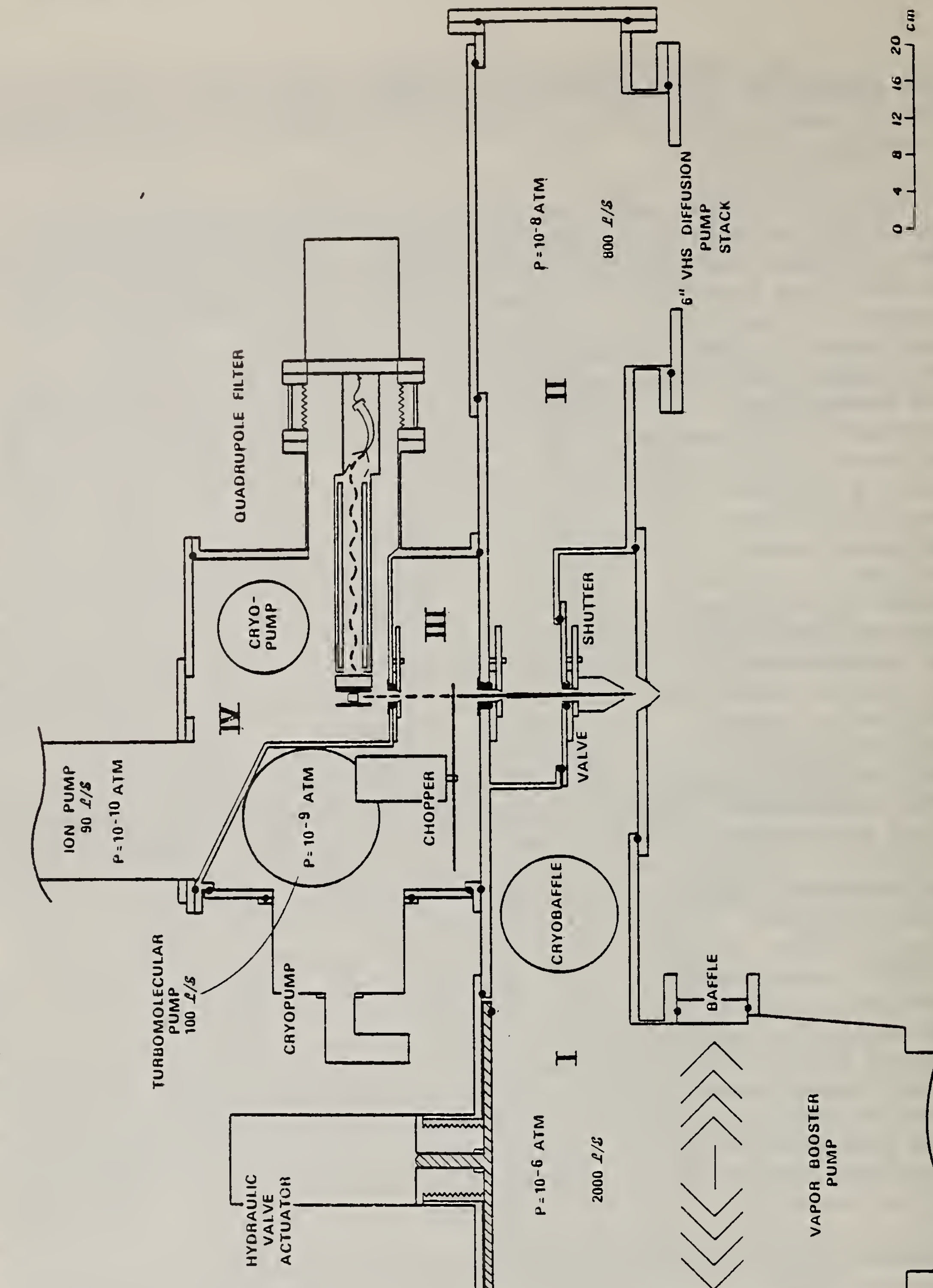

Figure 1. Scale drawing (to a good approximation) of the Vertical High Pressure Sampling Mass Spectrometer shown in a flame sampling mode. An assortment of premixed, diffusion and two phase (gas/liquid) burner assemblies may be coupled via a two-axis stage burning upward into the nozzle. The beam formation, collimation, modulation and detection process are depicted schematically stage by stage.

gaseous and heterogeneous systems at high pressures (ultimately 10-100 atm) and temperatures (to 1800 K), to operate in a vertical sample flow configuration, to handle large quantity (ca. 10^3 gm) samples, to have greater species detection sensitivity than the existing HPMS, and to handle particulate laden gases (e.g., smoky flames). The system has already operated satisfactorily at gas loads equivalent to 10 atm pressure with 10 ppm sensitivities.

(2) Design and construction of a coupled microwave-transpiration mass spectrometric system for use both with the HPMS and VHPMS facilities. The object of this work, which is being carried out cooperatively with scientists from the Center for Thermodynamics and Molecular Sciences, is to develop a method for simultaneous microwave and mass spectrometric characterization of high-temperature gas and vapor species. The techniques described above for sampling by supersonic expansion produce intense beams of high-temperature species in a "spectroscopically cool" form which avoids excessive thermal population of excited rotational and vibrational states. This will remove a major limitation in spectroscopic studies of the molecular species and provide the data needed for structural assignments. Coupling to the mass spectrometer will permit unequivocal identification of the species being examined. Quality structural information of unambiguously identified gas phase molecules will provide new statistical thermodynamic functions (necessary data base information for modeling efforts) for species of importance not accessible to classical high temperature spectroscopic methods.

(3) Development and application of a new method for determining molecular ionization cross sections for high temperature species using the TMS approach. Utilizing the transpiration environment, where applied gas concentrations can be precisely controlled and total system pressures accurately measured, direct relation of observed ion currents to external system conditions allows straightforward determination of pertinent ionization cross sections. When applied in simple systems under controlled conditions self consistent cross section data can be derived for a variety of condensible as well as volatile gas species of high temperature importance. Ionization cross sections are the single most important factor in converting mass spectral ion intensities to partial pressures and their determination has often been cited as an important problem in high temperature science.

(4) Vaporization characteristics of both actual and synthetic slag systems (species identity, relative concentration, vapor pressure, equilibrium constants, reaction enthalpies, and activity coefficients) were examined by TMS, and their reactivity in atmospheres of variable partial pressure of H_2 and H_2O determined. Complementary Knudsen effusion mass spectrometric (KMS) data, but at much lower system pressures, were also obtained. Both alkali metal and alkali hydroxide species were significant reaction products. The detailed information obtained indicated the inapplicability of ideal solution theory to slag systems and suggest that routine application of equilibrium calculations to these systems

may not be adequate expositions of the true conditions in these systems. The results of these measurements, which have not been available heretofore, provide an important input to the modeling studies described above.

(5) TMS vaporization thermodynamic data were obtained for the liquid systems KCl and KOH and existing literature discrepancies concerning vapor species and vaporization thermodynamics resolved. The relative amounts of monomer and dimer as well as the uncertainty in the heat of vaporization for the dimer molecules were refined. The previous uncertainties in species distribution place severe limitations on even routine calculation of equilibrium thermodynamic properties of systems containing these species, even relatively minor errors in the temperature dependence of monomer/dimer ratios having a profound effect when extrapolated to the very high temperatures and pressures typical of projected "real world" processes and corrosion problems. It was also demonstrated that $(KCl)_2$ clusters could be formed during the expansion process if the carrier gas to salt vapor concentration was too low. This ability to produce clusters should prove useful in future anticipated work on nucleation and condensation phenomena.

(6) The application of the TMS method to simple systems for demonstration and acquisition of data to elucidate complex vaporization systems has provided a unique opportunity to probe the characteristics of the molecular beam sampling process which promises to be a major tool for research in high temperature science. Evidence for high temperature cluster formation, unusual fragmentation processes, and small changes in thermodynamic functions magnified by the large available temperature and pressure range are providing clues which have the potential of direct access to data on molecular and electronic structure which at present is very uncertain.

Characterization Methodology for High Temperature Gaseous Service Environments

J. W. Hastie, D. W. Bonnell, L. H. Grabner, and P. K. Schenck

Objectives of this activity are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames, and to apply the methodology to assessing and predicting the performance of materials in those environments. During fiscal year 1979 the major thrust has been toward improved combustion diagnostic techniques and applying these to elucidating mechanisms of combustion modification, including flame retardance and smoke formation.

The development of the Vertical High Pressure Sampling Mass Spectrometer, described above, provides a capability for sampling diffusion and aerodynamically weak flames, and, because of its additional pumping capacity, allows use of larger sampling orifices for sampling particulate-laden environments. Experiments on smoky flames are being initiated.

Major emphasis has been given in the past year to development of optical characterization methodology for flames and other high temperature gases. A concerted effort has been to compare several approaches, such as Raman active rotation-vibration population distributions, OH rotational populations, and the sodium D-line reversal technique (electronic), to optical flame temperature measurements. The generally excellent agreements obtained, with critical evaluation of caveats among the techniques were presented at the Tenth Materials Research Symposium on Characterization of High Temperature Vapors and Gases. Observations were made via the position dependent techniques which indicated the occurrence of temperature inhomogeneities as well as non-equilibrium among degrees of freedom in hotter flames in/near the reaction zone.

In conjunction with the Center for Fire Research a laser induced two line fluorescence apparatus is also being developed for temporally and spatially resolved temperature measurements in turbulent flames. This is an important measurement problem as most practical combustion devices operate under turbulent conditions.

Also in conjunction with CFR, laser fluorescence and particulate scattering experiments are in progress on smoky diffusion flames. These experiments are designed to determine the relative role of neutral atoms versus ions in smoke and particulate formations in an alkali seeded flame. The increased thermal ionization of laser excited atoms (the opto-galvanic effect) is used to alter the neutral/ion ratio. The same burner will also be physically coupled to the VPHMS system for mass spectroscopic measurements to correlate with the optical particle scattering experiments.

In support of these experiments, modeling and additional experiments have been done on the rate of ionization of highly excited atoms. In these experiments two lasers (or a two photon absorption) is used to place the atoms within kT of the ionization continuum, resulting in almost total ionization. Ionization rates, which are important in the above studies, may be deduced from these experiments. In addition, the use of multiple laser excitation, has increased the sensitivity of metal atom detection in flames up to three orders of magnitude (joint with CAC). Since alkali metals are common contaminants in coal slag and other metals are added as flame inhibitors in plastics, increased sensitivity is important.

Other accomplishments in FY 79 include measurement of OH and H atom concentrations in representative model flames by optical absorption and emission methods to provide a needed base for planned work in alkali seeded flames and analysis of previously obtained Raman spectroscopic data on flame temperatures for HBr inhibited flames.

Solid-State Transport and Stability

A. D. Franklin, C. K. Chiang, A. L. Dragoo, and J. R. Bethin[1]

[1] Postdoctoral Research Associate

The Solid State Transport and Stability subtask is concerned with the general area of ionic mobility in ceramic and other ionic solids. The emphasis is on understanding the underlying processes and developing techniques for identifying and studying them and for monitoring materials performance in service. Experimental tools include not only ionic conductivity, but also other means of observing the position and motion of ions in crystals, such as dielectric relaxation, electron spin resonance, and anelastic relaxation.

Current focus is on solid electrolytes, with attention to two important aspects. One is the nature of the charge transport process itself, in the crystal lattice and across interfaces such as the grain boundaries and at the electrode-electrolyte interface. It is desirable in practice, for maximum efficiency, to minimize the resistance of a solid electrolyte device, such as a fuel cell or battery, including that arising at the interfaces. Lifetime of the device depends on the stability with respect to processes allowing this resistance to rise in service. At present no good technique exists for separately measuring these various contributions to the resistance, nor are the factors controlling the interface resistance at all understood. The other important aspect concerns directly the long-term stability of solid electrolytes with respect to both the gross and the atomic-scale structure, and especially with respect to such processes as defect clustering, order-disorder crystal structure transformations, and dopant-ion drift under steady electric fields. These are processes expected to influence the crystal lattice resistance and therefore to contribute to degradation of the desirable properties in service. Data on these changes and their rates in the fluorite-structure oxides are needed in assessing the potential of these materials as electrolytes in fuel cells and other devices.

This work is of direct interest to several industry groups using solid electrolytes in their products and processes. The technologies involved include fuel cells for utility power generation and transportation motive power; high energy density batteries for transportation applications; gas sampling probes for industrial and automobile process monitoring and control, and for air pollution monitoring; and research instrumentation for gas composition control and measurement. In a more indirect fashion, the techniques we are investigating for grain boundary studies may be useful in following the kinetics of sintering and grain growth in general, and as such should have wide application to the ceramic industry. They should also contain information concerning electron-hole recombination effects at grain boundaries in semiconductors, and may prove useful in that industry also. Finally, the work is directed toward identifying the basic atomistic processes governing the ionic transport in the lattice and across grain boundaries and interfaces, in terms of defect models and the influence of impurities and defect clustering and ordering. The models and techniques developed are expected to further the science of ionic conduction and mass transport in ceramics in a more general way.

We are currently studying cerium dioxide, doped with trivalent and divalent cations, chosen both because of its relation to practical devices and for theoretical interest as a model high-conductivity ionically-conducting ceramic. Considerable work on preparation of research material has resulted in ceramic specimens of apparently high purity and homogeneity, and whose porosity is about an order of magnitude lower than the lowest achieved elsewhere.

Nature of the Charge Transport Process

A. D. Franklin, C. K. Chiang, and J. R. Bethin

The dispersion of the impedance of polycrystalline conductors (with respect to the frequency of the measuring signal) contains information about charge transport in the interior of the grains, at grain boundaries and other inhomogeneities, and at the interfaces with electrodes. A major theme of the current work is to learn how to extract this information from the data on the frequency dependence of the impedance. Working with Y-doped CeO_2 as a model for high-conductivity ceramics, we have found we can represent the electrical properties in terms of the equivalent circuit shown in the inset of Fig. 1. The symbols are as follows: Cg is the geometric capacitance, R_B the lattice resistance, Z_{gb} represents a contribution that is presumably the grain boundary impedance and Z_{el} the impedance introduced by the interface with the electrodes. The latter two impedances are quite well represented with distributed time constants using the Cole-Cole distribution (K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 341 [1941]).

The figure displays both the experimental values of impedance, plotted in the complex plane with frequency as a parameter over the range from 10 Hz to 1 MHz, and the values derived from a computer fit of the equivalent circuit to the data. Current work is concerned with demonstrating that, in dense ceramics, Z_{gb} does indeed represent grain boundary properties, and in using this new measurement tool to study how materials preparation and treatment influence this part of the transport behavior.

Our data show that Z_{gb} is sensitive to how the material is prepared, a fact that should allow us to determine at least some of the factors influencing the "grain boundary" properties.

The sensitivity of Z_{gb} to preparation methods is shown by a comparison between two sets of Y-doped CeO_2 specimens. Type M materials were prepared by classical ceramic techniques, mixing the separate oxides, calcining the mixture, and either pressing and sintering (~ 1550 °C)

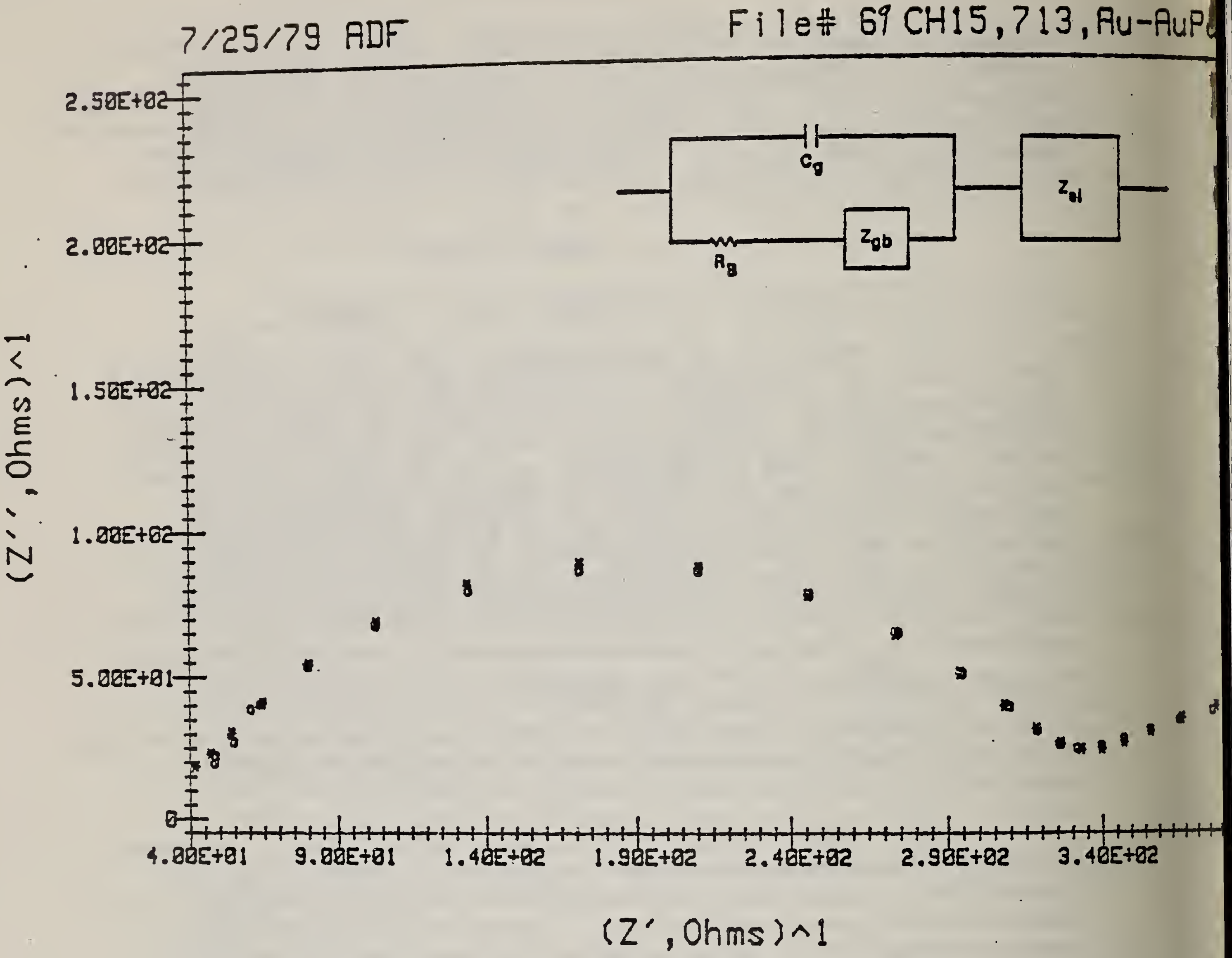

Figure 1. Plot of the impedance of a Y-doped CeO_2 ceramic specimen in the complex plane. The frequency of measurement increases from right to left from 10 Hz to 1 MHz. The open squares are observed values, and the asterisks show calculated values from the inset equivalent circuit with circuit parameters chosen using a non-linear steepest-descent least-squares computer fit.

or hot-pressing (~ 1340 °C) pellets. The mixed oxides for Type C materials, on the other hand, were prepared by homogeneous coprecipitation from aqueous solutions of the nitrates. The impedance parameters at about 236 °C are:

		Density	Lattice†		"Grain Boundary"‡	
Type	Conc.*	% Theory	$\rho, 10^5 \Omega \cdot cm$	ε	$\Delta Z_{gb}, 10^5 \Omega$	C_{gb}, pF
M	10	79	2.2	26	2.9	17
M	20	85	4.0	32	6.3	16
M	10	94	3.1	33	2.0	225
C	10	81	.26	45	1.6	1.7×10^4
C	10	95	.23	45	8.7	1.3×10^4
C	10	< 99.5	1.6	35	31.	0.3×10^4

Legend: * The concentration is the percent of cations represented by Y.

† The lattice properties have been reduced to resistivity (ρ) and dielectric constant (ε) using specimen geometry.

‡ The "grain boundary" parameters are those in the Cole-Cole expression $Z_{gb} = \Delta Z_{gb}/[1 + (jw\tau)^n]$ where j is the imaginary $\sqrt{-1}$, w the circular frequency, τ the relaxation time given by $\tau = \Delta Z \cdot C_{gb}$ and n the distribution parameter. For Type M materials n ~ .5, while for Type C n ~ .9.

While differences in composition and porosity may be reflected somewhat in the impedance parameters, the major difference between the two types lies in the effective grain-boundary capacitances C_{gb} and is much too dramatic to be accounted for in this way. Furthermore, the coprecipitated materials (Type C) exhibit narrow distributions of time constants while those for the Type M are quite broad. Thus a second major theme in current work using impedance measurements is to try to understand compositional and structural differences in the grain boundaries of these two types of materials to correlate with the differences in electrical behavior.

A third major topic in the impedance area is currently getting under way. We will be exploring the use of the impedance technique to examine the electrochemical reactions at the electrode/electrolyte interface, especially with respect to mixed electronic/ionic electrode materials and the influence of the kinetics of ionic motion on the electrode performance. We will again use Y-doped CeO_2 as our model material, and will use a number of electrochemical techniques to identify the controlling processes. An important aim of the work, in addition to delineating the electrochemistry of oxygen ionization on oxide ion-conducting solid electrolytes with oxide (e.g., SnO_2-doped In_2O_3) electrodes, will be to see how these processes appear in the impedance measurements and how the latter may be used to observe and monitor changes occurring during service.

Long Term Stability of Solid Electrolytes

A. D. Franklin and A. L. Dragoo

The basic transport process in ionic conductors is carried on by lattice defects, oxygen vacancies in the case of the doped CeO_2 we are studying. In materials whose conductivity is high enough to be of technological interest, the dopant ion and vacancy concentrations are so high that association among these defects plays a major role in determining the transport properties. This aspect of our work is concerned with elucidating these associations and their interactions with the transport process. We are approaching this problem from both ends of the concentration range, the high end where association will lead to ordered phases and order-disorder transformations, and the low where discrete clusters or complexes of a few defects can be detected.

The stimulation of an order-disorder transformation can be done by long-time anneals, over a range of temperatures and compositions to map the effect on the phase diagram. The furnaces and controls for such long-term anneals are about completed and the anneals will be started in the near future. In addition, by performing some anneals under steady applied fields we can study ion drift as well. The lower-concentration clustering is being studied using the electron spin resonance (esr) of manganese and gadolinium ions serving as dopants in single crystals. The esr signal reflects the symmetry of the surroundings to the dopant ions and therefore indicates the arrangements of nearby point defects (in our case, oxygen vacancies). Because the Mn and Gd esr signals persist to high temperatures, thermally-activated motions of the surrounding defects can be followed. We have obtained lightly doped crystals from Oak Ridge and have detected both Mn^{2+} and Gd^{3+} esr signals. Partial reduction of the crystal, which introduces oxygen vacancies, converts some of the Mn^{2+} ions in cubic surroundings to trigonal symmetry, indicating the formation of Mn^{2+} oxygen vacancy pairs. By studying the temperature dependence of both the intensity and breadth of this pair signal, we should be able to learn much about the kinetics of motion of the oxygen vacancy in the pair and the energetics of formation.

DIVISION 561 ACTIVITIES SUPPORTING NBS RECYCLED OIL PROGRAM

During Fiscal Year 1979, the program of the Chemical Stability and Corrosion Division was augmented by transfer into the Division of a technical group previously assigned to the Bureau's Recycled Oil Program (ROP). The short-term objective of this Tribochemistry Group is to provide a technical base of data and measurement methodology to support the ROP in responding to its mandate, under the Energy Policy and Conservation Act, to develop test procedures to establish the substantial equivalency of new and re-refined oils.

Tribochemistry

S. M. Hsu, J. Comeford, R. S. Gates, C. S. Ku, K. N. Hartman, D. Mathews, and R. G. Crumley[1]

[1] WAE

Current technical activity is directed mainly toward development of measurement methods and standards for re-refined petroleum oil used as automotive crankcase oils. There are four individual project areas:

Chemical and Physical Properties

J. Comeford, S. M. Hsu, and K. N. Hartman

The chemical and physical properties of a lubricating base oil reflect the chemical composition, and hence, at least in theory, determine the performance. There are some twenty tests commonly used to characterize basic chemical and physical properties of base oils. Most of these are ASTM test procedures, such as viscosity, boiling point distribution, sulfur, sulfated ash, water, aniline point, etc. For the purposes of the NBS Recycled Oil Program, each test must be evaluated for applicability and relevance for use with re-refined base oils. Some tests, such as ash, total acid number (TAN), and halogen content, will require modification or new test development.

During the past year, the major effort in this area had been to establish the laboratory capability to evaluate these tests. To facilitate development of in-house capabilities, our staff has made extensive visits to industrial laboratories. Sixteen tests have been set up in our laboratory. Data are being collected on re-refined virgin base oils.

Hydrocarbon Type Analysis

S. M. Hsu, C. S. Ku, and R. G. Crumley

Lubricating oil base stocks are complex mixtures of several types of hydrocarbons. Their detailed molecular composition, while difficult to elucidate, is critical to their performance. Structural characteristics, for example, may hold the key to some observed but as yet unexplained phenomena, such as the observation that sulfur compounds can increase or decrease base oil additive response depending on the crude source.

This portion of the program is concerned with methodology for separation of base hydrocarbon materials into aromatic, saturate, and polar fractions. Gradient elution liquid chromatography is the method of choice for this separation. The polar fraction separated by this technique is of particular interest, since it comprises the most active molecular species in a lubricating base oil. Detailed analytical information on the polar material can then be obtained with a variety of techniques including high pressure liquid chromatography, gas chromatography, mass spectrometry, nuclear magnetic resonance, and IR and UV spectroscopy.

Progress to date in this area has included evaluation of three analytical procedures and data are being collected on seven re-refined lubricating base oils. Information of this type will be correlated with physical and chemical properties and performance.

Oxidation Stability and Deposit Simulation

S. M. Hsu and C. S. Ku

In the area of performance tests for automobile crankcase oils, the industry-accepted tests include the current engine sequence tests (IIC, IIIC, VC, L-38), laboratory truck engine tests (1H2, 1G2, 1D, EMD, T02), full-scale truck engine tests (Mack T-5), fleet tests (Aunt Minnie type, taxi/police fleet heavy duty type, commuter type, tire-track, and EPA cycle type). The expenses involved in running these tests are enormous. There are no commonly accepted chemical/physical laboratory bench tests for indicating in-service performance.

The performance requirements of an automobile crankcase oil are: rust protection; corrosion resistance; low temperature dispersancy (to prevent sludge formation); detergency (to keep engine parts clean); solvancy (to solubilize oxidized products); high temperature stability (to keep piston rings from sticking); viscosity-temperature characteristics (to maintain hydrodynamic lubrication); anti-wear properties; and low frictional resistance. In addition, the oxidation stability of the oil is common to most of these requirements. Laboratory equipment and test procedures for these various performance requirements are numerous (over 100 variations of equipment and test procedures for measurement of friction and wear are contained in a single ASLE publication).

The program plan of the performance testing areas will make use of ASTM Reference Oils as a tool to screen promising procedures. The reference oils are currently being used to monitor all the certified engine test stands in the various testing laboratories all over the U.S. and in some foreign countries. Some of these Reference Oils even have fleet test data available. These oils can be classified into good, bad, and borderline performance oils. By using these Reference Oils, test procedures can be screened for correlation with in-service performance.

A laboratory module has been modified to satisfy the special safety requirements of these tests. Equipment is being set up to simulate the engine service conditions in oxidation stability, high temperature stability, and corrosion.

Friction and Wear

S. M. Hsu and R. S. Gates

The emphasis in this area is on the chemical aspects of friction and wear. In re-refined base oils derived from many sources of used oils, potential contamination by cutting oil additives, and metal-forming oils could have significant effect on friction and wear characteristics of the final product.

A laboratory module had been specially equipped to accommodate three wear test apparatus: ring-on-block, 4-ball, and pin-and-V. Two additional research grade wear test instruments are on order. These are commercial apparatus modified by NBS to facilitate the collection and analysis of wear debris. These machines will allow realistic simulation of automotive power train wear. Other equipment acquired includes a Ferrograph and a profilometer.

A wear debris analysis procedure has been developed to examine the chemical composition of debris. The debris is filtered and solvent extracted into four major fractions: iron, iron oxides, organo-iron compounds which are soluble in oil, and organo-iron compounds which are soluble in pyridine. Coupling this analysis with information obtained from Ferrography (particle size distribution), we can monitor the basic chemical aspects of anti-wear effectiveness of oils. The polar fractions from the hydrocarbon type analysis area will then be examined in wearing contacts.

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Other Division Activity

Invited Talks

Corrosion Protection Principles for Organic Coatings
Mobil Chemical Company, Edison, New Jersey
J. Kruger
September 19, 1978

The Effect of Soil Properties on Underground Corrosion
NACE Northeast Corrosion Control Conference, Newport, Rhode Island
E. Escalante
October 2, 1978

The Role on Noncrystalline Films in Passivation and Breakdown of Passivation
7th International Congress on Metallic Corrosion, Rio de Janeiro, Brasil
J. Kruger
October 5, 1978

Stress Corrosion Testing at Elevated Temperatures in Simulated Coal Conversion Gases
7th International Congress on Metallic Corrosion, Rio de Janeiro, Brasil
J. Kruger for C. E. Johnson
October 9, 1978

An Electrochemical Study of an Al-Zn-Mg Alloy
7th International Congress on Metallic Corrosion, Rio de Janeiro, Brasil
J. Kruger
October 9, 1978

Detection and Analysis of Electrochemical Noise for Corrosion Studies
7th International Congress on Metallic Corrosion, Rio de Janeiro, Brasil
J. Kruger for U. Bertocci
October 9, 1978

Laser-Induced Chemistry
American Chemical Society, Columbus Section, Columbus, Ohio
T. D. Coyle
November 13, 1978

Approaches Toward Designing Corrosion Protective Coatings
Massachusetts Institute of Technology, Cambridge, Massachusetts
J. Kruger
November 30, 1978

Recent Developments in the Bio- and Environmental Chemistry of Tin
34th American Chemical Society Southwest Regional Meeting, Corpus Christi, Texas
F. E. Brinckman
November 30, 1978

Optical and Electrochemical Studies of Corrosion
Joint Physics and Chemistry Symposium, University of Maine, Orono, Maine
J. Kruger
December 1, 1978

New Corrosion Protection Principles for Organic Coatings
Dwight P. Joyce Research Center, Glidden Coatings and Resins, Strongsville, Ohio
J. Kruger
January 16, 1979

New Approaches Toward the Design of Corrosion Protective Organic Coatings
Combined meeting of Detroit Sections of Electrochemical Society and National Association of Corrosion Engineers, Detroit, Michigan
J. Kruger
February 15, 1979

Qualitative Use of Ellipsometry to Study Localized Corrosion Processes
Ford Motor Co. Research Labs, Dearborn, Michigan
J. Kruger
February 15, 1979

The Morphology of Immersion Deposited Zinc on Aluminum
Chemical Stability and Corrosion Division Seminar, NBS
D. S. Lashmore
February 16, 1979

A Field Study on the Corrosion of Concentric Neutral Cables
National Association of Corrosion Engineers, Atlanta, Georgia
E. Escalante
March 1979

Economic Effects of Metallic Corrosion in the U.S.
National Association of Corrosion Engineers, Atlanta, Georgia
J. Kruger
March 1979

Underground Corrosion of Metals
National Association of Corrosion Engineers, Atlanta, Georgia
E. Escalante
March 13, 1979

Important Issues in the Breakdown of Passivity
National Association of Corrosion Engineers, Atlanta, Georgia
J. Kruger
March 13, 1979

Corrosion Induced by an Alternating Voltage. A Comparison Between Theoretical Predictions and Experimental Results
National Association of Corrosion Engineers, Atlanta, Georgia
J. L. Mullen
March 1979

Studies on the Biomethylation of Tin, Arsenic, and Mercury
American Chemical Society, Chemical Society of Japan International Chemical Congress, Honolulu, Hawaii
F. E. Brinckman
April 4, 1979

Applications of High Vacuum Techniques in Laser Chemistry
Introduction to Chemistry Class, NBS
J. J. Ritter
April 1979

Ultra-Black Coating for High Absorptance of Solar Energy
Institute of Environmental Science, Seattle, Washington
C. E. Johnson
April 1979

Chemical Aspects of Fire Retardancy
American Chemical Society, Western Section, Buffalo, New York
T. D. Coyle
April 17, 1979

Corrosion Enhancement Due to Large Voltage Modulations. Experimental Results for Electrodes Under Charge-Transfer Control
ASTM Meeting, San Francisco, California
U. Bertocci
May 1979

Morphology of Immersion Deposits on Aluminum
American Electroplaters' Society, Atlanta, Georgia
D. S. Lashmore
June 25, 1979

Corrosion in Soil
New England Gas Assoc., Gas Operations School, Boston, Massachusetts
E. Escalante
June 1979

New Developments in the Economics and Science of Corrosion
Washington Chapter-American Society of Metals, Bethesda, Maryland
J. Kruger
June 1979

Abiotic and Biogenic Transformations of Organotins in Aqueous
Media: The Problem of Speciation
Department of Chemistry, University of Noddingham, Noddingham,
England
F. E. Brinckman
July 5, 1979

Corrosion, Sagamore Army Materials
Research Conference, Bolton Landing, New York
J. Kruger
July 1979

Microbial Transformations of Heavy Metals
XIth International Congress of Biochemistry, Toronto, Canada
W. P. Iverson
July 13, 1979

New Methods for Speciation of Bioactive Organotinleachates from
Antifouling Paints and Polymers
6th International Symposium on Controlled Release of Bioactive
Materials, New Orleans, Louisiana
K. L. Jewett
August 7, 1979

Ellipsometric Studies of Film Growth Under Organic Coatings on Iron
Fourth International Conference on Ellipsometry, University of
California, Berkeley, California
J. J. Ritter
August 1979

Soils and Underground Corrosion
Liberty Bell Corrosion Course, Philadephia, Pennsylvania
E. Escalante
September 1979

Biological and Abiotic Transformations of Organometallics in
Aqueous Media
IXth International Conference on Organometallic Chemistry,
University of Dijon, Dijon, France
T. D. Coyle
September 1979

Important Issues in the Breakdown of Corrosion
National Association of Corrosion Engineers, Canadian Regional Meeting, Ottawa, Ontario, Canada
J. Kruger
October 1979

Economic Effects of Metallic Corrosion in the U.S.
National Association of Corrosion Engineers, Canadian Regional Meeting, Ottawa, Ontario, Canada
J. Kruger
October 1979

A Review of Techniques for Measuring the Corrosion of Metals in Soil
ASTM Underground Corrosion Symposium, Williamsburg, Virginia
E. Escalante
November 1979

The Biosphere as a Perturbation of the Cosmic Environment--The Question of Elemental Availability and Essentiality
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
April 19, 1979

Considerations of Chemical Solubility and Biological Mobilization
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
April 20, 1979

Materials Cycles--Natural and Anthropogenic
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
April 26, 1979

Heavy Metal Pollution--Scope and Prospect
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
April 27, 1979

What Can We--What Must We--Measure?
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
May 3, 1979

Status Report on Biogeochemical Mobilization of Heavy Metal Species
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
May 4, 1979

Synthesis--What Can We Expect for Heavy Metal Pollution?
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
May 10, 1979

Technology to the Rescue--Maybe
Johannes Gutenberg University, Mainz, F.R.G.
F. E. Brinckman
May 11, 1979

Biotransformations and Speciation of Organoarsenicals and Organotins in Aquatic Systems
Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), Zurich, Switzerland
F. E. Brinckman
August 13, 1979

Biotransformations and Speciation of Organoarsenicals and Organotins in Aquatic Systems
University of Stockholm, Stockholm, Sweden
F. E. Brinckman
August 20, 1979

Opto-Galvanic Spectroscopy: A New Look at Atoms and Molecules
University of Maryland, College Park, Maryland
P. K. Schenck
February 1979

Vapor Pressure Measurements of Potassium Over K_2O-SiO_2 Solution by a Knudsen Effusion Mass Spectrometric Method
10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, NBS
E. R. Plante
September 18-22, 1978

Optogalvanic Spectroscopy: A New Look at Atoms and Molecules
10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, NBS
K. C. Smyth, P. K. Schenck, W. G. Mallard, and J. C. Travis
September 18-22, 1978

A Comparison of Optical Flame Temperature Measurements: Na Line Reversal, Rotational and Vibrational Raman, and OH Absorption Spectroscopy
10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, NBS
M. Drake, L. Grabner, and J. W. Hastie
September 18-22, 1978

Transpiration Mass Spectrometry of High Temperature Vapors
10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, NBS
D. Bonnell and J. W. Hastie
September 18-22, 1978

Raman Spectroscopy in High Temperature Chemistry
10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, NBS
M. C. Drake and G. M. Rosenblatt
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Slag and Metal Oxide Vaporization in Reactive Atmospheres
International Colloquim--Use of Refractory Oxides for High Temperature Energy Sources, Toronto, Canada
J. W. Hastie
July 15-20, 1979

Molecular Chemistry of Inhibited Combustion Systems
ARO--Engine Combustion Workshop, Madison, Wisconsin
J. W. Hastie
July 22-24, 1979

Synthesis, Structure and Electrical Properties of Doped Polyacetylene
International Conference on Transport Processes in Macromolecular Systems, Konigstein/Ts., Germany
C. K. Chiang
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F. Ogburn and D. Ballard
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Spectroscopy and Photophysics of the $CF_2\tilde{A}{}^1B_1-X{}^1\tilde{A}_1$ System
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Improved Sensitivity for Laser Enhanced Ionization Spectrometry in Flames Using Stepwise Excitation
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Inorganic Chemistry, 18, No. 7, 1947-1951 (1979)

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T. D. Coyle and A. R. Siedle
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      1: Terminology, Delegate
      2: Methods of Inspection and Coordination of Test Methods, Delegate
      3: Electrodeposited Coatings and Related Finishes, Delegate
      7: Corrosion Tests, Delegate

  TC156: Corrosion of Metals
    J. Kruger, Delegate:
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Offshore Technology Conference
  Executive Committee
  J. Kruger, Member

Surgeon's General Review Panel on Special Surveillance Program for Leaking Weteye Bombs
J. Kruger, Member

Seminar Summary

Current Understanding of Stress Corrosion Cracking
E. N. Pugh
University of Illinois, Urbana, Illinois
June 27, 1978

Microstructure of Electrodeposited Metals
R. Weil
Stevens Institute of Technology, Hoboken, New Jersey
September 26, 1978

Electrodeposition Research in the Communications Industry
D. R. Turner
Bell Telephone Laboratories, Murray Hill, New Jersey
November 1, 1978

Cryptate Complexes of Lanthanide(III) Elements
O. Gansow
Michigan State University, Lansing, Michigan
January 25, 1979

Electrochemical Corrosion Research at the Rockwell Science Center
F. Mansfeld
Rockwell International Science Center, Thousand Oaks, California
February 9, 1979

The Morphology of Immersion Deposited Zinc on Aluminum
D. S. Lashmore
NBS Research Associate, Aluminum Association
February 16, 1979

Organotin Chemistry--New Compounds and Applications. The Existence of the Tin-Tin Double Bond
J. J. Zuckerman
University of Oklahoma, Norman, Oklahoma
February 27, 1979

Electrochemical and Mechanical Aspects of Stress Corrosion Crack Propagation in Face-Centered Cubic Metals
J. C. Scully
University of Leeds, Leeds, England
March 19, 1979

The Role of H_2S and Sulfide Films on the Hydrogen Entry into Iron and Steel in Sour Environment
T. Murata
Nippon Steel Company, Japan
March 19, 1979

The IGSCC of Austenitic Stainless Steels in High Temperature Water Containing 8 ppm O_2
H. Hanninen
Technical Research Center of Finland
March 20, 1979

Studies of Early European Iron Slags
G. Sperl
Erich Schmid Institute, Loeben, Austria
April 18, 1979

Preparation and Characterization of Thin Oxygen-Ion Conducting Ceramics
A. L. Dragoo
NBS, Division 561
April 27, 1979

Conservation Treatment of Oil Paintings and the Detection of Forgeries
C. H. Olin
Great Falls, Virginia
June 13, 1979

High Resolution NMR of Solids
J. Riemer
California Institute of Technology, Pasadena, California
June 29, 1979

External Recognition

Richard Merton Visiting Professor
Johannes Gutenberg University
Mainz, Federal Republic of Germany
April-May; June-September, 1979
F. E. Brinckman

George Kimball Burgess Memorial Lecture for the year 1979
Washington Chapter
American Society of Metals
June 1979
J. Kruger

Books

Organometals and Organometalloids: Occurrence and Fate in the Environment
Edited by F. E. Brinckman and J. M. Bellama
American Chemical Society Symposium Series No. 82
Washington, D. C., 448 pages
1978

Passivity of Metals
Edited by R. P. Frankenthal and J. Kruger
Electrochemical Society, Princeton, New Jersey, 1072 pages
1978

Characterization of High Temperature Vapors and Gases
Edited by J. W. Hastie
Proceedings of the 10th Materials Research Symposium, NBS, September 18-22, 1979
in press

Special Reports

A Bibliography on the Corrosion and Protection of Steel in Concrete
E. Escalante and S. Ito
NBS Special Publication 550 (August 1979)

Stress Corrosion Behavior of 7049-T76510, -T73510, and -T7351]
Aluminum Alloy Extrusions
B. T. Sanderson and W. F. Gerhold
NBSIR 78-1587 (Report to Naval Air Systems Command) (1979)

A Review of Techniques for Measuring the Corrosion of Metals in
Concrete
E. Escalante
NBSIR, (Report to the Federal Highway Administration)
in press

Passive Films, Surface Structure, and Stress Corrosion and Crevice
Corrosion Susceptibility
J. Kruger, J. J. Carroll, A. J. Melmed, J. J. Ritter, and J. R.
Ambrose
NBSIR, (Report to the Office of Naval Research)
in press

Recycled Oil Program: Phase 1--Test Procedures for Recycled Oil
Used as Burner Fuel
D. A. Becker and J. J. Comeford
NBSIR 78-1453 (1979)

Standard Reference Materials

The Division produces coating thickness SRMs, used to calibrate coating thickness gages. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one surface of which has an electroplated coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are made ranging in thickness from 0.7 μm to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) They are designed for use with either magnetic type or beta backscatter type thickness gages.

These SRMs are packaged in sets and the SRM catalog lists some 31 different sets. About 3000 individual coating thickness standards were produced during FY 78, and the same number were produced during FY 79.

The Division is also in the process of developing NMR SRMs to be used for calibration of NMR spectrometers. A single SRM will consist of two seven-inch long NMR tubes, 5 mm and 10 mm (or 12 mm) in diameter, respectively. The tubes will contain a mixture of organic liquids sealed in an inert atmosphere and will be calibrated for proton line positions (five lines) and carbon-13 line positions (eight lines). It is expected that the initial stock will consist of 200 NMR tubes.

Patents

Enrichment of Chlorine Isotopes by Visible Laser Techniques
J. J. Ritter
May 24, 1977
U. S. Patent 4,025,406

Ultra-Black Coating Due to Surface Morphology
C. E. Johnson
NBS Case No. 1760
Filed April 1979

Apparatus for Galvanic Detection of Optical Absorptions
R. B. Green, R. A. Keller, G. G. Luther, P. K. Schenck, and J. C. Travis
April 10, 1979
U. S. Patent 4,148,586

Sponsored Conferences

Corrosion General Session, Corrosion Division
Electrochemical Society, Boston, Massachusetts
May 8, 1979
J. Kruger

Progress in Electrochemical Corrosion Testing
ASTM, San Francisco, California
May 21-24, 1979
U. Bertocci

Corrosion General Session, Corrosion Division
Electrochemical Society, Pittsburgh, Pennsylvania
October 17, 1979
J. Kruger

Underground Corrosion Symposium
ASTM, Williamsburg, Virginia
November 26-27, 1979
E. Escalante

Early Pyrotechnology
Smithsonian Institution and NBS, Washington, DC
April 19-20, 1979
A. D. Franklin and J. Olin

FRACTURE AND DEFORMATION DIVISION

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FRACTURE AND DEFORMATION DIVISION

Richard P. Reed, Acting Chief
Sheldon M. Wiederhorn, Deputy Chief
D. C. Shields, Administrative Assistant
C. J. Montgomery, Secretary
P. L. Salpino, Secretary
D. L. Mills, Secretary

The Division research emphasizes mechanical property and fracture mechanics theory and experiment. Fracture and deformation mechanisms are explored. New test standards are developed and characterized. Techniques of microscopy and nondestructive inspection are used in failure analyses and evaluation of fracture mechanisms, deformation, wear, oxidation, and effects of defects. Research relates predominantly to metals and alloys, ceramics, and composites.

During this past year, the NBS-Boulder fracture mechanics and mechanical property group has been integrated into the Fracture and Deformation Division. The Boulder-based group complements the Division, since it has specialized in low-temperature mechanical properties and, recently, in elastic-plastic fracture mechanics. This combination encompasses most of the NBS mechanical property research and all of the NBS fracture mechanics activities. Research at both high and low temperature extremes is represented. A core group in fracture mechanics will provide the means to grow in that area in the near future.

The strengths of the new Division can be generalized by the following categories: deformation and fracture of ceramics, failure analysis, low-temperature mechanical properties and fracture, development of test standards, fracture control, and effects of weld defects. Research this past year related to these five Division specialties is briefly summarized here. Studies of ceramics include creep rupture at elevated temperatures; erosive wear and strength degradation from particle impact; high-temperature, high-pressure compressive strengths of castable refractories; flexural and compressive strength characterization of geothermal cements; effects of microstructure on stress-corrosion cracking of aluminum oxide for prosthetic applications; and electron microscopy studies. Special failure analysis tasks this past year have included the second Silver Memorial Bridge failure (Pt. Pleasant, West Virginia), a seamless welded steel pressure vessel that ruptured while being filled with natural gas, and railroad wheel and tank car failures. Low-temperature research included an assessment of carbon and nitrogen additions to the strength and toughness of austenitic stainless steels at liquid helium temperatures (4 K), the tensile, shear, and compressive characterization of fiberglass/epoxy composites at low temperatures, the characterization of the temperature dependence of the flow strength of austenitic stainless steels from 4 to 100 K, and further development of welding alloys and processes for the use of stainless steels in cryogenic applications. Research has progressed on J-integral, precracked Charpy impact, and on assistance to ASTM in the establishment of standard test procedures and specimen parameters. Research to establish alternative allowable defect size standards, based on fitness-for-service, previously conducted for the trans-Alaska oil pipeline, is now progressing for the Alaska Natural Gas Transportation System and includes pipe and weldment material properties, elastic-plastic-model development and verification, and nondestructive inspection to measure defect length and depth.

Our technical outputs are directed toward a broad range of government and industrial users. The emphasis on fusion, magnetohydrodynamics (MHD), coal gasification, and geothermal energy by the Department of Energy has led to low-temperature research for structural containment of the large magnetic fields produced by superconducting magnets, an assessment of future low-temperature material requirements for superconducting magnets used in MHD, characterization of castable refractories at high temperatures and pressures, the development of an in situ evaluation test to assess metal susceptibility to high-temperature, high-pressure environmentally assisted metal cracking, and property characterization of geothermal cements.

Transportation-related research includes the establishment of inspection and alternative allowable defect size standards for pipeline girth welds, mechanical property and microstructural characterization of pressure tank-car steels and railroad wheels, fracture mechanics assessment of tank-car behavior, and numerous structural metal fracture analyses.

The research for the Department of Defense is diverse with the objectives to assist the Navy in the eventual up-grading of their fracture control plans, to identify material limitations in ultrasensitive gyroscopes used in inertial guidance systems, study of the applicability of proof testing to nitride and carbide ceramics that have potential use in gas turbine engines, to conduct erosion and wear experiments of ceramics to attempt to reduce machining costs, to examine the low-temperature material properties related to the use of superconducting motors and generators for ship propulsion, and to assist the Air Force in using advanced composites in light-weight superconducting magnet airborne power packages.

The Division manages as well as conducts research for three programs: (1) Evaluation of Pipeline Girth Welds for the Department of Transportation, (2) Structural Materials Research at Low Temperatures for Superconducting Magnets for Fusion Applications for the Department of Energy, and (3) Cryogenic Materials and Welds for the US/USSR Science and Technology Program of the National Science Foundation. In these programs, the collaboration of industries and universities is beneficial, and research subcontracts are issued to contributing laboratories.

Considerable emphasis is placed on technology transfer. We currently have two books in preparation: Materials at Low Temperatures (containing tutorial chapters on mechanical and physical properties, materials, and special considerations for use of materials in cryogenic applications) and a "Summary of Fracture Mechanics Concepts" (by R. deWit in collaboration with G. R. Irwin, University of Maryland). Workshops on Materials at Cryogenic Temperatures are held annually at Vail, Colorado, in collaboration with the Department of Energy. This year, in collaboration with various coordinating groups, four Workshops related to ceramics were held at NBS-Gaithersburg. The Division plays a major role in the establishment (1975) and operation of the International Cryogenic Materials Conference, which holds yearly international conferences, that are growing rapidly. It organized and leads a group of six other industrial concerns and universities in the US/USSR Science and Technology Joint Exchange Program on Electrometallurgy. The Failure Information Center is maintained to provide materials information on failures in coal gasification and conversion plants; we are collaborating with the Department of Energy and Battelle Memorial Institute in this effort.

Because of the NBS Materials Durability Initiative, in this next year our Division will have the opportunity to emphasize new research thrusts. The need for extension of workmanship codes to fitness-for-service alternatives for reduction of repair welds, for assessment of specific defects in critical structures, for fracture control plans of critical structures, and for lifetime estimates of structural integrity has placed increasing emphasis on elastic-plastic fracture mechanics. Elastic-plastic fracture mechanics models and methodologies are needed, instead of the more traditional elastic mechanics approach, since essentially all structural alloys for critical applications are selected to ensure against crack instability preceding plastic deformation. Therefore, research concentrating on test methodologies, model development and verification, effects of defects and subcritical crack growth, all related to elastic-plastic or fully plastic conditions, will be initiated.

Secondly, although the Division has studied the high-temperature aspects of ceramic durability, we have not placed emphasis on high temperature or time-dependent studies of metals. Such research is timely, since new energy conversion systems, plasma containment systems, and nuclear systems all have current serious material selection and durability problems associated with the understanding and characterization of time-dependent fracture processes in structural alloys. Study of crack-tip fracture mechanisms, characterization of fracture processes and generation of property data, emphasizing creep and fatigue, will provide new insight to assist in high-temperature design and material selection.

These new directions, plus the addition of the staff from Boulder, have led our Division to modify and expand our primary research tasks for the next year. This past year our two tasks have been:

1. Fracture and Deformation Science for Durability and Reliability of Metallic Structures and

2. Fracture and Deformation Science for Durability and Reliability of Ceramic Structures

To replace these two tasks, we will establish three new tasks for the Fracture and Deformation Division:

1. Fracture Mechanisms and Analyses
2. Durability of Ceramics and Composites
3. Elastic-Plastic Fracture Mechanics

Research within our Division will be discussed under Subtasks of these three tasks. It must be considered, however, that these objectives have been established just recently and that the research for the past year was directed primarily toward the objectives established for the earlier tasks. Tasks 1 and 3 will receive greater emphasis from the opportunities under the Materials Durability Initiative; included as part of the introduction to each task will be a brief discussion of this expected new research.

FRACTURE MECHANISMS AND ANALYSES

Fundamental understanding of crack-tip processes is vital to an understanding of fracture and to the development of long-term failure prediction techniques for structural materials. The influences of atomic structure and chemical reactions at the crack tip are demonstrated from atomistic models of fracture in a solid, but these influences remain to be confirmed quantitatively by experimental studies of subcritical crack growth and environmental effects. Ductile processes in the high-stress region of the crack tip must be introduced into these atomistic models to assess the role of plastic deformation and to extend the theoretical models to describe crack growth phenomena such as fatigue. High-temperature fracture is complex; the influences of microstructure, impurity content and segregation, processing history, and environment combine to influence competitive fracture mechanisms, such as subcritical crack growth, cavity nucleation and growth, and grain boundary sliding.

Failure analysis studies perform a valuable service for those government agencies that have no facilities and indicate that research is required for safe performance of structural materials. By using modern metallographic, x-ray, fractographic, and chemical analyses techniques and maintaining a Failure Information Center, our Division serves as a focal point for analyses and compilation of many critical structural failures.

Because of the Materials Durability Initiative, there will be increased emphasis on high-temperature fracture processes and mechanisms. Crack-tip theory coupled with high-temperature tensile, creep, and fatigue research will be directed toward increasing our understanding of the fracture of metals under time-dependent conditions.

The Fracture Mechanisms and Analyses Task is subdivided into four subtasks: Fracture Theory, Plastic Deformation of Metals, Failure Deformation Center, and Failure Avoidance Services. Each of these is summarized below.

Fracture Theory

E. R. Fuller, R. M. Thomson, and S. W. Freiman

Lattice theories of fracture were extended to include the effect of corrosive environment for the simple one-dimensional model of a crack. The solid in which the crack is enclosed consists of two one-dimensional chains of atoms that form a border for the crack and the projected crack plane. The two chains are bonded in the projected crack plane by linear springs; the atoms within each chain are bonded by bendable springs. At the tip of the crack is a nonlinear spring that can also react with the corrosive environment, which is composed of diatomic molecules. Predictions of the stress dependence of the activation energy for crack motion indicate a power law dependence whose exponent varies from 3/2 to 2 depending on the form of the atomic bonds of the solid. General conclusions are: (1) chemical activity accentuates and extends the intrinsic slow crack-growth phenomenon because of the surface absorption activation barrier, and (2) the "chemical" and "mechanical" contributions to the activation energy for slow crack growth are not separable.

Tensile experiments are now being conducted on silicon to attempt to correlate chemical activity, mechanical stress, and crack-tip opening. Optimum selection of environment and temperature is necessary to ensure chemical absorption yet to prevent crack-tip blunting from dislocation processes.

Plastic Deformation of Metals

B. W. Christ and R. S. Polvani

Tensile microcreep in various metals and alloys is measured. Current focus is on instrument-grade beryllium. The overall goal of this work is two-fold: (1) to develop a data base on microcreep (10^{-12} cm/cm-s) for improved design of gyroscopes used in inertial guidance systems for naval applications, and (2) to develop a fundamental understanding of microcreep. This program is a joint effort of two groups within NBS and the Draper Laboratory, Cambridge, Massachusetts.

Microcreep testing of instrument grade beryllium has been carried out at about 63 °C (145 °F), and temperature control is held to ± 0.005 °C (0.01 °F) on a testing system designed to detect strains in the range of 10^{-7}. A major finding is the phenomenon of microcreep exhaustion, i.e., loss of the ability for continued microcreep. This phenomenon is attributed to the exhaustion of glide dislocations through an as-yet-to-be-identified microstrain hardening process. The potential of microcreep exhaustion for promoting ultradimensional stability in gyroscope structural components will be explored.

The building of a second testing system designed like the first is nearing completion. A third testing system designed to detect strains in the range of 10^{-8} has been completed. Testing for zero-applied-stress dimensional stability of instrument-grade beryllium is being undertaken. A fourth testing system to obtain biaxial microcreep data is being designed. A review paper surveying the micromechanical properties of beryllium is nearing completion.

Failure Information Center

R. C. Dobbyn and W. A. Willard

The Failure Information Center assists the coal conversion industry in extending the useful life and reliability of plant components by maintaining a central source of information on the performance, especially failures, of materials and components used in coal conversion environments. It provides an integrated materials properties data base for materials of construction to aid the coal conversion industry in the design, construction, and operation of plants converting coal to alternate energy forms, including MHD power generation. Finally, it collects and evaluates the appropriate information, maintains suitable computer files for ready retrieval, and disseminates the data in convenient form to the users.

Sources of the information compiled by the Failure Information Center include operators of all gasification and liquefaction processes, from bench-scale units through operating pilot plants participating in the DoE voluntary failure reporting program. Informational detail varies from one-page failure occurrence reports to final reports of laboratory analyses of failed parts.

A computerized data base of approximately 500 reported failures has been established and is continually being updated, refined and increased as additional failure reports are received. Separate information items addressing the same failure are collated when possible. In addition, direct contact with operating personnel at the various process locations and with failure analysis laboratory staff has enhanced the quality and the flow of information and assisted plant operators in problem solving.

Several draft reports have been assembled and other dissemination schemes are being explored. One output mechanism that has proved successful is the failure experiences feature in DoE's Materials and Components Newsletter, in which NBS and Battelle-Columbus cooperate. Requests for additional details are received regularly from Newsletter readers.

At present, the Center produces sets of abstracts covering all reported incident and sorted according to material, component type, failure mode, and conversion process, or any combination of these. The abstracts are intensive summaries constructed from the source document and contain all reported data.

During the past year, the Failure Information Center has completed a detailed study of the performance of materials used in the Conoco Lignite Gasification Pilot Plant (CO_2 Acceptor Process). The study is based on the information contained in plant operating records and is not limited to reported failures. A complete report is now available. In addition, the Center responded to 68 requests for information and supplied over 2800 reports and abstracts summarizing the details of in-service materials performance.

Failure Avoidance Services

B. W. Christ, C. G. Interrante, J. G. Early, T. R. Shives, and
G. E. Hicho

Failure avoidance services are provided to other government agencies and to other NBS Divisions. Services provided include diagnostic failure analysis, mechanical testing, metallographic analysis, and metallurgical consultation. Sponsoring agencies include the Office of Pipeline Safety Regulations and other branches of the Department of Transportation, the National Transportation Safety Board, the Department of Defense, the Consumer Product Safety Commission, the Bureau of Engraving and Printing, and the Department of Agriculture. These sponsoring agencies have responsibilities in matters of public safety, productivity, national defense, and the promotion of effective and responsive regulations. When structural failures occur or when metallurgical problems arise, NBS responds immediately to help the sponsoring agency. NBS provides a prompt and objective assessment of the cause of failure based on metallurgical evaluation and nondestructive examination of the material and a structural analysis based on mechanical properties measurements and fracture mechanics concepts.

This past year, 15 reports were issued to sponsoring agencies; they are listed later in this report. These are reports of structural failures that occurred in pressure vessels, aircraft components, railroad tank cars, gas distribution lines, amusement park rides, seat belts, fuel pumps, printing plates, bicycle parts, and building construction materials. Highlights are listed below:

A seamless steel pressure vessel in natural gas service ruptured violently via hydrogen embrittlement arising from 600 ppm H_2S impurity in the gas reacting with extremely hard microzones (HRC 40) in the steel.

A year-old steel gas distribution line rupture was due to stress corrosion.

A bicycle crank fracture was due to brittle zones that developed during improper heat treatment.

DURABILITY OF CERAMICS AND COMPOSITES

The durability of ceramic and composite materials is studied to provide assurance of the reliability of these materials in structural applications. Ceramic materials are used in many critical applications where properties, such as chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and physical resistance to temperature extremes, are required. Ceramics, such as glasses, refractory concretes, geothermal cements, porcelains, and high density ceramics, are used in commercial applications, such as containers for nuclear waste disposal, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, thread guides and wear surfaces for paper and clothing manufacture, cutting tools and cutoff wheels for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for the coal conversion and petrochemical industries. In defense applications, these materials are used as radomes, missile nose cones, turbine components in portable electric generating facilities, and bearing surfaces in gyroscopes. In many applications resistance to mechanical abuse is crucial in determining the successful use of ceramic materials. Because they are brittle, structural ceramics are usually overdesigned to satisfy engineering requirements or are not used, even though they have other outstanding properties. By investigating the fracture and deformation properties of these materials, many difficulties associated with their brittle behavior may be overcome.

In contrast to metals or ceramics, composite materials are highly engineered, heterogeneous materials designed to impart unique, superior properties not achievable with conventional materials. Composites offer the possibility of high strength, light weight, and durable structures. In typical advanced composites, the strength-to-weight ratio is an order of magnitude larger than normal grades of steel. Extensive commercialization of composites will realize major energy and materials savings, enhanced productivity, improved product safety, and enhanced U.S. technological innovative capabilities. The key to effective industrial utilization of composite materials lies in an improvement of our understanding of wear-out and fracture mechanisms in these materials. By investigating the mechanical strength and fracture behavior of a variety of composite materials (ceramic/ceramic, ceramic/ metal, ceramic/polymer, and metal/polymer), many of the problems associated with mechanical degradation will be solved, and composites will be used in a wide variety of industrial applications for their unique properties.

The Fracture and Deformation Division program on ceramics and composites can be divided into the following parts: the development of basic fracture and fracture mechanics information on structural materials, development of new engineering data for design purposes, the investigation of processes that result in erosive and abrasive wear of ceramics and composites, and an investigation of the microstructure of composites and ceramics through the use of light and electron microscopy. Experimental techniques developed by the Division permit us to conduct measurements on the mechanical properties of composites and ceramics over a wide range of experimental conditions: in vacuum at temperatures to

2700 °C, in corrosive environments at temperatures that range from room temperature to 1000 °C, in air at temperatures that range from room temperature to 1500 °C, and at cryogenic temperatures as low as -259 °C. This range of experimental capabilities within the Division is unique.

Fundamentals of Fracture

S. W. Freiman, B. J. Hockey, S. M. Wiederhorn, and E. R. Fuller

The effects of proof testing on the strength of materials were investigated. A theoretical study was conducted to evaluate the effect of single-region and multi-region crack propagation on strength of components after the proof test. In this study, two single-region Weibull-type strength distributions were studied: one with a slope of m at high cumulative failure probability levels; the other with a slope of R-2 at low failure probability levels.* Truncation of the strength distribution always occurs as the result of proof testing; the truncation strength depends on the rate of unloading. In contrast to these results for single-region crack propagation, multi-region crack propagation results in a more complicated strength distribution after proof testing. Bimodal strength distributions occur as a consequence of region-II-type crack growth (i.e., R-0). Theoretical results confirm experimental findings that proof tests must be conducted at rapid unloading rates and with good environmental control to be effective. Experimental investigations are currently underway to check the predictions of this theoretical model of proof testing.

Secondly, a new analytical technique, electron scanning for chemical analysis (ESCA), was applied to analyze the type of chemical reactions that occur during the stress corrosion of ceramic materials. This, coupled with other techniques, will enable analysis of chemical species that form on freshly fractured surfaces that are exposed to active environments. During the past year, the surface analysis system, which includes ESCA, SIMS, and Auger spectroscopy, arrived and was put into operation. The thin-film deposition system, which will be used to make test specimens, is being attached to the surface analysis system so fresh uncontaminated surfaces of ceramic material can be analyzed when the equipment is fully operational. To study the effect of stress on the chemical reactions, a specimen holder that can stress the thin film has been designed and built. The holder is held in a shuttle that goes between the film deposition chamber and the analysis chamber. A thin film of ceramic is formed on a substrate, which is then stressed using a micromanipulator, reacted with an environment and transferred into the analysis chamber for examination. To date, thin films of aluminum oxide have been deposited on aluminum using an electron beam deposition system that is part of the apparatus. In the coming year, we hope to use the

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* m is the shape factor of the Weibull Strength distribution before proof testing; R is the exponent of the stress intensity factor, K_I, assuming that the crack velocity can be expressed as a power function of the stress intensity factor: $v = AKI^n$.

apparatus for chemical analysis of stressed ceramics and glasses. This project is being conducted jointly between the Fracture and Deformation Division (S. W. Freiman) and the Ceramics, Glass, and Solid State Science Division (D. M. Sanders).

New Techniques for Obtaining Fracture and Deformation Information

E. R. Fuller, S. W. Freiman, S. M. Wiederhorn, R. J. Fields, and N. J. Tighe

Fracture mechanics provides engineers with new design techniques for estimating the total allowable lifetime under load. Fracture mechanics techniques can be used in this application when mechanisms of failure are well understood. For ceramic materials, the primary mechanism of failure at low temperatures is subcritical crack growth, whereas that occurring at elevated temperatures is creep and creep cracking. By characterizing creep and fracture processes in ceramic materials, estimates of the creep rate or the crack growth rate can be made, and the lifetime of structural components can be determined. The success of this approach depends, in part, on the quality of the creep and crack growth data used to characterize the fatigue behavior of structural materials.

To improve our ability to collect useful data for lifetime predictions, a new type of loading apparatus was developed for dead-weight loading of structural ceramic materials. The technique involves the use of pneumatic loading as a substitute for the dead-weight loading usually used for constant-load experiments. The pneumatic system has several advantages over the dead-weight system. It is inexpensive and compact; a number of them can be used simultaneously for experimental purposes without requiring a great deal of space for operations. Their advantage of space efficiency was used in the construction of a high-temperature fracture mechanics facility, which was designed so that three loading fixtures were operated within each furnace. A similar facility is now under construction for evaluating the creep resistance of refractory materials for regenerative heat exchangers in large MHD facilities. The pneumatic test facilities have the further advantage that when the static load test has been completed, it is possible to load the specimens pneumatically so the strength can be measured. A pneumatic loading facility is also being constructed as an integral part of our bioceramic test program. Here the compactness of the system has an advantage for the construction of a multiple test facility that has the proper biological environment for testing materials that are intended for use as prosthetic devices.

Often our ability to assess materials in new environments depends as much on the way we view the engineering information available on a material as it does on the information itself. In the past year, a new method of expressing crack growth data has been developed that clearly delineates mechanisms of crack growth as a function of temperature and stress intensity factor. The experimentally controllable parameters, I_I and T, are plotted as ordinate and abscissa related by contours of constant material response, i.e., crack velocity. This sort of map emphasizes changes in a materials fracture resistance as either the temperature or the stress intensity factor change. In general, the resistance of a material to slow cracking or fracture depends upon the temperature and the load level. Any change in mechanism of cracking or fracture will manifest itself as a change in dependence on these two controlling parameters. On the map, such a change would be indicated by an abrupt change in slope of the constant velocity contour lines. The loci of such slope changes define boundaries between different mechanisms of slow crack growth or fast fracture. The boundaries may be sharp or diffuse, but within a set of boundaries exists a region in which one mechanism of slow crack growth or fracture is dominant. This new type of map has been applied to high-temperature fracture data on hot-pressed silicon nitride, providing a clear picture of the regions over which each mechanism of crack growth is dominant. During the coming year, it is intended to apply this new mapping procedure to other ceramic and metal materials to see if mechanisms for crack growth can also be clearly represented for these materials.

Engineering Evaluation of Ceramics

E. R. Fuller, N. J. Tighe, S. M. Wiederhorn, S. W. Freiman,
D. E. Roberts, C. L. McDaniel, and R. F. Krause, Jr.

Extensive studies are being conducted on the strength of ceramic materials that are intended for use in a number of important commercial and defense applications. Materials being studied include: castable refractories for coal gasification application, geothermal cements that will be used to line the wells that tap hot reservoirs of water deep within the earth, specialty ceramics that are intended for use in heat engines, dense ceramic materials for prosthetic devices, alkali halides for scintillation counters in deep space NASA gamma ray observatories, dielectric materials for ceramic capacitors intended for defense applications, and refractories for regenerative heat exchangers used in MHD applications.

Work on castable refractories is being conducted because of the intended use of three refractories in coal gasification applications, where strength must be maintained under severe environmental conditions. The objectives of the project are to characterize the mechanical properties (strength, erosion resistance, and fracture toughness) that relate to the structural integrity of refractory concretes intended for use in coal conversion systems, to correlate these mechanical properties with microstructural changes that are induced by the reactive environment and to develop equipment and test procedures to assess the reliability and durability of castable refractories. Our major accomplishment last year was the completion of a high-pressure, high-temperature mechanical test machine that will be capable of measuring strength in gasification environments at extreme temperatures (100 °C) and pressures (7 MPa, 1000 psi) for these environments. The unit has been operated at design conditions. Initial experiments were conducted in steam at temperatures as high as 1000 °C on both a low (56%) aluminum oxide refractory and a high (94%) aluminum oxide refractory. Results of these initial experiments are consistent with results from previous experiments in which the strength was tested after high-temperature, high-pressure exposure. Results indicate that the lower purity (and cheaper) 56% aluminum oxide refractory is superior for coal gasification reactor linings. As noted in earlier reports on the Department of Energy, this result should contribute to substantial savings in the construction costs of gasifiers through the use of the less expensive refractory.

The program on geothermal cements was initiated to develop a laboratory test facility for screening candidate cementing materials that are to be used in finishing operations of geothermal well holes. The program will provide the technical data necessary for an evaluation of the structural integrity of these cements after they have been exposed to high-pressure, high-temperature brine. The suitability of these cements for more costly tests in down hole facilities will be evaluated for the Department of Energy. The program is divided into several tasks aimed at establishing the physical properties of cements after they have been exposed to simulated geothermal environments. Physical properties to be measured include flexural and compressive strengths, strengths of cement pipe interfaces, and cement permeability at elevated pressures and temperatures. The equipment for this study has been designed and is being built. Proposed procedures for these tests have been drafted and submitted to an American Petroleum Institute Task Group for evaluation. These procedures have been approved tentatively with a final vote expected in the fall of 1979.

At the request of the Department of Energy, a special series of screening tests was conducted on geothermal cements to evaluate the performance of a special group of cements. The structural stability of the cements was evaluated after exposure to water at temperatures of $\sim$ 200 °C and pressures of $\sim$ 20 MPA ($\sim$ 2800 psi) for extended intervals of time. Among the cements that were tested were candidates that had been proposed for use in a remedial cementing operation of a hot-dry-rock well at Los Alamos Scientific Laboratory. A series of shear-bond strength tests was also conducted to examine the influence of thermal cycling on the interfacial bond between a steel rod and the cement.

Because ceramic materials offer the potential for significant increase in operating temperatures and efficiency for gas turbine engines, silicon nitride is being considered by the Department of Defense and the Department of Energy for application in heat engines. Work at NBS on the subject of proof testing as a method of ensuring the reliability of this material at high temperatures is being conducted under the auspices of the Department of Energy. The objective of this study is to determine if the strength distribution of population of test specimens can be truncated by proof testing. Earlier studies for the Department of Defense showed that truncation as a practical technique was viable at room temperature and for rather large cracks at high temperatures. In addition, there is an upper limit to the proof test load that can be used to achieve reliability without destroying too many specimens. During the past year, this work was extended to include reaction-sintered silicon nitride and hot-pressed silicon nitride doped with yttrium oxide. Work on the reaction-bonded silicon nitride indicates that proof testing as a means of ensuring component reliability will be applicable to this material. Results at room temperature and at

1200 °C show that, regardless of test conditions, the strength distribution of the reaction-bonded silicon nitride is truncated by proof testing. This conclusion is based on several hundred strength tests conducted on this material after exposure to 1200 °C at load for periods as long as 1000 hours. We conclude that, when subjected to stress at 1200 °C, the material will either fail upon loading or will support its load indefinitely at elevated temperatures. This conclusion is consistent with the fact that subcritical crack growth, as determined by fracture mechanics techniques, does not occur in this material at 1200 °C. At room temperature, subcritical crack growth does occur, but in a predictable manner, so that the framework of fracture mechanics can be used to predict lifetime. These conclusions do not seem to be applicable to yttria-doped, hot-pressed silicon nitride, which can fail unpredictably when subjected to high temperatures (1200 °C) under sustained load conditions. Flaw generation and subcritical crack growth seem to be a real problem with the hot-pressed material. Work is continuing on this material to determine the causes of failure.

Another new and interesting application of ceramic materials is in the field of medicine. Certain types of ceramic materials (aluminum oxide, glass ceramics) are useful as structural components of prosthetic devices because they are biologically inert to the body environment and are relatively strong compared with bone. As a consequence, these materials are being introduced into the body in several applications: total hip replacements, anchors for artificial teeth, and artificial knee joints. In these applications, ceramic materials will have to sustain structural loads for periods that may last for forty years or longer. Given the tendency for ceramic materials to undergo stress corrosion cracking owing to water in the environment, there is concern over the ability of these materials to perform their function in the body environment for extended periods. Because of this concern, the Fracture and Deformation Division has been conducting a study to determine the effect of microstructure on stress-corrosion cracking of aluminum oxide.

During the past year, one of the major tasks has been to assemble the test rigs to perform long-term delayed failure studies on biomaterials. This setup has been nearly completed. It consists of 10 pneumatically loaded test rigs. The specimens will be held in tanks through which the selected liquid environment will flow using a peristaltic pump. We are in the process of assembling a microcomputer system that will monitor the stresses on the test specimens and from which the failure times can be determined. Data will be displayed on a video screen in the laboratory.

Initial data have been obtained in air on 30 to 50 specimens of the Friedericksfeld Al_2O_3. The crack growth parameters calculated from these data agreed with those obtained at the University of Florida under the same conditions.

Considerable discussions have been carried out with Dr. Larry Hench of the University of Florida and Dr. Jerry Klawitter of Tulane University regarding a joint research program with NBS. The result of discussions with Dr. Klawitter is a proposal summary that has been submitted to FDA. In this study Tulane University would perform the in vivo studies on stressed ceramic specimens. NBS would conduct the accompanying mechanical property experiments before and after implantation.

Discussions with Dr. Klawitter have also been held regarding the development of an ASTM standard on the strength and mechanical testing requirements of Al_2O_3 for implants. The writing of a draft standard is planned within the coming year.

A new project for the coming year will evaluate the mechanical properties of alkali halides to be used as scintillation material for the NASA Gamma Ray Observatory. Data on mechanical properties are needed by NASA to aid in the efficient design of the support housings for the scintillation materials. Materials to be studied include NaI and CsI, both of which will be used in the Observatory. The type of information needed includes compressive and flexural strength measurements for the NaI and the CsI, creep measurements for the CsI, and fracture toughness and static fatigue measurements for the NaI. Equipment is currently being designed and constructed to perform the required mechanical tests. The work is expected to be completed by the end of the 1980 fiscal year.

A second new project for the coming year will be directed toward the development of screening tests to assess the performance and expected lifetime of ceramic capacitors for defense applications. These studies will be conducted on multilayered ceramic capacitors that are currently being used in a number of critical military applications, among which is the guidance system for the Trident missile. The need for reliability in these systems is obvious, so mechanical or electrical reliability of these capacitors should be ensured to technically achievable levels. Studies on this project will involve the use of ultrasonic signals combined with sophisticated computer analysis techniques as a means of deleting delaminations and cracks in capacitor parts. In support of this screening development, studies will be concluded to characterize the microstructure of ceramic capacitors and to establish the susceptibility of the ceramic material in the capacitor to strength degradation resulting from internal stresses and subcritical crack growth. This research is a joint effort between Divisions 562 and 564 to provide technical assistance to the Navy to improve the reliability of chip capacitors for defense applications.

The final project on our program of engineering evaluation of ceramic materials is concerned with refractory materials for MHD air preheaters. The high temperature plasma (2400-2700 °C) necessary for operable and economically attractive open-cycle MHD power generation is achievable through the combustion of fossil fuels using air preheated to

∿ 1500 °C. Temperatures of this level require the operation of regenerative heaters at temperatures as high as 1650 °C, which requires refractory materials that are capable of maintaining their mechanical integrity at this extreme temperature. Creep resistance is one of the primary properties that will determine the ability of refractories to perform adequately as components in regenerative heaters. Although several types of commercial refractory bricks have been selected to serve in this application, creep data on these materials are not available at temperatures in excess of 1500 °C. Consequently, there is a need to collect such data if regenerative heaters are to operate successfully in the necessary temperature range. The objective of this research project is to obtain data on the high-temperature compressive creep of the refractories being considered for use in MHD air preheaters and to rank the proposed refractories in terms of their creep resistance at the proposed service temperature of 1400 to 1650 °C. To date, equipment has been designed for multiple creep experiments on candidate materials at temperatures as high as 1650 °C in air. The equipment uses the pneumatic loading fixtures described above in this report. When completed, the test facility will be capable of measuring creep on 12 specimens simultaneously. All components for the test facility are currently being ordered or constructed at NBS. An existing dead-weight loading apparatus was modified to obtain preliminary data on candidate materials and to eliminate any potential problems that might arise in the course of the study.

Friction and Wear of Ceramics

S. M. Wiederhorn, B. J. Hockey, and H. Johnson

Friction and wear are important phenomena that determine the cost and reliability of precision-ground ceramic parts. Since machining often accounts for 90% of the cost of these parts, a considerable reduction in costs may be achieved through an understanding of the machining process. Furthermore, since machining and erosion leave residual damage that reduces the strength of ceramic components, an understanding of these processes may lead to improvement in the strength of these materials. To achieve these ends, this project has been initiated to study the friction, wear, and erosion resistance of commercially important ceramic materials.

In an extension of work conducted last year on sharp particles, impact data (SiC grains against glass) were collected to evaluate the effect of impact angle on contact-induced strength degradation. These studies were conducted to determine if impact at oblique angles leads to local damage that is greater than that predicted by elastic-plastic strength degradation theories developed to explain strength degradation at normal impact. If enhancement of damage does not occur, then existing analyses can be used as a conservative basis for design. It was also felt that such a study might throw light on the damage mechanisms themselves and so add to our understanding of similar angular effects in erosion phenomena.

Strength degradation tests were run on crown glass discs using 150 μm SiC particles at a velocity of $\sim$ 94 m/s. Various angles of exposure were used in the study with at least 10 specimens per angle. Strength results from ring-on-ring tests indicate an increase of strength as the impact angle becomes more oblique. However, the strength increase is less than that predicted from current theories, assuming that only the normal component of the velocities is effective in providing the driving force for crack formation. Plastic stresses arising from the shear component of velocity appear to contribute to crack formation and thus to strength degradation. However, the degradation appears to be small relative to that occurring at normal impact, so the elastic-plastic theory of strength degradation proposed earlier can be applied to obtain a conservative estimate of strength.

The above observations suggest that a shear component of velocity contributes to strength degradation. These observations are consistent with earlier observations on the erosive wear of ceramic materials, which indicate a contribution to erosion is a result of oblique impact of erosive particles. Shear stresses that occur during oblique impact apparently enhance the intensity of the plastic zone that results in crack formation and, therefore, increase the size of the cracks that are formed at impact.

Our data base for the erosion of brittle materials was expanded by obtaining erosion data on silicon (room temperature, 500 °C, 1000 °C), fused silica (room temperature, 500 °C) soda-lime silicate glass (500 °C and 600 °C) and sapphire (room temperature, 500 °C and 1000 °C). These data were combined with erosion data on aluminum oxide and hot-pressed silicon nitride obtained in earlier studies to show the dominant effect of fracture toughness (K_{IC}) and hardness (H) on the erosion rate. Resistance to erosion was found to be largest for materials for which the ratio of the toughness to the hardness, K_{IC}/H, was high. Therefore, K_{IC}/H appears to be an important parameter for evaluating the erosion resistance of ceramic materials. In the year to come, these data will be used to summarize the effect of material properties, such as K_c and H, on the resistance of materials to erosive wear. Comparisons between data obtained from these studies and theoretical expressions for the erosion rate will be made to determine the applicability of the erosion theories to brittle materials.

Microstructural Analysis of Ceramics

B. J. Hockey and N. J. Tighe

The objective of this subtask is to investigate the relation between structural and mechanical properties of ceramic materials. This subtask develops and applies techniques of high resolution transmission and scanning electron microscopy to study deformation and fracture and wear processes in hard materials.

Earlier transmission electron microscopy studies on impact damage were extended this year by the use of scanning electron microscopy. This technique was used to evaluate the role of microstructure in determining the extent and type of impact damage that occurs during erosion. Temperature and particle velocity were used as parameters in studies on glass, silicon, sapphire, 30 μm grain-size alumina, 3 μm grain-size alumina, and hot-pressed silicon nitride. As indicated by the size of lateral cracks formed during impact, brittle behavior was enhanced as the fracture toughness (K_{IC}) decreased. For example, Si_3N_4, which has a fracture toughness of ~ 6 MPa-$m^{1/2}$, showed very little chipping or crack formation associated with the damage at the contact area. In contrast, glass and silicon, which have relatively low values of toughness (~ 0.8 and 0.7 MPa-$m^{1/2}$, respectively), exhibited well-developed crack structures, with both lateral and median vents extending far beyond the immediate impact site. The type and extent of damage appeared to correlate with erosion rates measured on these materials (discussed below), confirming the importance of high fracture toughness to good erosion resistance.

Perhaps the most interesting observation made in these microstructural studies was on glass impacted at room temperature with 150 μm SiC particles at a velocity of ~ 94 m/s. Under these conditions, the temperature elevation was so high that pools of molten glass formed at the impact site. At oblique angles of impact, molten glass attached itself to the impacting particles and glass fibers were pulled from the surface of the glass. Simple theoretical estimates indicate glass temperatures in excess of 900 °C. A more detailed model, which was developed to explain thermal effects during erosion, confirmed these high-temperature estimates.

The effect of ambient temperature on erosion damage was investigated by comparing surface damage occurring at room temperature with that occurring at elevated temperatures (500 °C, 600 °C, and 680 °C for glass; 500 °C for silicon; 500 °C and 1000 °C for Al_2O_3 and Si_3N_4). Despite the higher ductility of these materials at elevated temperatures, the damage during impact was very similar to that observed at room temperature. However, qualitative differences between room temperature and elevated-temperature erosion were observed. In glass, lateral cracks did not extend as far at 500 °C and 600 °C as they did at room temperature. Furthermore, plastic deformation at the contact site was enhanced at high temperatures. These differences in appearance of the contact site account for the observed decrease in the erosion rate of glass at elevated temperatures. For the crystalline materials studied (Al_2O_3, Si_3N_4, Si), differences in appearance of the contact site occurred, but were not as obvious as those observed for the glass, which probably accounts for the fact that the erosion rate at elevated temperatures was virtually identical to that obtained at room temperature.

Engineering Evaluation of Composites

M. B. Kasen and R. E. Schramm

This effort began in 1973 with a comprehensive literature review of the existing state of knowledge on the effect of cryogenic temperatures on the mechanical and thermal properties of composite materials. An increasing use of composite materials in high-technology cryogenic areas had created the need for a reliable data base on low-modulus (glass-reinforced) and high-modulus (graphite, boron, Kevlar) polymer-matrix composite laminates. These reviews, published in Cryogenics, June and September 1975, provided the background for establishing test programs. Data available in 1975 indicated that all of these composite types were viable structural materials for cryogenic use. But the temperature dependence of the mechanical properties and the values for the properties showed a large scatter. It was apparent that this variability reflected inadequate test methodology and relatively poorly characterized materials.

The NBS testing programs were initially funded by ARPA as part of a program to acquire data relevant to the construction of superconducting machinery. A continuation of these studies was funded by the U.S. Air Force Aero Propulsion Laboratory (AFAPL), Wright-Patterson AFB, Ohio. The object of the latter program was to provide composite property data relevant to construction of lightweight, airborne superconducting power packages based on either generator or magnetohydrodynamic designs.

These studies required development of improved testing techniques capable of producing valid tensile, compression, and shear data from all types of composite materials from 295 K to 4 K. Information derived during this phase was communicated to Committee D-30 of ASTM, which is primarily responsible for establishing standard methods of composite testing. M. B. Kasen of the Fracture and Deformation Division is a member of this Committee. Participation was timely, since such standards were almost nonexistent.

Development of test methods proceeded concomitantly with the acquisition of systematic data on the cryogenic temperature effect. The NBS objective was to characterize the major mechanical properties of state-of-the-art boron-, glass-, graphite- and Kevlar-reinforced epoxy products from 295 K to 4 K. Twin outputs of the program were the establishment of the first systematic data base reaching to liquid helium temperature and an assessment of the need to develop special epoxy resin formulations for cryogenic use.

Key properties are those required for prediction of crossply laminate performance using macromechanical composite theory developed in the aerospace industry. Required data are longitudinal and transverse uniaxial strengths, moduli, and Poisson's ratios, plus in-plane shear strength and modulus. These data have been acquired for epoxy-matrix laminates reinforced with 0.14 mm (5.6-mil) boron, S-glass, Kevlar 49, and Types AS, HM-S, and GY-70 graphite fibers. A 0.14 mm (5.6-mil) boron-reinforced aluminum was also characterized. The data have thus far failed to define performance regions, therefore the development of special composite formulations is necessary for cryogenic use. But the possibility that such a development might be justified under cyclic loading conditions remains to be investigated.

A second major direction in the program reflected the need to use large quantities of low-cost, high-pressure industrial laminates as structural support and electrical insulation in large superconducting magnets for magnetic fusion energy and magnetohydrodynamic power generation in the consumer area. The commercial high-pressure industrial glass-epoxy laminates produced under NEMA (National Electrical Manufacturer's Association) designations G-10 and G-11 are normally selected for this application. But such materials display large property variability at cryogenic temperatures. Therefore NBS has cooperated with NEMA and the U.S. laminating industry to establish a uniform specification for cryogenic grades of such laminates. These products, designated G-10CR and G-11CR, are now in commercial production. Their mechanical, electrical, and thermal properties have been extensively characterized at NBS-Boulder with the participation of the Massachusetts Institute of Technology, Los Alamos Scientific Laboratory, Westinghouse, and General Electric. The performance of these materials under neutron and gamma radiation at 4 K is under assessment at Oak Ridge National Laboratory.

The composite program during the past year included characterization of the performance of graphite-epoxy laminates at cryogenic temperatures. Additionally, we served as a consultant to the USAF on composite materials selection for the prototype advanced-composite superconducting generators being designed for the Air Force by General Electric, and the lightweight magnetohydrodynamic power systems being designed by General Dynamics/Convair in association with the Magnet Corporation of America. Characterization of the mechanical properties of the cryogenic-grade G-10CR and G-11CR materials also continued.

ELASTIC-PLASTIC FRACTURE MECHANICS

Safety and durability are primary considerations in the design and construction of engineering structures. Sophisticated methods to assess structural safety and durability have been developed on the basis of linear elastic fracture mechanics. These analytical methods are applicable to the high-strength alloys used for aerospace vehicles and to the heavy section steels used for nuclear pressure vessels. Unfortunately, the methods of linear elastic fracture mechanics are not applicable to a wide range of metal structures, including bridges, pressure vessels, ships, offshore structures, and pipelines. In these applications, the materials of construction (steels and aluminum alloys are typical) exhibit substantial plasticity (nonlinear behavior) before fracture. Consequently, linear elastic methods are not applicable and the assessments of structural safety and durability are based on empirical methods and extensive prior experience. Although current methods generally provide a reasonable record of structural safety, improved efficiency and productivity could be achieved if more rational methods were used to establish material toughness requirements, allowable stress levels, minimum service temperatures, and weld quality standards. The objective of this task is to contribute to the scientific basis (i.e., elastic-plastic fracture mechanics) for developing fracture prevention procedures applicable to materials that exhibit extensive plasticity before fracture.

The Fracture and Deformation Division program consists of five subtasks:

1. J-integral evaluations are used to characterize the fracture resistance of structural alloys and to determine the driving force for fracture under elastic-plastic conditions.

2. Current fracture control procedures are being reviewed and we are contributing to the development of test standards for improved procedures.

3. The significance of defects, particularly in weldments, are being evaluated on the basis of plastic strain cycling tests and analytical studies.

4. The elastic-plastic fracture properties of alloys and weldments used for low-temperature applications, such as LNG tankage and superconducting-magnet structures are being evaluated.

5. Elastic deformation phenomena are being studied to contribute to our understanding of the fundamental basis of strength.

Fracture Control

H. I. McHenry, R. deWit, D. T. Read, and B. W. Christ

Many engineering practices contribute to the prevention of fracture in metal structures. Elastic-plastic fracture mechanics is a technology that can contribute to development of improved practices based on consideration of material toughness, operating stress levels, and probable defect sizes. As discussed elsewhere in this report, work is underway in the Fracture and Deformation Division relating to improved measures of material toughness, improved means of fracture mechanics analysis, and significance of defects. Other fracture control activities are discussed here: a survey of fracture control practices used by American industry, a tutorial report on fracture mechanics concepts, and participation in the standardization of fracture test methods.

A survey of fracture control practices used by American industry was conducted for the U.S. Navy. The specific objectives of the resulting report were: (1) to review the elements of fracture control and to prepare a detailed summary of industrial practice relative to each element, and (2) to identify fracture control concepts potentially transferable to the Navy. Twelve classes of structures were reviewed including ships, offshore structures, bridges, pressure vessels, aircraft, piping, cryogenic tankage, electrical power generation equipment, space vehicles, and pipelines.

A tutorial report on fracture mechanics is being prepared in collaboration with Professor G. R. Irwin of the University of Maryland. This report includes both linear elastic and elastic-plastic fracture mechanics. Fracture and subcritical crack growth owing to fatigue and stress corrosion are discussed. A summary of fracture mechanics concepts has been completed.

Minimum toughness requirements are frequently included in material procurement specifications. Standard test methods are essential to ensure the buyer and seller of the material that the toughness meets specified requirements. The Fracture and Deformation Division is contributing to the standardization of test methods for evaluating the fracture toughness using the J-integral, the J-resistance curve, and the crack opening displacement methods. Division activities include membership in the responsible ASTM committees and participation in round-robin testing programs.

J-Integral Evaluations

D. T. Read, R. L. Tobler, T. A. Whipple, and H. I. McHenry

The J-integral is a characterization of the elastic-plastic field in the vicinity of the crack tip. The value of the J-integral for any contour surrounding the crack tip has been shown experimentally to be a criterion for the onset of crack extension. Experimental methods have been developed to determine the critical value of J, J_{IC}, which is a measure of the plane strain fracture toughness. The Fracture and Deformation Division is conducting research using the J-integral to characterize the fracture toughness of structural alloys, to measure the driving force for fracture under elastic-plastic loading conditions, and to conduct analytical studies to evaluate the influence of geometric configuration and stress-strain characteristics on the J-integral value.

During the past year, we have made substantial improvements in our test facilities, experimental methods, and analytical capabilities. A 1 MN capacity servohydraulic fatigue test machine has been procured and installed. It is being used to apply a uniform strain field to tensile panels with flaws that are small compared with the overall panel size. A minicomputer has been procured and computer-interactive J-integral test procedures have been developed. These advanced test procedures are now being used to evaluate the fracture toughness of stainless steel alloys and weldments for cryogenic service. A finite element computer code for elastic-plastic fracture mechanics analysis, developed by the Navy, has been obtained and is operational on the NBS computer. The two-dimensional analysis code features crack-tip-singularity elements that enable simplified grids for calculating the J-integral and thereby substantially reduce the computer time requirements for elastic-plastic analysis. The computer analyses are being used to study the influence of strain hardening and geometric configuration on the plastic strain field in tensile panels with through-thickness cracks.

A major new experimental effort has been started to measure directly the J-contour integral on tensile panels under elastic-plastic loading conditions. Single-edge-notch tensile panels are instrumented with strain gauges along the vertical boundaries and displacement gauges along the horizontal boundaries. Gauge signals are recorded by a computer and the strain energy density is calculated on the basis of the stress-strain characteristics of the test material. The rotational contribution to J is computed from displacement signals from LVDT transducers mounted along the top and bottom of the specimen. Tests to date have confirmed the feasibility of the method and have provided a positive check on the finite element analysis predictions. This represents a start on the goal of relating the J-integral to the applied strain and flaw size for a variety of geometric configurations and structural alloys. Measurements of this type are being conducted for the Navy to establish a J-integral design curve and for the Office of Pipeline Safety Regulation to develop an analytical model for prediction of critical flaw sizes in pipeline girthwelds.

Significance of Defects

R. deWit, J. H. Smith, D. T. Read, M. B. Kasen, J. G. Early, and H. I. McHenry

The Fracture and Deformation Division is conducting programs for the Navy and for the Office of Pipeline Safety Regulation regarding the significance of defects, particularly in welded structures. Weld quality standards usually stipulate allowable defect sizes on the basis of workmanship considerations, i.e., what level of quality can generally be achieved by a qualified welder using the proper welding materials and procedures under reasonable working conditions. These quality levels may differ significantly from the quality required to ensure structural integrity.

In the Navy programs, a J-integral design curve is being developed along the lines proposed in the Draft British Standards Rules for Derivation of Acceptance Levels for Defects in Fusion Welded Joints. The program involves the experimental determination of the relationship between the J-integral fracture toughness, the applied strain, and the defect size. Initial tests, currently in progress, involve tensile panels of ship steel with edge cracks. Future work will progress to center cracks, surface cracks, and cracks in welds. The influence of residual stress on the design curve will be assessed using wide plate tests currently being fabricated by the Navy. The program is being conducted in collaboration with the Naval Ship Research and Development Center and Professor S. T. Rolfe of the University of Kansas.

The program for the Office of Pipeline Safety Regulation is being conducted to establish weld quality requirements for the Alaska Natural Gas Transportation System. Initial studies involve analytical modeling of the significance of defects using methods comparable to those used for the trans-Alaska pipeline assessment conducted previously. Future work will involve J-integral studies comparable to the Navy program and verification testing on small-scale and full-scale pipe specimens. In addition to the fracture studies, fatigue tests are being conducted to evaluate the effect of plastic-strain cycling on nonplanar defects, such as porosity and slag. Load-controlled fatigue tests are planned to determine the influence of simulated service loading on the growth of planar defects, such as lack of fusions and lack of penetration.

Low-Temperature Properties

R. P. Reed, H. I. McHenry, D. T. Read, R. L. Tobler, and R. E. Schramm

The increased use of natural gas, usually shipped and transported in liquefied form (LNG), has led to materials research on economical structural alloys and insulation materials. Such research has been necessary to satisfy regulations based on fracture control plans for LNG ships and stringent safety requirements for LNG storage sites inspired by the potentially dangerous consequences of LNG. Our research, sponsored by the Gas Research Institute and the Maritime Administration, now focuses on development of improved low-temperature LNG ship hull steel plate, and characterization of the mechanical properties of concrete and foam insulations used by the LNG industry. To develop economical steel plate more tolerant to high heat input welding techniques, major ship plate producers and LNG ship builders were assembled and combined with NBS in a joint program. Better steels have been identified and characterized for use by the shipbuilding industry.

A major developing technology is the use of superconducting magnets for energy applications. High magnetic fields are required for fusion plasma and MHD plasma confinement and guidance. Superconducting machinery, under prototype development, provides the potential for better performance coupled with lighter weight and reduced space requirements. Power transmission, via superconducting underground cables, is under intensive development. Energy storage, using large superconducting rings, is being considered. In all applications, the magnet or superconductor, with appropriate structural supports is expected to operate at liquid-helium temperature (4 K) for times up to 20 years.

Such emphasis on liquid helium design and material use has led to rather large national materials programs, sponsored by DARPA and DoE and managed by our Division. These programs have produced a low-temperature materials handbook; mechanical, thermal, electrical, and magnetic characterization of economical structural alloys including austenitic stainless steels, aluminum alloys, and superalloys; an annual Low-Temperature Materials Workshop held each October in Vail, Colorado; and joint research programs between NBS and its subcontractors, which have included Battelle, Westinghouse, General Electric, Martin-Marietta, Teledyne-McKay, Alcoa, Armco, and Belfour-Stulen. Major research emphasis has been to characterize the austenitic stainless steels (AISI 304, 316, and 310 grades) and to develop reliable welding processes and filler metals for welding austenitic stainless steels for use at low temperatures. The development and characterization of low-temperature composite insulator standards is discussed in the previous task.

Research highlights this past year include the following: Additions of 0.2% nitrogen to an iron-chromium-nickel austenitic stainless steel (AISI 304) achieve yield strength increases of a factor of five at liquid-helium temperatures. Since nitrogen alloying is inexpensive and the preliminary J-integral measurements indicate sufficient toughness, additional research will proceed to characterize high-nitrogen stainless steels at 4 K.

The temperature dependence of the flow strength of austenitic stainless steels has been measured and analytically characterized. Anomalous regions of decreases of strength with decreasing temperature have been identified and correlation with the martensitic transformation is progressing.

A correlation between low-temperature fracture toughness and ferrite concentration in stainless steel weldments has been obtained; higher ferrite concentrations reduce the low-temperature toughness.

Our Division plays a major role in world-wide low temperature materials research. It organized the International Cryogenic Materials Conferences (ICMC), held annually in various countries (average number of papers = 100), and the ICMC current Board Chairman is from our Division. A series of bound volumes, Cryogenic Materials Series, contains the proceedings of these conferences. The Division, collaborating with the Thermophysical Properties Division (NEL) personnel, is in the final stages of completing a tutorial book, Materials at Low Temperatures. Division personnel organized and led a group of U.S. scientists (from Alcoa, Armco, Westinghouse, University of California, University of Illinois, Rensselaer Polytechnic Institute) collaborating with the USSR under the US/USSR Science and Technology Exchange Program, Electrometallurgy Working Group. The exchange research emphasizes development of a ferritic weld metal and processes for use with iron-nickel alloys, development of a ferrite-free, microfissure-free austenitic filler metal, and characterization of low-temperature flow strengths of austenitic Fe-Cr-Ni alloys.

Elastic Deformation Phenomena

H. M. Ledbetter

A solid's elastic constants provide fundamental information to both the solid-state physicist who wonders what holds solids together and to the materials engineer who wonders what tears them apart.

Our effort on solid-state elastic constants comprises three categories: (1) critical reviews of elastic-property data, (2) experiment, and (3) theory.

Our critical reviews focus on materials of both scientific and technological importance: iron, nickel, copper, zinc, iron-nickel alloys (completed); copper-zinc alloys, aluminum (in progress) magnesium, titanium, and others (planned). Besides recommending "best" elastic constants, these reviews, consider effects of variables such as temperature, pressure, alloying, magnetic field, and mechanical deformation. Also identified are suggested areas for further study. From both university laboratories and industrial laboratories, we have received considerable encouragement for more studies of these kinds.

Our experimental studies deal with metals, alloys, composites, and polymers; with single crystals and with polycrystals. Notable recent studies include the paramagnetic spin-glass transition in manganese stainless steels, the omega-phase effects in niobium-titanium alloys, and precise measurement of the complete set of elastic constants of a boron-aluminum composite and their reconciliation with theory. Laser-induced bulk and Rayleigh waves have been used to study composite superconducting wires. Because superconducting wires are used in critical design applications such a magnets, these studies are important, especially in terms of rule-of-mixture predictions and in the compositional variation of the wire's physical properties, especially those that are design parameters.

Our theoretical efforts focus on three principal problems: (1) relationships between elastic constants and other physical properties, particularly the Debye characteristic temperature; (2) relationships between physical properties of single crystals and polycrystals, that is, the tensor averaging problem; and (3) elastic constants and interatomic potentials. On the latter problem, collaborating with T. Suzuki, using pseudopotentials, we have recently calculated the elastic constants of the alkali metals and related these to their phase-transition behavior. An exciting new concept for low-temperature solid-state nucleation of the new phase is emerging from these calculations. Basically, the traditional surface-energy-term approach, which fails to predict reaction rates, is replaced by a lattice-deformation-energy term that might predict them.

Test Methods and Standards

B. W. Christ, J. G. Early, C. G. Interrante, G. E. Hicho, and J. H. Smith

The development of test methods and standards often follows closely the failure analysis tasks carried out for other agencies. In addition, ASTM and ASME often call on NBS expertise for assistance in formulating test methods and standards. Staff members of the Fracture and Deformation Division are contributing to the following work.

Hydrogen Embrittlement: This project carries out research to establish guidelines to be used for developing standard fracture mechanics test methods for hydrogen embrittlement of steel exposed to aqueous media. Emphasis is on pressure vessel steels and structural steels of moderate strength. These steels are of commercial significance in the petrochemical industry and the transportation industry. Ties have been established with the Pressure Vessel Research Committee of the Welding Research Council.

ASTM Subcommittee E24.03-Alternative Fracture Test Methods: Chairmanship of this Subcommittee involves fostering fracture test methods which differ from ASTM Standard E399, which is a plane strain fracture toughness test. Alternative methods apply to high toughness structural metals and include the Pre-cracked Charpy and Dynamic Tear Test Methods. Applications of the Equivalent Energy Method of data analysis are being looked into by this Subcommittee.

ASTM Subcommittee E24.05 Fracture Terminology: Chairmanship of this subcommittee involves developing standard terminology for Fracture Toughness Testing. Numerous definitions have been developed and balloted already.

ASTM Committee E38-Resource Recovery: Membership on this Committee involves contributing to the development of standards. Two standards have been prepared: "Standard Methods of Test for Municipal Ferrous Scrap," and "Standard Specifications for Municipal Ferrous Scrap." The data base for the former method was developed in the following technical paper: "Determination of Combustible Material in Ferrous Scrap Recovered from Refuse," by J. G. Early (to appear in The *Journal of Resource Recovery*).

ASTM Task Group E28.04.03-Verification of Alignment: Chairmanship of this task group involves developing a standard method for verifying alignment under tensile loading. This method applies to tensile, stress rupture, creep, uniaxial fatigue and microstrain testing. A draft method is ready for subcommittee ballot.

U.S. Coast Guard-Equivalence of Codes and Standards: This task was recently undertaken with the sponsorship of the U.S. Coast Guard-Department of Transportation. The objective is to make recommendations to the sponsor concerning the equivalency to U.S. specifications of structural materials made to foreign specifications. The German DIN specification and the Japanese JIS specification are being examined first.

United Nations Specification For Compressed Gas Containers: This task is being performed for the Materials Transportation Bureau-U.S. Department of Transportation. An international specification for seamless and welded steel containers has been prepared.

Other Division Activities

Sponsored Conferences

NBS-DoE Workshop on Materials at Low Temperatures
Kiandra/Talisman Lodge, Vail, Colorado
October 1978

Basic Science Division Meeting of the American Ceramic Society
National Bureau of Standards, Washington, D.C.
November 1978

Science of Ceramic Machining and Surface Finishing, II
National Bureau of Standards, Washington, D.C.
November 1978

Ninth Meeting of Interagency Coordiantion Group for Application of Ceramics to Heat Engines
National Bureau of Standards, Washington, D.C.
November 1978

ONR Workshop on Erosion of Materials
National Bureau of Standards, Washington, D.C.
June 1979

International Cryogenic Materials Conference (ICMC)
University of Wisconsin, Madison, Wisconsin
August 1979

Invited Talks

Summary of Fracture Mechanics Concepts
Oak Ridge National Laboratories, Oak Ridge, Tennessee
R. deWit

Operational Experiences in Nuclear Power Plants, Regulation and Research
Panel for Special Symposium on In-Service Data Reporting and Analysis
American Society of Mechanical Engineers, San Francisco, California
R. C. Dobbyn
December 1978

The Performance of Materials in Advanced Coal Conversion Pilot Plants
Oak Ridge National Laboratory, Oak Ridge, Tennessee
R. C. Dobbyn
May 1979

How Should We Handle the Subjective Component of In-Service Data Reporting and Analysis
Materials and Fabrication Committee, PVP Division
American Society of Mechanical Engineers, San Antonio, Texas
R. C. Dobbyn
August 1979

Some Effects of Geometry on the High Temperature Fracture Notched Components
Oak Ridge National Laboratory, Oak Ridge, Tennessee
R. J. Fields
October 1978

Investigation of Appropriate Fracture Criteria for Si_3N_4 at High Temperatures
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
R. J. Fields
April 1979

Effective Heat Treatment on the Oxidation of Hot-Pressed Si_3N_4 as Determined by Infrared Reflection Analysis
American Ceramic Society Conference on Composites and Advanced Materials, Cocoa Beach, Florida
S. W. Freiman, J. M. Barrett, L. L. Hench, S. Bernstein, and D. E. Clark
January 1979

Fracture Mechanics Applied to Ceramics
ASTM Subcommittee E24.02 Meeting, Atlanta, Georgia
S. W. Freiman
February 1979

Effect of Crack Velocity on Fracture Morphology in Ceramics
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
S. W. Freiman, J. J. Mecholsky, and A. C. Gonzalez
May 1979

Current Status of Predicting Service Lifetimes for Ceramic Implants
Biomaterials, Gordon Conference, Tilton, New Hampshire
S. W. Freiman
July 1979

Effects of Surface on the Mechanical Properties of Ceramics
Sagamore Conference, Sagamore, New York
S. W. Freiman, J. J. Mecholsky, and P. F. Becher
July 1979

Atmospheric Influences on Brittle Crack Propagation
Ceramic Engineering Seminar, University of Illinois, Urbana, Illinois
E. R. Fuller, Jr.
December 1978

Cementing of Geothermal Wells-Property Verification
API Task Group on Cements for Geothermal Wells, Houston, Texas
E. R. Fuller, Jr.
January 1979

The Ductile-Brittle Character of Fracture
American Physical Society 1979 March Meeting, Chicago, Illinois
E. R. Fuller, Jr.
March 1979

Kinetics of Chemically Assisted Brittle Fracture
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
E. R. Fuller, Jr., and R. M. Thomson
May 1979

Mechanical Property Testing of Refractory Concretes at High Pressure and Temperature
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
E. R. Fuller, Jr., S. M. Wiederhorn, and D. E. Roberts
May 1979

Considerations of the Ductile-Brittle Character of Fracture
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
E. R. Fuller, Jr., and R. M. Thomson
May 1979

Stress Waves from Particle Impact
Office of Naval Research Workshop on the Erosion of Materials, NBS, Gaithersburg, Maryland
E. R. Fuller, Jr.
June 1979

Computer Assisted Impact Testing
ASTM Symposium on Computer Automation of Materials Testing, ASTM Committees E-24 and E-28, Philadelphia, Pennsylvania
C. G. Interrante
November 1978

A System for Studies of Crack-Growth Rate in Aggressive Environments
ASTM Symposium on Computer Automation of Materials Testing, ASTM Committees E-24 and E-28, Philadelphia, Pennsylvania
C. G. Interrante
November 1978

Railroad Tank Car Problems
Seventh Fracture and Deformation Division Seminar, NBS, Washington, D.C.
C. G. Interrante
December 1978

Analysis of Railroad Tank-Car Failures
The American Welding Society, Northeast Tennessee Section,
Oak Ridge, Tennessee
C. G. Interrante
March 1979

Impact Testing of Metallic Materials with Emphasis on Test Methods,
Instrumentation, and Acquisition and Analysis of Data
Building Composites Group Seminar, NBS, Washington, D.C.
C. G. Interrante
April 1979

Status of DoT Fracture Mechanics Pipeline Welding Research
Pipeline Welding and Inspection Conference, Houston, Texas
M. B. Kasen
February 1979

Significance of Flaws in Girth Welds of Pipelines
Paton Institute of Electrowelding, Kiev, USSR
M. B. Kasen
June 1979

Practice for Property Testing of Geothermal Cements
Standardization Conference of American Petroleum Institute,
San Diego, California
R. F. Krause, Jr.
June 1979

Proposed Practice for Testing Geothermal Cements
API Task Group on Cements for Geothermal Wells, San Diego, California
R. F. Krause, Jr., and E. R. Fuller, Jr.
June 1979

NBS/DoE Welding Program
NBS/DoE Workshop on Materials at Low Temperatures, Vail, Colorado
H. I. McHenry
October 1978

Ship Steels with Improved Toughness and Weldability
AWS Conference on Welding in Shipbuilding: Productivity and
Economics, San Diego, California
H. I. McHenry
March 1979

Fitness for Purpose Evaluation of Defects in Pipeline Girthwelds
ASME Conference on Structural Integrity, Washington, D.C.
H. I. McHenry
May 1979

Structural Alloys for Superconducting Magnets in Fusion Energy Systems
Fifth International Conference on Structural Mechanics in Reactor Technology, Berlin, West Germany
H. I. McHenry
August 1979

Mechanical Properties of Austenitic Stainless Steel Base- and Weld-Metal
NBS/DoE Workshop on Materials at Low Temperatures, Vail, Colorado
R. P. Reed
October 1978

Structures, Insulators, and Conductors for Large Superconducting Magnets
First Topical Conference on Fusion Reactor Materials, Miami, Florida
R. P. Reed, F. R. Fickett, and E. N. C. Dalder
January 1979

Low Temperature Effects of Defects in Stainless Steel Welds
Paton Institute of Electrowelding, Kiev, USSR
R. P. Reed
June 1979

The Effect of High Temperature Processes on Predictive Testing
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
N. J. Tighe
May 1979

Analysis of the Refractories from a Coal Gasification Plant (CO_2 Acceptor Process)
American Ceramic Society, Bedford Springs, Pennsylvania
S. M. Wiederhorn
October 1978

Erosion of Ceramics
NACE Conference on Erosion/Corrosion of Coal Conversion System Materials, Berkeley, California
S. M. Wiederhorn
January 1979

High Temperature Fracture of Ceramic Materials
DoE Workshop on Time Dependent Fracture, Germantown, Maryland
S. M. Wiederhorn
February 1979

Effect of Fluid Viscosity on Crack Propagation
American Ceramic Society, 81st Annual Meeting, Cincinnati, Ohio
S. M. Wiederhorn
April 1979

Structural Ceramics
DoE Workshop on Coal Conversion Systems, Knoxville, Tennessee
S. M. Wiederhorn
June 1979

Erosion of Ceramics
Energy Materials Coordinating Committee Conference on Structural
Ceramics, sponsored by DoE, Knoxville, Tennessee
S. M. Wiederhorn
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POLYMER SCIENCE AND STANDARDS DIVISION

Ronald K. Eby, Chief
Darrell H. Reneker, Deputy Chief
P. C. Colbert, Secretary
H. E. Kistler, Secretary

In the 70 years since Baekeland introduced the first commercial plastic produced entirely by the reaction of small molecules, plastics have left little of our culture and our technology untouched. We have moved rapidly into an age in which an overwhelming number of the needs of mankind are served by plastics.

In 1976, the last year for which comprehensive figures are available, over 22 teragrams of synthetic polymer were produced. This amounts to tens of billions of dollars worth of materials produced in hundreds of manufacturing plants where hundreds of thousands of workers are employed. Plastics production is currently growing at a rate of 9% per year. In addition to the domestic needs served, the polymer industry presently produces a two billion dollar favorable balance of trade.

Important trends in the polymer industry include increased use of polymers in packaging, in automobiles to reduce weight and improve fuel economy, in electronic and information handling applications, and in medical implants. These increasingly sophisticated and demanding applications have created new needs for concepts, measurements, standards, and data that can be used to insure that plastics perform as intended not only in the use environment, but in processing and other phases of the materials cycle as well.

Long-range planning activities included visits by the Division managers to the polymer research laboratories of Proctor and Gamble, Army Research and Development Command, General Motors, Boeing Commercial Airplane, and Lawrence Livermore Laboratory.

The costs associated with the limited durability of plastics were estimated by a survey of industrial trade associations and academic sources. It appears that this survey is the first of this sort ever attempted for plastics. The uncertainties in our estimates are therefore large because of the sparse data base. Significant economic costs related to limited durability appear in the following applications of polymers: Building, Transportation, Energy Transmission, Appliances, Dental and Medical Applications. Costs associated with limited durability of plastics in all areas appear to be in the range of 6 to 12 billion dollars per year.

A survey of polymer processing science and technology was also completed. Attention was focused on the processing of polymer blends and on the biaxial orientation of polymers because of the large growth potential of these processes. Many contacts with experts in industry and university laboratories were made to gather information about the future prospects for these areas of polymer processing. The report also contains information about more conventional polymer processing methods, including injection molding, extrusion blow molding, thermoforming, structural foam, rotomolding and reaction injection molding.

These planning activities help insure that the future efforts of the Division will be responsive to the themes outlined by the Director of NBS in his State of the Bureau address. These are the healthy growth of industrial productivity, prudent utilization of energy sources, a reasonable system for the regulation of the effects of technology and a wise policy of materials utilization.

Major problems now being addressed by Division projects include:

- A cooperative effort with the Bureau of Foods to produce methods of improved reliability for predicting both the rates of migration of small molecules from plastic containers into foodstuffs and the equilibrium concentrations that will be reached.

- Elucidation of the molecular level processes that are responsible for piezoelectric effects in polymers. Applications of devices based on piezoelectric polymers led to solutions of measurement problems ranging from improved control of presses used to print currency to monitoring the intensity of ultrasonic energy used in medical diagnosis and treatment.

- Evaluation of the fatigue resistance of elastomers needed in efforts supported by the National Institutes of Health to develop artificial heart components and improved circulatory assist devices.

- Improved polymer-based dental restorative materials and ad hesives to make durable bonds between restorative materials and tooth tissue. This work involves extensive cooperation with the American Dental Association and the National Institute for Dental Research.

- Characterization of the elastomers used as seals in equipment used to collect energy from geothermal sources in Department of Energy sponsored projects. More durable elastomeric seals will allow greater use to be made of this potentially large and cost effective energy source.

- The mechanical durability and permeation behavior of plastics used in containers for the safe transport of hazardous materials needed to insure reasonable regulation of such containers by the Office of Hazardous Materials of the Department of Transportation.

These problems and the others detailed in the following pages lead the scientists in the Division into productive examination of those properties of polymers which are (or should be) of concern to people who design and produce useful objects from plastics. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of plastics.

The activities of the Division are associated into six Tasks, each described separately below. The Task titles are:

DIELECTRIC PLASTICS DESIGN AND PERFORMANCE

POLYMER STANDARDS FOR CONTROL AND EQUITY

CHEMICAL DURABILITY OF POLYMERS IN USE

MIGRATION AND THE DURABILITY OF PLASTICS IN USE

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

DIELECTRIC PLASTICS DESIGN AND PERFORMANCE

Trends in dielectric application of polymers include use of higher working voltages in electrical apparatus and transmission lines to conserve materials, save space, and reduce weight. This work provides manufacturers (polymer manufacturers, film fabricators, transducer manufacturers), trade associations (EPRI), and government agencies (DoE, DoD) with data measurement methods, and concepts which identify limitations in polymer performance traceable to manufacturing practices. For example, steam curing of extruded polyethylene insulated cables results in lifetime limiting voids and inclusions. With a trend toward increased use of underground transmission of electric power, improved insulation performance is required. Data and recommendations from this work go directly to cable manufacturers and funding organizations (i.e., EPRI, DoE) who are able to specify and require manufacturing changes leading to improved products.

Other trends are new, rapidly growing applications of polarized polymers as pyro- and piezoelectric transducers. Transducer manufacturers as well as private and government transducer users (DoD, EPA, HEW) need reliable information connecting polymer structure and polymer performance for the design of improved transducers. This work will help transducer material and device manufacturers design and develop commercial polymer transducers for use in health and safety applications (pulse monitors, therapeutic and diagnostic sound measurements, auto crash sensors, prosthetic fitting devices, nontoxic antifouling coatings, mine disaster warning devices) and in the areas of national security (microphones, hydrophones, intrusion detectors, ultrasonic and infrared imaging devices, fusing devices, etc). Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement methods which are becoming possible with newly developed polymers. For example, this work attempts to show how polymers interact with electronic and ionic charges, how structure control can be modified to optimize piezoelectric, pyroelectric, and semi-conducting properties.

Technical Activity

Polymer Insulation for Superconducting AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

This project, sponsored by and carried out in collaboration with Brookhaven National Laboratory (BNL) with DoE funds, is part of a program for evaluating the suitability of various types of polymer films for use (in tape form) as the electrical insulation in high power superconducing AC transmission cables operated at 6 K - 9 K. Such cables, in which the superconductor is Nb_3Sn, are currently under development at BNL. Among the guidelines used for selecting the insulation for such cables is that the dielectric constant (ε) should be 2.5 or less, and that the dielectric loss ($\tan \delta$) should preferably not exceed 20×10^{-6} at the cable operating range and 60 Hz.

This subtask is primarily concerned with the measurement of the dielectric properties (ε, $\tan \delta$) of polymer films at cryogenic temperatures. These measurements, for which NBS has a unique instrumental facility, are coupled with studies of aspects of the fine structure of the films in an effort to determine the influence of various structural parameters (e.g., crystallinity, molecular orientation, voids) on the dielectric properties of the films. In addition to determining whether specific types of commercially available films meet the established criteria for dielectric properties, these studies are aimed at providing data relevant to the design and production of films exhibiting optimum dielectric properties for the intended end use. In a less extensive effort, the compressibility of the polymer films is measured. This latter feature is among others, relevant to the determination of the optimum conditions (e.g., tape tension) necessary for winding the films (slit in the form of tapes) around the cable core, so as to yield a cable exhibiting appropriate flexibility for winding onto storage drums 10 ft. in diameter.

For FY 1979 the main concern was to characterize the dielectric loss of polyurethane board polypropylene laminates. These laminates consist of polypropylene tapes bound together with a polyurethane adhesive. The laminates were made in order to form a tape strong enough to withstand the necessary winding tensions in making a cable and also be rigid enough not to wrinkle when the cable is wound onto the storage drums. Also, usually one of the urethane layers was dyed so that the tapes could be visually monitored during the winding process.

Several laminates using three layers of 25 μm polypropylene tape with different urethane formulations and dyes were studied. In addition tapes were delaminated and put back together so that both dyed and undyed urethane layers could be measured separately. The results showed that the major sources of dielectric loss in the temperature range of 4 to 10 K were the sub 4.2 K loss peak in the original polypropylene, which decreases with increasing temperature and the loss due to the polyurethane which increases with increasing temperature. The $\tan \delta$ at 100 Hz ranged from 18 to 41×10^{-6}, which is somewhat higher overall than the desired value of 20×10^{-6}. The only effects dye had on the loss in these laminates was at higher temperatures above 150 K.

In addition, several laminates made from two layers of a new 50 μm polypropylene were investigated together with the new polypropylene. These laminates had $\tan \delta$ of $13\text{-}18 \times 10^{-6}$ at 100 Hz in the temperature range of 4 to 10 K. The lower loss of these laminates was established as being due to a reduced urethane content and either less antioxidant or a different type of antioxidant.

Compressibility measurements were made on the laminates in order to predict cable bendability. In addition, the laminates were examined for void content in the urethane layers in order that control of the laminating process could be established to minimize the presence of voids which could serve as a source of electrical discharge.

Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

Oil impregnated paper (cellulose) tape has been for many years one of the most commonly used types of electric insulation in high power AC transmission cables. The current and projected needs for more efficient power transmission systems have elicited considerable interest in the development of oil impregnated or oil filled cables operated at 700 Kv-1000 Kv in which polymer tape insulation will be used instead of the conventional paper tape which is unsuitable because of its large dielectric loss.

In a project, sponsored by Brookhaven National Laboratory with DoE funds, a program has been initiated in the Polymer Science and Standards Division for evaluating the suitability of various types of impregnated AC transmission cables. The goals of this study are: (a) the measurement of the dielectric constant and dielectric loss of candidate films between 273 K and 423 K; (b) the determination of the dependence of the dielectric loss of the fine structural characteristics of the films; and (c) the specification of the dielectrically most suitable type of film for the intended end use.

In FY 1979, the special dielectric cell needed to measure polymer films was tested and modified so that it now gives reproducible loss measurements on polymer films in the temperature range of 300 to 420 K to a resolution in $\tan \delta$ of 1×10^{-6}. In addition, several polymer films were studied in this temperature range of 100 Hz and 1 kHz. The samples were studied as a function of several temperature cycles in order to see if elevated temperatures cause changes in the observed dielectric loss, possibly signaling aging in the polymer itself. The samples studied to date include several of the films studied previously at cryogenic temperatures and several new films prepared by Battelle Institute for BNL that were extruded, rolled, and drawn from commercial polymers.

The main features found in the dielectric measurements where the presence of a loss peak at about 300 K, as seen in earlier measurements, using the cryogenic equipment and a loss minimum around 350 K followed by rapidly accelerating loss above this temperature up to maximum test temperature at 423 K. No sign of the α loss peak near 390 K was found. The loss varied appreciably among the different samples studied with minimum $\tan \delta$ at 353 K of 30×10^{-6} which is a very low value. In addition, mechanical and dielectric instabilities were observed in the Battelle samples.

The Battelle samples are currently undergoing x-ray diffraction and morphological studies to characterize them and comparisons will be made with the heated samples in order to determine the nature of any temperature induced aging which may have occurred.

Porous Polymer Tapes for High Voltage Transmission Cables

A. J. Bur, M. G. Broadhurst, and W. P. Harris

Existing underground high voltage transmission cables are made with an insulation consisting of layers of paper tape saturated with a dielectric oil. This system has proved to be adequate for voltages up to 325 kV. At higher transmission voltages dielectric dispersion in the paper produces unacceptable dielectric losses. In the foreseeable future electrical transmission at voltages higher than 235 kV will be necessary and a substitute for paper is being sought. A polymer material is a logical choice. Some work on solid polymer films has been carried out in the past but the permeation of oil throughout the lapped tapes and encapsulated voids in the films are problems which impede other uses of solid films. It is possible that porous polymer tapes can overcome these problems through improved oil permeation and decreased occurrence of unfilled voids.

The Electric Power Research Institute (EPRI) is supporting this porous polymer tape project. The objective of the project is to establish a screening program by which candidate materials can be tested and a judgment made regarding their suitability as cable insulation. The screening program which we have developed consists of criteria for physical properties which the tapes must have and a description of the tests by which these physical properties can be measured. On the test schedule there are 21 tests to measure the following physical properties: dielectric constant, dielectric loss, dielectric breakdown, softening temperature, mechanical moduli in three directions, coefficient of friction, yield strength, fracture strength, solubility, creep and recovery, swelling, and degree of void filling.

With the exception of the degree of void filling and solubility tests, a description of these tests was obtained from literature sources and ASTM test schedules. The degree of void filling and solubility tests have been developed through our own laboratory experience. For these two tests, we have used a method which is designed to measure the buoyant force of a sample immersed in a dielectric oil.

To measure the degree of void filling, the density of a porous sample is first measured in a calibration fluid which is chosen because of its efficient permeation into the material being investigated. (For example, heptane is known to permeate into polyethylene filling microvoids in the material). It is assumed that this calibration fluid fills all pores and voids so that the true material density can be obtained from the buoyant force measurement. A buoyant force measurement is then made for the sample immersed in a dielectric oil. The difference between the true specific volume and the immersed-in-oil specific volume is equal to the specific volume of unfilled pores. Solubility can be measured by weighing the dry sample before and after immersion in the fluid being tested.

Oil permeation into the sample is a common conditioning step in many of the dielectric and mechanical tests which must be carried out in oil. Temperature and vacuum cycling are often necessary in order to increase the permeation of oil and decrease the unfilled void volume. The buoyancy measurements are being developed to observe these conditioning parameters.

Four materials and two oils have been used in these experiments. The materials are a polypropylene synthetic paper (PPSP), a porous polypropylene (PP), a polyethylene synthetic paper (PE) and a paper-polypropylene-paper laminate (PPP). The oils are an alkyl benzene oil and a polybutene oil. The results show a range of void filling from very little for PPSP to complete filling for PP.

A final report for this project has been submitted to EPRI for publication.

Thick Electrode Transducers

A. J. Bur, H. E. Gilpin, and M. G. Broadhurst

The fabrication of transducer specimens of PVF_2 with thick, well adhering electrodes was attempted. The objective was to study the influence of the mechanical properties of the electrodes on the PVF_2 transducer behavior. It is expected that the hydrostatic response will be enhanced by a factor of 2 to 3, if the electrodes maintain their own integrity and exert a stress on the polymer film during temperature and/or pressure changes. Up to this time transducers fabricated in our laboratory have had very thin evaporated electrodes, several hundred angstroms thickness. Because the electrode is so thin, the mechanical properties of the polymer substrate dominate.

Metals such as Ni, Au, Ag, and Cu have moduli which are 30 to 40 times larger than that of PVF_2. A metal electrode of 0.4 μm thickness will have the same rigidity as 12 μm of PVF_2. A metal electrode of 4 μm thickness will have 10x the rigidity of the polymer. Relative to the polymer, a thick electrode can be considered rigid so that when the polymer contracts, a stress between electrode and polymer develops. The effect of this stress is to decrease the thickness of the polymer film via Poisson's ratio. The factor which controls this effect is $1 + \nu/1 - \nu$ (ν = Poisson's ratio). For $\nu = 1/2$, this factor is 3, i.e., threefold enhancement of the change in thickness. Correspondingly, there should be a threefold increase in the piezoelectric response.

At this time we have not successfully made a thick electrode specimen. Several approaches have been attempted. Initially the approach which we took was to evaporate 1000 Å Ni electrodes onto PVF_2. The speciman was then poled and its piezo- and pyroelectric coefficients were measured. The speciman was then placed in an electroplating bath and an attempt was made to plate Cu on top of the Ni to a thickness of 3 μm. This plating, however, did not adhere well to the Ni. It either did not plate at all or after plating, flaked off. In spite of the flaking Cu, one apparently intact speciman was measured and found to have the same piezo- and pyroelectric coefficients as before plating. The speciman was observed to be electrically noisy and to have a large background current in the shorted condition, presumably due to ions injected into the polymer from the plating process.

Other attempts at electroplating included Au plating on Ni, electrodeless Ag plating followed by Cu plating; and Au plating on top of Ag spray painted electrodes. In all cases where electroplating was used the specimens became electrically noisy so that in some cases, it was not possible to measure the coefficients. In other cases the Au and Cu plated electrodes flacked off. Although two specimens were measured, no conclusions could be drawn from these data.

Brass shim stock, 25 μm thick, was also used for electrodes. In this case, the brass shim was glued onto an evaporated Ni electrode. No change was observed for the coefficients. It is not known whether or not the adhesion of the brass shim is adequate enough to effectively clamp the PVF_2.

An attempt was made to simulate the mechanical rigidity of a thick metal electrode by placing a speciman in a ring collar which held the speciman fixed at the perimeter of the ring. Measurements on those specimens with the collar in place were found to be approximately 10% higher than those without the collar. It has been suggested that the time scale of the experiment is too slow and these collared specimens relax before the effect can be observed.

A series of specimens with evaporated aluminum electrodes of various thicknesses were prepared. The thickness range from 4000 Å to 32,000 Å. Measurements of the piezo- and pyroelectric coefficients showed no significant differences for this series of specimens.

At this time specimens are being prepared with evaporated Ni electrodes at 5000 Å and 10,000 Å thickness. Although these electrodes can not be called "thick", the amount of deposited metal may be enough to produce the expected effect of enhanced response due to electrode rigidity.

ASTM Activities

W. P. Harris

ASTM Committee D-9 met three times in this period:

October 17-19, 1978, in New Orleans
March 19-21, 1979, in Cincinnati
June 18-20, 1979, in Philadelphia

Mr. Harris, Chairman of D-9 and of its Executive Subcommittee, attended and chaired these meetings, and also took part in the activities of several of the subcommittees.

At each meeting 20-30 standards were balloted for revision or reapproval. The Committee had been working hard to bring all its standards into conformity with the "Blue Book" by including a section on sampling as required. However, as a result of a special conference on revision of the "Blue Book" held at ASTM headquarters in Philadelphia in September 1978 (attended by Mr. Harris), it was decided to relax the requirement, as applied to test methods. The revised "Blue Book" is expected to appear in October 1979, with the section on sampling no longer mandatory for test methods. Because of this, D-9 is no longer automatically inserting a sampling section, but is looking at each document to see if such a section would be helpful, or whether reference to standards on sampling can suffice. Committee D-9 has prepared such a general standard, D 3636, "Sampling and Judging Quality of Solid Electrical Insulating Materials," with sampling tables adapted from MILSTD-105D.

During this period the following new standards prepared by D-9 were approved by the Society and issued:

D 3638	"Standard Test Method for Comparative Tracking Index of Electrical Insulating Materials"
D 3755	"Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials Under Direct-Voltage Stress"
D 3756	"Standard Test Method for Evaluation of Resistance to Electrical Diverging Fields"

Mr. Harris attended the Biennial Conference for ASTM Technical Committee officers in Philadelphia in September 1978. Several problems were addressed, including that of getting increased participation in Technical Committees. As a result of this meeting, Headquarters is preparing promotional letters to send to selected lists of prospects. One of the first to be scheduled is one for D-9, to be sent to persons who purchase Parts 39 or 40 of the Book of Standards, but are not members. Mr. Harris participated in the preparation of the letter, and it is now in the process of being printed and sent.

Subcommittee 91 on International Standards continues to be very active. D-9 shared support of several delegates to TC-15's meetings in Zurich, Switzerland, in April 1979. Inflation has so increased the cost of such support that the D-9 Fund is nearly depleted. Two steps were taken to alleviate the problem. First, Mr. Harris prepared and sent a follow-up letter asking those who hadn't contributed to the D-9 Fund for 1978-79 to please consider doing so now. Second, the Executive Subcommittee decided to ask for $30 per person for the 1979-80 year, up from $20 last year.

The new section on Electrical Safety formed last year in the S/C on Electrical Tests has been moved to S/C 94 and broadened to include all aspects of safety during the making of tests on solid electrical insulating materials.

Several new standards are in preparation, and a major revision of one of D-9's most widely-used standards, D-150, is underway.

Space Charge Studies

A. S. DeReggi and M. G. Broadhurst

The thermal pulse method of measuring the distribution of charge or polarization across the thickness of dielectric films continues to be relevant to advancing our understanding of space charge phenomena in polymers and the electrical properties of polymers in general. Evolutionary improvements in the data processing and in the data analysis methodology have been made recently and new results on PVF have been obtained in collaboration with Dr. Sidney Lang of the Ben Gurion University of the Negev (Israel) who was a guest worker at NBS for two months. In addition, survey measurements of charging phenomena in non-polar polymers have begun.

Previous theoretical work at NBS showed that the information which can be obtained unambiguously from thermal pulse data consists of Fourier coefficients of the charge or polarization distribution. However, the diffusive nature of the thermal conduction process results in unfavorable conditions for recovering a large number of Fourier coefficients, particularly if the charge distribution is concentrated at a depth removed from the thermally pulsed surface. To offset this disadvantage, a first-rate data acquisition scheme including signal averaging for the enhancement of the signal-to-noise ratio is required. In addition, carefully programmed numerical computations are needed as part of the data analysis if all the information contained in the data is to be extracted. During the past several months, the existing data acquisition system has been interfaced to an Interdata minicomputer in the Division. Programming to handle the data stream is complete. Programming to extract information about charge and polarization distributions on the Interdata is currently underway. During Sidney Lang's visit and thereafter, curve fitting programs were written and run in the NBS computer to interpret qualitatively new data on PVF in terms of adjustable parameters including the effective depth and width of the polarization. It was confirmed that during the initial stages of poling, polarization first becomes significant towards the poling cathode, in contrast to the situation of PVF_2 where polarization first tends to concentrate towards the poling anode. The two types of behavior strongly suggest effects due to space charge of opposite signs in the two polymers. It was also found that polarization grows and spreads while the poling voltage is progressively increased. This work is currently being prepared for publication. Thermal pulse measurements of a survey nature have also been performed on charged non-polar polymers including polyethylene and polytetrafluoroethylene, which are two commonly used materials in the electrical power industry. Charging was accomplished by subjecting samples for a period of time to an applied voltage at various temperatures. The preliminary results have indicated that charging occurs and that the sign of the charge depends on the electrode material as well as other parameters. Systematic data are being developed for a range of metal/polymer interfaces and for a range of charging voltage and temperature. An attempt is being made to understand the charging data in terms of a simple picture where a polymer can act as a donor or acceptor of electrons depending on the properties on the metal/polymer interface. In the case of 30 μm thick PE charged at 80 °C using a charging voltage of 1750 V and a charging time of 90 minutes, it was found that as the electrode material (anode side/cathode side) was changed from Al/Al, Au/Al, Al/Au, Au/Au the signs and amplitudes of the thermal pulse responses changed. These results suggest that PE was an acceptor relative to Al and a donor relative to Au. Some aspects of this research seem directly pertinent to the insulation problem in electric power cables. In particular, it is relevant to ask whether a particular combination of polymer, or polymer blend, and metal electrode could be found which is resistant to space charge accumulation and hence minimize the space charge enhancement of local fields in the polymer. This space charge enhancement is one probable cause of aging and failure of cable insulation.

Piezoelectric Polymer Fuzing

S. C. Roth, A. S. DeReggi, and S. Edelman

This project is sponsored by the U. S. Army Armament Research and Development Command. It developed from previous work by NBS in cooperation with Frankford Arsenal reported in NBSIR 75-724 (R). NBS is to assist ARRADCOM to determine the feasibility of using piezoelectric polymer film in impact sensors for fuzing applications in several particular geometries.

Two male forms have been built to facilitate mounting an irregularly shaped polymer sensor inside the ogives (forward part of the casing) of selected projectiles. The two forms built so far differ slightly in the length of the forward sections. The machining of the forms was done by numerical control and the directions were preserved on tape so that additional modified forms can be constructed with a minimum of additional design.

Six pre-prototype polymer sensors were designed, constructed, and delivered to ARRADCOM. After some minor modifications and testing at ARRADCOM, they are to be subjected to reverse ballistic tests in an air gun at HDL.

Some preliminary tests have been performed on our drop tester to study the effect of impacts of limited area on the output of large area (several wavelengths) sensors fixed to metal backing.

Structure and Performance of Piezoelectric Polymers

G. T. Davis and M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

Although the best piezoelectric and pyroelectric activity from polymers is still less than that from good ceramic materials, the other properties of polymers often made them the preferred transducer material. Some of the polymer properties which made them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. The interest in the use of polymeric transducers continues to increase as evidenced by the requests from other government agencies, by the large number of requests for information by mail, phone, and personal visits, and by the 17 papers presented at the American Physical Society meeting in March 1979.

In principle, any polar polymer can be made piezoelectric by preferentially aligning its dipoles in an applied electric field while in the liquid phase, then freezing in the alignment by cooling below the glass transition before removing the electric field. Practical use requires that T_g be greater than ambient temperature but amorphous polymers have other limitations in that the degree of alignment (polarization = net dipole moment/unit volume) is only weakly linear with applied field, and the electric fields that can be applied are limited by rather low electrical breakdown strengths above T_g. The polymer of primary interest continues to be poly(vinylidene fluoride) in which the polarization resides in the crystalline phases of the polymer and the polarization attainable is an order of magnitude larger than that of typical amorphous polymers.

The model developed here for piezoelectric and pyroelectric response from a polymer composed of this lamellar crystals with preferentially aligned dipoles dispersed in a randomly oriented amorphous matrix was published in J. Appl. Phys. 49, 4992 (1978). Data relating piezoelectric and pyroelectric response to measured polarization using the expressions developed from the model were submitted to ONR as technical report number 11 and have been submitted to the Journal of Applied Physics. The data obtained indicated that the polarization charge was compensated by real charge at the external electrodes rather than at the crystal-liquid interfaces throughout the polarmer film. Further evidence for this conclusion was obtained from measurements on a thick (0.13 mm) specimen of PVDF supplied by EMI of Great Britain. The ratio of piezoelectric to pyroelectric response for this sample was about two times larger than usually observed which was traced to the fact that the film had many tiny voids and was therefore more compressible than solid material while thermal expansion properties were unaltered. The enhanced effect of voids could be expected only if the polarization is compensated externally.

A cooperative model has been developed to describe ferroelectric polarization in polyvinylidene fluoride (PVDF). The molecular dipoles within the crystal are assumed to have two or more orientations available to them and the lattice energy of a given orientational site is assumed to be proportional to the fraction of molecules having that orientation. An analytical solution was obtained for the 2-site model which predicts polarization hysteresis typical of ferroelectrics. However, a more complex 6-site model, which can be analyzed numerically was needed to account for observed infrared hysteresis data and electric-field-induced x-ray structural changes. Although the model is simple, rather complex behavior is observed including a gradual increase or decrease in the remnant polarization with number of cycles of electric field application. Though the agreements with various experimental data are good, an obvious need to include kinetic effects in the model was indicated. These results have been communicated to ONR as technical report number 13 and submitted to the Conference on Electrical Insulation and Dielectric Phenomena.

All the available data indicate that only about 50% of the maximum polarization that can be expected in PVDF has actually been achieved. This is probably due to the incomplete alignment of dipoles in the electric field. A study of the effect of crystal orientation on poling has been initiated using x-ray diffraction. A Phillips diffractometer has been modified so that a polymer film can be oriented at any position in the beam and a transmission scan obtained. The electric-field-induced phase transitions from alpha to the polar alpha phase and then to beta phase which were reported here last year are particularly useful for this investigation. This phase transition from α to polar-α results in the loss of 100 and 120 peaks while increasing the intensity of the 200 peak.

Conversion to the beta phase at still higher fields results in even greater changes in the diffraction peaks. After several unsuccessful attempts to apply high electric-fields to PVDF samples in the alpha phase which were obtained from suppliers in that form, we resorted to melting the mixed phase biaxially oriented films and stretched them at high temperature to obtain uniaxially oriented alpha films. These samples still withstand electric fields in excess of 2 MV/cm.

A fourth crystal form of PVDF has been reported. It is thought to have a tttgtttg' chain conformation and is also thought to crystallize in a polar unit cell. We have confirmed literature reports that annealing through the melting point of alpha phase in the presence of a polymeric surface active agent results in complete conversion to this gamma phase. The poling characteristics of unoriented films of gamma phase PVDF are now being investigated.

An important aspect of piezoelectricity in PVDF which requires much further investigation is the mechanism through which the polymer gradually loses its electrical activity at elevated temperatures. Future work will be directed toward determining the parameters that most affect the thermal stability. The influence of the initial crystal phase on the ultimate stability will be an important part of this study.

Polymer Sensors for NDE of Bearings

S. C. Roth, S. Edelman, J. F. Mayo-Wells, and J. M. Kenney

The 1979 NDE work of the Bulk Properties group consisted of a comparison of the usefulness of polymer sensors and conventional accelerometers for monitoring the condition of bearings. The study led to the publication of a paper in the Proceedings of the 28th Meeting of the Mechanical Failures Prevention Group, NBS Special Publication 547, pp. 303-314, July 1979.

The study used a horizontal shaft supported on ball-bearings, a quiet bearing at one end and a noisy bearing at the other. An isolated electric motor was coupled to the shaft by a flexible belt so that only the bearings contributed measurable noise to the structure supporting the shaft. A polymer sensor was fixed to the stationary race of each bearing and a miniature piezoelectric accelerometer was mounted on the supporting structure as close to each bearing as practicable.

It was found that polymer sensors have several advantages. The principal advantage derives from the flexibility and low density that allow the polymer sensor to be mounted directly to the bearing. So mounted, it responds only to the bearing noises. Conventional accelerometers are relatively massive and require specially prepared mounting surfaces of appreciable area. These characteristics require them to be mounted some distance from the bearing where they can be unaffected by noise from other sources. The extraneous noise can cause uncertainty as to which of several bearings is bad.

It has been suggested that polymer sensors can provide a non-invasive means for detecting cracks of the kind affecting DC-10 airplanes recently. A polymer gauge cemented to a metal surface responds to surface strain in all directions and detects a signal which can be analyzed into a spectrum of resonances of the metal panel. A change in the structure of the metal preliminary to cracking and certainly development of a crack will cause a significant shift in resonance frequencies and amplitudes. Polymer sensors are cheap so that one can be attached to each critical surface. The sensor and lead constitute a continuous thin sheet of polymer that would not affect the behavior of the panel. All resonances of the panel would be excited any time the engines were operating. Before each takeoff, a superposition of the current spectrum would detect any change in the integrity of the panel.

Other proposed NDE work consists of the use of polymer sensors to detect broken strands in airplane control cables and the use of polymer sensors in a non-resonant method to measure the real and imaginary parts of the elastic moduli of long, thin rods as continuous functions of frequency and static load.

Polymer Stress Gauge for Intaglio Printing Press

S. C. Roth, J. M. Kenney, A. S. DeReggi, and S. Edelman

This work, which is supported by the Bureau of Engraving and Printing, U. S. Department of the Treasury, involves the development of a gauge to measure the dynamic pressure at critical points in the presses used to print money. It is the continuation of work reported last year.

The first phase of the work was completed this year. The accomplishments of the first phase included measurement of the width of the area of contact between the two cylinders of the press, 18.7 millimeters, the duration of contact of a point on the upper cylinder with the lower cylinder, 0.25 milliseconds, and a qualitative (uncalibrated) determination of the change of the pressure with time during contact. The successful measurement was made with a gauge having an active area two millimeters wide and 14 centimeters long with very narrow inert shoulders. The electrodes were evaporated indium about one micrometer thick. The gauge was mounted directly on the steel cylinder of the upper drum of the press below all of the layers of paper and rubberized canvas used to distribute the printing pressure.

The work of the first phase was described in a report to BEP and in a paper by the authors listed above which was presented to the 10th Annual Symposium of the Paper and Pulp Foundation at Miami University, Oxford, Ohio.

Piezoelectric Polymer Deposition

S. C. Roth, S. Edelman, and M. G. Broadhurst

This project is sponsored by the U. S. Army Research Office. It is a continuation of work described in the previous annual report.

Fused powder films were formed of PVDF-TFE copolymer by fusing a coating of electrostatically-charged, spray-deposited, polymer powder on a metal substrate. Subsequent attempts at poling such films were only marginally successful. Attempts to use the same procedures, which might be expected to give greater piezoelectric activity, resulted in films of uneven appearance, apparently caused by incomplete fusing. Attempts to form smoother films depend on procurement of PVDF powder of low molecular weight.

In order to produce films with better mechanical properties and to pole them so that they exhibit satisfactory piezoelectric activity, it is necessary to have a better understanding of the mechanisms involved. However, the detailed physics of piezoelectricity in polymers is still controversial to some extent. Also, on a different scale of magnitude, the mechanical and dielectric properties of fused and incompletely fused films are not well-known. Available experimental data on piezoelectric polymers consists of measurements made on samples prepared in various ways and performed on different samples by a number of different methods under different conditions. The properties of piezoelectric polymers are more dependent on history and treatment than those of crystals and ceramics. As a means of accumulating data which would form the basis of theory to provide the guidance needed for this project, a set of measurements was worked out which yield all of the pertinent mechanical, dielectric, and piezoelectric properties of a polymer sample. The measurements are made in a short time under uniform conditions. The necessary apparatus has been built or assembled, a pair of capacitance bridges has been calibrated and each has been shown to have adequate sensitivity. Apparatus for measuring suitable small displacements by a microphone with a film micrometer eyepiece illuminated by straposcopic light synchronized with the motion of the sample has been provided.

Development of Piezoelectric Polymer Stress Gauges for Rock Studies

S. C. Roth and S. Edelman

This work, funded by the Denver Mining Research Center of the Bureau of Mines, is a continuation of work described in the report for last year.

Most of the gauges having single circular active areas were delivered early in this fiscal year. These gauges were similar to those developed for the National Highway Traffic Safety Administration (described in NBSIR 76-1078). Three sizes of active area were built: 5, 3.5, and

1 cm, respectively. These, especially the one centimeter size, have been effective in detecting and measuring the acoustic emission from rock samples under stress. Also, they have been found to survive collapse and crushing of the rock specimens unless a crack develops directly across the active area.

Considerable difficulty was experienced in designing and building the masks for a 16-element array. This has been successfully accomplished; twelve of the arrays have been built; one has been delivered to the Bureau of Mines; and the remainder of the contracted number of gauges will be delivered before the end of the fiscal year. Future work on rock and soil transducers is expected to result from tests on these transducers.

Automated Dielectric Measurements

F. I. Mopsik, S. J. Kryder, and S. C. Roth

The automated dielectric spectrometer is nearing completion. This instrument will record the transient response of a dielectric sample in real time and using numerical transforms automatically determine the dielectric constant and loss of the sample over the frequency range of 10 kHz to 0.001 Hz or below. The instrument should have a resolution of 10^{-5} which is an order of magnitude improvement over most designs. This will allow determination of the dielectric properties of low loss polymers with much greater speed than previously possible.

Work completed in FY 1979 includes a step function generator that can put out simultaneous positive and negative steps of 100 V matched to one part in 10^5 with a 10 μs rise time. This matching is necessary to accurately subtract out the constant capacitance term. A detector has been completed and is being trimmed. This detector will be able to resolve charge changes to 0.1 pC with a 10 ms response time. These and previously completed or obtained components complete the instrumentation.

One other needed piece of support work that has been completed is the development of an efficient numerical Laplace transform technique. The transform gives accurate results over six decades in log time and uses 36 preselected data samples. This performance is quite superior to methods in the literature.

The recording of data for the thermal pulse experiment and the transfer of these data to the Interdata Laboratory computer has been completed and work has started on writing the needed programs for data analysis. When completed this automation will provide a convenient method of determining polarization distributions in polymer films as an aid to studying their piezoelectric and charge transfer properties.

Ultrasonic Hydrophone

A. S. DeReggi, S. C. Roth, J. M. Kenney, and S. Edelman

This project is sponsored by the Bureau of Radiological Health which is also contributing the service of a guest worker. The early work was described in the annual report for last year.

The objective of the project is to develop a piezoelectric polymer hydrophone for characterizing, point-by-point, the acoustic field beamed by ultrasonic transducers such as those used in biomedical equipment. Accurate knowledge of the details of the acoustic field is not otherwise obtainable. The knowledge can be used to ensure both the safety and adequacy of ultrasonic dosage and for research in ultrasonic treatment.

During this year, a number of prototype hydrophones were built and tested at NBS and at the Bureau of Radiological Health. The hydrophone is a taut membrane of polyvinylidene fluoride (PVDF), 50 μm thick, with a piezoelectrically active central spot of about one millimeter diameter. The close impedance match of PVDF to water makes the hydrophone acoustically transparent in use. Thus, whether the hydrophone is held stationary or is scanned across the field, the acoustic impedance presented to the source is essentially the same as it should be if the probe were not present. The response of the probe is flat between 0.5 and 10 MHz. The thickness resonance is about 20 MHz.

The hydrophone was described in a paper presented by the authors listed above and G. Harris of the Bureau of Radiological Health at the joint meeting of the Acoustical Society of America and the Acoustical Society of Japan, November 27-December 1, 1978. J. Acoust. Soc. Am., 64, S.55 (1978).

Plans are currently under way to extend the work to linear arrays, planar arrays to two-dimensional arrays conformed to special shapes such as parabolic dishes. These arrays are of interest in medical imaging systems.

Fabrication of Piezoelectric Polymer Film

A. J. Bur, J. M. Kenney, and M. G. Broadhurst

The Department of the Navy is supporting a project to fabricate piezoelectrically active PVF_2 specimens with thicknesses of 0.81 mm (32 mil). A thick transducer is described because, relative to the thin film PVF_2 transducers which we have routinely prepared, a thick transducer will have a lower capacitance and a correspondingly higher voltage response for a given strain. A relatively large voltage response is the benefit of fabricating a thick transducer.

The problem in preparing thick transducer specimens is that the dielectric strength of the specimen is usually lower than that of a thin film of the same cross section. A commercially available thick film was found to have such a low dielectric strength that the minimum poling field of 800 kV/mm could not be reached. Consequently, we began to prepare thick specimens from PVF_2 powder starting material. The planned fabrication procedure will be: (1) vacuum molding of bubble-free disked shaped specimens; (2) converting the PVF_2 crystal structure from α to β phase by tensile extension or by rolling; (3) evaporating electrodes; (4) poling at 800 kV/cm or higher at 80 °C. At this time, bubble-free disk shaped specimens have been prepared but poling has not been carried out.

POLYMER STANDARDS FOR CONTROL AND EQUITY

Molecular weight and molecular weight distributions are the most important determinants of the useful properties of high polymers. They are of primary importance in determining both the processability of the raw materials and the characteristics of the fabricated products. Directly or indirectly, molecular weight is an important part of the specifications used in the commerce involving the tens of millions of tons of plastics produced every year. The ability to determine molecular weight reliably and reproducibly in different laboratories is thus important to both plastics producers and fabricators.

This task has four main technical activities, all aimed at this overall objective of providing a reliable base for the measurement system of molecular properties for use in commerce. First, the current needs of the measurement system used in industry are addressed by projects on the production of standards for molecular weight calibration and research on methods of improving the utilization of gel permeation or size exclusion chromatography which has become a widely used industrial measurement technique. Classical absolute molecular weight determinations are highly labor intensive, which limits the speed of standard reference material production and consumes large amounts of capital per standard. Our highest priority is therefore placed on the development of an absolute molecular weight detector for a gel permeation chromatograph which will be able to produce standards at a much faster rate without a sacrifice in quality. Elastomer SRM's are produced for quality control and specification by the rubber industry. The second technical activity provides the scientific basis for the molecular characterization methods of the future by exploring techniques and theories which meet needs we see growing in the plastics industry. Examples of this are our projects concerned with block copolymers and blends which are rapidly growing segments of total plastics use. The third and fourth activities involve the development and application of molecular characterization methods to particularly critical plastics applications where market forces are not sufficient to attract sufficient industrial effort. Our present work in these activities relates to the use of ultra high molecular weight polyethylene for orthopedic implant use and the development and application of gas permeation measurement methods and standards.

Technical Activity

Self-calibrating Gel Permeation Chromatography

P. H. Verdier

Gel permeation chromatography (GPC) is a widely accepted technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular-weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material, so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape, and in any event is inadequate for quantitative determinations. Some instruments, an example of which is commercially available, attempt to circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required in principle to relate scattering intensity to molecular weight. In addition, qualitative information on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

We are designing and constructing a light-scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle, and which is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of scattering angle and concentration and the results extrapolated to zero scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers.

During the current fiscal year, we have completed construction of a prototype of the scattering cell and its mounting, the two most critical components of the instrument. In the coming fiscal year we expect to complete design and construction of the remainder of the instrument and to begin testing it.

Recycle Gel Permeation Chromatography

F. L. McCrackin and H. L. Wagner

Recycle gel permeation chromatography (GPC, also called size exclusion chromatography) was studied theoretically and experimentally as a method to measure the column spreading parameter and the polydispersity of nearly monodisperse polymer standards. The width of the recycled chromatograms could be accounted for by four causes: (1) the volume of solution injected into the column, (2) the column spreading, (3) the molecular weight distribution of the polymer, and (4) spreading due to the pump. A method was developed to separate the spreading into contributions due to each of the individual causes. Previous analysis of recycled GPC considered the width of the chromatograms as due to only the column spreading and molecular weight distribution of the polymer. By taking the other contributions of the spreading of the chromatograms into account, much more accurate values of the column spreading parameter and polydispersity of the polymer are obtained.

The recycle experiments were carried out with a set of crosslinked polystyrene columns of nominal pore size of 10^3, 10^4, 10^5 and 10^6 Å in a GPC system with a differential refractometer as a detector. The columns were calibrated in tetrahydrofuran and toluene with 5 narrow distribution anionic polystyrenes ranging in molecular weight from 9,000 to 498,000, including SRM 1478 at 36,000 and SRM 705 at 175,000.

To reduce the extent of interference by spurious peaks, which normally occur at high retention volumes after the polymer peak has eluted with distortion of the subsequent recycle peaks, most recent runs were made in toluene. The use of this solvent, together with additional changes in the injection procedure, reduced this interference but did not eliminate it entirely.

Previously, all the various components of spreading were obtained by a least squares fitting of a function of the total spreading to a polynomial in the number of cycles. To improve the precision of the results, we made use of the observation that the spreading due to the injection and the pump was the same for all the samples. These two components of the spreading were then determined separately by measuring the spreading with the columns removed from the chromatograph. Knowing these, it was possible to determine the remaining components, the column spreading and polydispersity, from a least squares fitting of a function of the total spreading to a simple linear relationship in the number of cycles.

Results from this analysis are shown in Table 1. The polydispersities, M_w/M_n of the anionic polystyrenes are quite low, ranging from 1.0027 to 1.09. The spreading due to the columns increases with molecular weight from 0.2 ml at a molecular weight of 10^4 to 0.6 ml at a molecular weight of 2×10^5.

Such measurements now allow the spreading to be measured for <u>any set of columns</u> without using recycle by measuring SRM 750 or 1478.

A chromatogram is obtained for one of these polystyrenes run through the columns, and the spreading due to the columns is then found by subtracting the spreading due to the known polydispersity from the total spreading.

Table 1

Polydispersities and Column Spreading Parameters for Polystyrene Samples

Sample	Solvent	$M \times 10^{-3}$	M_w/M_n	Spreading Parameter, ml
SRM 1477	Toluene	9.1	1.124	0.259
SRM 1477	THF	9.1	1.050	0.158
SRM 1478	Toluene	36	1.0095	0.395
"	"	"	1.0099	0.436
"	"	"	1.0091	0.437
"	THF	"	1.0090	0.394
PC25170	Toluene	51	1.0028	0.336
PC4b	Toluene	111	1.0030	0.581
"	"	"	1.0043	0.449
SRM 705	Toluene	175	1.0062	0.592
"	THF	"	1.0090	0.505
PC50124	Toluene	233	1.0028	0.551
PC3b	Toluene	390	1.0027	0.538

Standard Reference Materials for Rubber and Rubber Compounding

G. W. Bullman and G. B. McKenna

Many of the procedures used by industry for quality control and commercial specifications of rubber depend on standard reference materials (SRM) which are maintained by the Polymer Science and Standards Division. This project renews SRM's as stocks are depleted and produces new SRM's needed by industry for control of processes and commercial specifications which are outside the range of properties available with current SRM's.

The limited resources of the SRM program have prompted us to try to elicit support for an industrial research associate program that would assist in the maintenance of the current program and in the development of new SRM's. Although ASTM Committee D-11 on Rubber and Rubberlike Materials has set up a task group to try to get support for the rubber SRM program from the rubber industry, nothing has been accomplished in this regard since December 1977 and the industry appears content to let the rubber SRM program remain static. In response to this, the Polymer Science and Standards Division has been making efforts to maintain the important SRM's and to eliminate those which are selling at very low levels. The net result will be a streamlined rubber SRM program which serves industry in an efficient manner with materials which are certified by NBS to have certain physical and/or chemical properties rather than having NBS serve as a warehousing distributor for industrial grade materials.

As part of the program to maintain the current important SRM's, we have contracted for the production of a new Butyl Rubber SRM, which will be certified for Mooney Viscosity. In addition, one material, N-t-butyl-2-benzothiozole sulfenamide, a rubber accelerator, will be renewed as an SRM. This material is certified only for homogeneity and fits into the category of warehousing an industrial grade material, but will be renewed to avoid a major disruption in the ASTM standards which rely on this material.

Work within ASTM has also indicated a requirement for a high temperature, high viscosity, Mooney Viscosity reference material. Work will be undertaken to develop such a material during the coming year.

Quasielastic Light Scattering

C. C. Han

Quasielastic light scattering uses the photon correlation technique to measure the two time correlation function of scattered light from polymer solutions. This two time correlation function at any momentum transfer, q, is related to the intermediate scattering function, S(q,t), which in turn is a double Fourier transform of the space and time correlation function of monomer pairs. Therefore, in principle, measurement of S(q,t) can provide not only a measure of the properties associated with the equilibrium distribution of polymer segments such as the radius of gyration, R_G, or the statistical segment length, but also measure physical properties associated with the time evolution of polymer segment distributions, such as the hydrodynamic radius, R_H, or the hydrodynamic interaction strength.

Our most recent efforts have been centered on the development of theories for the intermediate scattering function, S(q,t), and the characteristic frequency, Ω(q), for polymer solutions. Such theories are essential for the interpretation of quasielastic light and neutron scattering data. Our theory includes both temperature and molecular weight dependence specifically. We have also successfully applied this theory to a different characterization technique, intrinsic viscosity.

Interpretation of Scattering Experiments on Polymer Solutions

A. Z. Akcasu[1] and M. Benmouna[1]

[1]University of Michigan

Interpretation of dynamic scattering experiments require, ideally, a theory that can predict the intermediate scattering function, S, as a function of t and q, under actual experimental conditions, which are characterized by the temperature and concentration of the solution, and by a chain model consistent with the chemical structure of the polymer. Unfortunately, exact expressions of S(q,t) are available, at present, only for a single unperturbed (θ-condition) gaussian chain without hydrodynamic interaction (Rouse model), or, in the infinite chain limit, with hydrodynamic interaction and preaveraged Oseen tensor (Rouse-Zimm model). In this sense, a complete interpretation of scattering experiments on polymer solutions is an unsolved problem. By using linear response theory, we have been able to express S(q,t) of both linear and circular chains for Rouse and Rouse-Zimm cases for infinite chain limit in a closed form. Also we can express S(q,t) for finite chain lengths of linear chains in the Rouse limit and for circular chains in both Rouse and Rouse-Zimm limits in a closed form. All these can be compared with the method of eigenfunction expansion and the method of solving diffusion equations directly. Advantages of our current scheme have been demonstrated. In the case where an exact solution of S(q,t) can not be obtained, the characteristic frequency, Ω(q), which is the initial slope and defined by

$$\Omega(q) = -\lim_{t \to 0} \frac{dS(q,t)}{dt}$$

can be calculated. The temperature and concentration dependence of Ω(q) in terms of the "blob model" chain statistics can be calculated not only for the intermediate scaling region but also for the upper and lower transition region where information about polymer chain parameters such as radius of gyration, R_G, statistical length, a, and hydrodynamic interaction, B, can be extracted.

Temperature and Molecular Weight Dependence of Polymer Chain Dimensions and Application to Intrinsic Viscosity

A. Z. Akcasu[1]
[1]University of Michigan

The molecular weight, M_w, and temperature, T, dependence of the radius of gyration, R_G, and hydrodynamic radius, R_H, of a polymer in dilute solution have been investigated. Theoretical predictions were compared with experimental results on polystyrene in various solvents as a function of M_w and T, where the lower critical solution temperature is high and has negligible effect[1]. The existing data fell in a region where R_H can not be represented by a simple power law, $R_H \sim M^{\nu'}$, whereas most of data on R_G satisfy $R_G \sim M^{\nu}$. A power law fit to data would yield a $\nu' < \nu$ in this region, even though the theory yields $\nu' = \nu$ in the asymptotic region.

The same molecular weight and temperature dependence has also been successfully applied to intrinsic viscosity[2] using the dynamic argument of Weill and des Cloizeaux. Without any parameters besides the one which has been obtained previously in an R_G measurement, the intrinsic viscosity of polystyrene in various solvents and temperatures can be represented over a range of 5 decades as shown in the Figure 1. This scheme could overcome the difficulty of empirical Mark-Houwink equations $[\eta] = KM^a$, which only apply for limited molecular weight ranges and require a different set of parameters (K and a) for different experimental conditions. Our scheme can be used as a characterization method for polymers with any desired solvent and temperature. Also, it may provide a better universal calibration for gel permeation chromatography.

References:

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(2) "Molecular Weight and Temperature Dependence of Intrinsic Viscosity of Polymer Solutions," C. C. Han, Polymer, (in Press).

Our theoretical predictions of $[\eta]/[\eta]_\theta$ through the static argument of Flory-Mandelkern where $[\eta] \sim R_H^3$ and the dynamic argument of Weill-des Cloizeaux where $[\eta] \sim R_G^2$ are also shown in solid lines. The discrepancy with experimental results of the static argument is due of its failure in differentiating R_G and R_H and in predicting the slower cross-over of R_G from the θ-region to the good solvent limit. The dotted line represents the limiting slope of $[\eta]$ at high M and T.

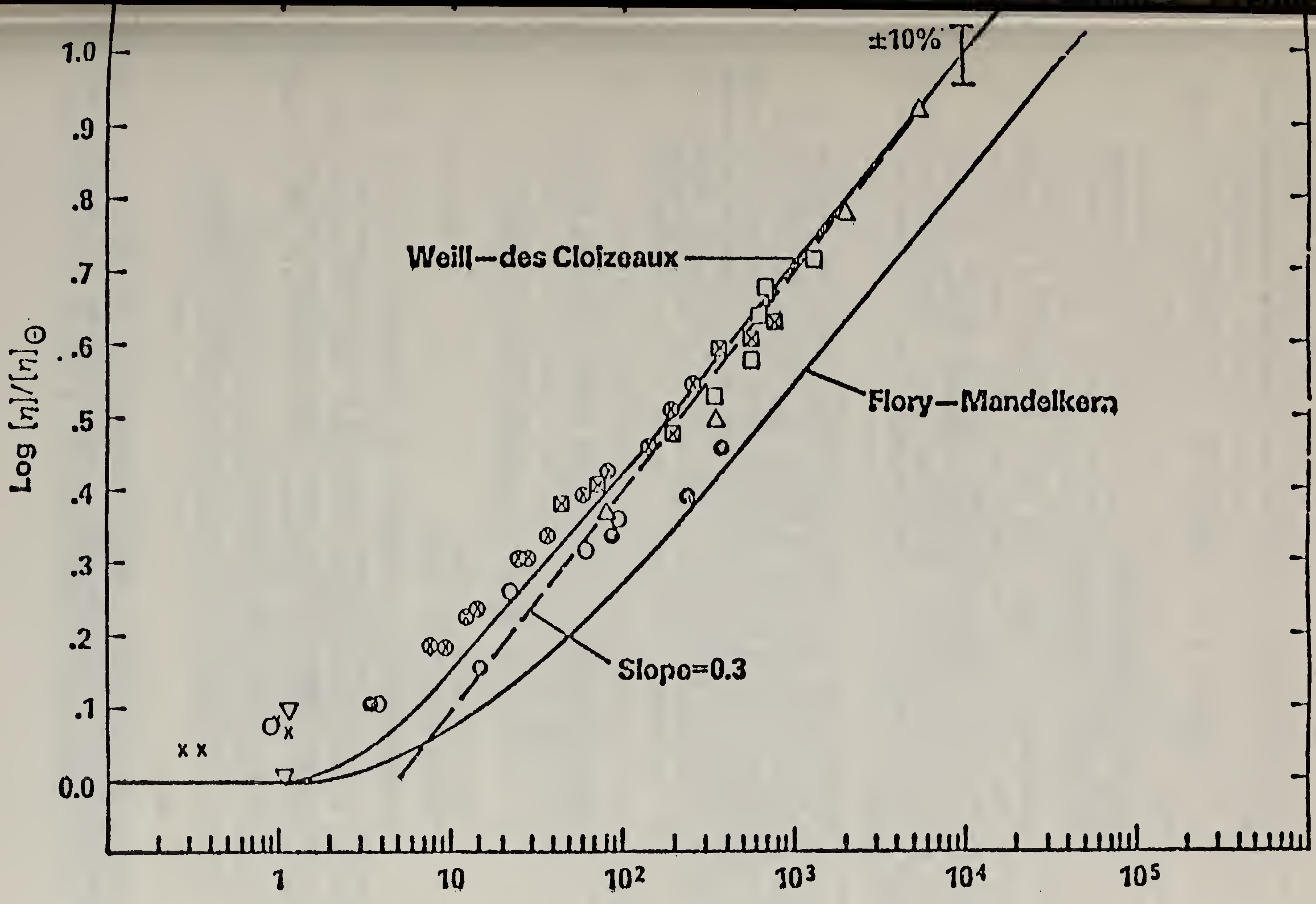

Figure 1

The variation of intrinsic viscosity of polystyrene in various solvents and temperature, with a combined scaling parameter N/N_τ, where $N/N_\tau = Mt^2/M_0(n\alpha)$ and $\tau = T-\theta/T$ with M as molecular weight of the polymer, M_0 as the molecular weight of the monomer, τ as the reduced temperature, θ^0 as the theta temperature and $(n\alpha)$ is the only parameter which has been fixed by a different experiment (R_G measurement in our case).

Single Chain Neutron Scattering in Concentrated Solutions and Melts

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Measurements of the single chain configuration in neutron scattering have always involved taking the limit of small relative concentration of the deuterated polymer. This is done to eliminate interference effects in scattering from different chains. The difficulty with this procedure is, of course, that it emphasizes the least reliable results, namely those from the small relative concentrations of labeled polymers.

A general method for extracting the single chain scattering function by performing experiments at two different concentrations of labeled chains while keeping the total polymer concentration constant has been developed. This method has been tested experimentally by using 10,000 molecular weight polyisoprene and matched deuterated polyisoprene mixtures. Signal to noise ratios so obtained during 40 hour runs at the NBS facility are excellent and are comparable with results obtained using the D17 instrument in Grenoble, France, with a two dimensional detector.

Characterization of Polymers and Domain Structure Study of Block Copolymers

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Characterization of polymers with different architecture such as branched star and comb polymers, and stiff chain polymers will be carried out by small angle neutron scattering. Also, the domain interface structure of linear and star shaped block copolymers will be studied by SANS. Samples and specimens are currently being prepared and characterized by conventional techniques.

Excimer Fluorescence in Dilute Solutions of Block Copolymers

F. W. Wang

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths with respect to the fluorescence spectrum of the isolated molecule. Similarly, excimer formation may take place by intramolecular processes in polymers carrying excimer-forming groups. Thus, excimer fluorescence has been observed in dilute solutions of polymers such as polystyrene, polyvinylnaphthalene, and poly(1-naphthyl methacrylate).

Our experiments[1] as well as those of others[2,3] have shown that in solutions of polymers carrying excimer-forming groups, excimer formation becomes more efficient as the polymers become more compact or as the intermolecular interaction among polymers increases due to aggregation or an increase in concentration. Therefore, excimer fluorescence may serve as a probe for conformational change or aggregation taking place in solution.

We have measured excimer fluorescence in dilute solutions of a polystyrene and of a four-branched block copolymer, each branch of which has a polystyrene block at the free end and a polybutadiene block at the branch point. The solvents used were cyclohexane and a mixed solvent consisting of 5:1 by volume methylene chloride and cyclohexane. As expected, phenyl-group excimer formation for both polymers was found to be more efficient in cyclohexane, a poorer solvent for polystyrene, than in the mixed solvent, a better solvent. But what is more interesting is this: in both solvents, excimer fluorescence was found to be more efficient for the block copolymer than for the homopolymer. These observations suggest that intramolecular or intermolecular aggregation takes place even in the dilute solutions (about 0.03%) of the block copolymer.

Additional experiments will be performed to study the variation of excimer formation with temperature, solvent power, and the number of branches. Experiments based on the fluorescence energy transfer technique are being made to determine whether the aggregation is intermolecular or intramolecular and whether intermingling of the polystyrene block and the polybutadiene block takes place.

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Fluorescence Energy Transfer Technique for the Study of Polymer Compatibility

F. W. Wang and R. E. Lowry

There has been growing interest in the potential value of reusing scrap plastics as blends of generic mixtures. Because such blends often have very poor mechanical properties, there have been some efforts to develop additives or "compatibilizers" which can improve the properties of the blends. Since a convenient technique is needed to test polymer compatibility, we have initiated a program to evaluate the utility of the fluorescence energy transfer technique for the study of polymer compatibility.

Fluorescence energy transfer can take place between a fluorescence energy donor and a suitable energy acceptor over distances as large as 70 Å. Since the efficiency of transfer depends on the inverse sixth power of the distance between the donor and the acceptor, in a blend containing two polymers labeled with donor and acceptor, respectively, the efficiency of transfer will be small if the two polymers are incompatible and segregated but will be large if they are compatible and form a single phase. Some results of our energy transfer measurements to evaluate the effectiveness of a compatibilizer are described as follows:

Although poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) are incompatible[1], Kwei and co-workers[2] found it possible to render these two methacrylate polymers compatible with the use of poly(vinylidene fluoride) (PVF_2) as "compatibilizer" or a common solvent. We prepared methacrylate polymers labeled with donor or acceptor. The efficiencies of energy transfer in three polymer blends with the following components were determined: 1) donor-labeled poly(ethyl methacrylate) polymer(D-PEMA)/acceptor-labeled poly(methyl methacrylate) polymer(A-PMMA); 2) D-PEMA/A-PMMA/PVF_2; and 3) D-PMMA/A-PMMA. It was found that, at the compositions studied, the efficiency of energy transfer for the second blend with PVF_2 was close to that for the third which should be homogeneous, while the efficiency for the first blend without PVF_2 was much lower. Thus, in agreement with calorimetry results[2], energy transfer measurements showed that, at some compositions, PVF_2 serves as a compatibilizer for the two methacrylate polymers.

To establish the utility of the fluorescence energy transfer technique for the study of polymer compatibility, we plan to investigate some well understood polymer blends by this technique and compare the results with those from more conventional techniques.

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Statistical Mechanics of a Generalized Lattice Model: A Model for Interacting Polymer Molecules

D. H. Lohse[1] and I. C. Sanchez

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We have considered the statistical mechanics of N indistinguishable particles distributed on a lattice of ω sites. The model is a generalization of the usual lattice model in the sense that up to m particles can be accomodated at each lattice site. The potential energy E of the system is assumed to be given by

$$E = \sum_{n=0}^{m} \omega_n E_n$$

where ω_n is the number of lattice sites (cells) containing n particles and E_n is the potential energy of a cell containing n particles.

In the thermodynamic limit ($N, \omega \to \infty$, N/ω = constant) the canonical partition function can be evaluated exactly for this model. Some interesting properties of this model include:

1) No first order phase transition is possible.

2) For $m = 1$, or equivalently, $m > 1$, $E_2 = E_2 = \ldots = E_m \to +\infty$, the free energy is that of a lattice gas without attractive interactions and the distribution law for cell occupancy corresponds to Fermi-Dirac statistics.

3) For $m = N$, $E_n = n\varepsilon$, a Bose-Einstein distribution law is obtained for cell occupancy.

4) For finite $m (m \geqq 2)$ and $E_n = n\varepsilon$ an intermediate distribution law is obtained.

The above assumption that the potential energy of the system is equal to the sum of cell energies is in general invalid for interacting particles. However, there exists a class of intermolecular potentials for which this assumption is correct. This important result is expressed in the following theorem which we state without proof:

Theorem

Consider a system of N spherical particles of diameter d whose potential energy is pairwise additive. The system is divided into a lattice of ω cells each of volume $(\pi/6)d^3$. A system configuration in which all N sphere centers are at lattice positions is defined as a lattice configuration. Any system configuration can be converted to a lattice configuration by translating all spheres which are located at off-lattice positions to the centers of their respective cells. If the pair potential $\mu(R)$ between spheres separated by a distance R is proportional to the covolume (the common volume), i.e., if

$$\mu(R) = \begin{cases} \mu_0(1 - R/d)^2(1 + R/2d) & R < d \\ 0 & R \geqq d \end{cases}$$

then the mean potential energy of the system $\langle E\rangle$ is equal to the mean potential energy of the translated lattice system, $\langle E\rangle_{\text{lattice}}$, with

$$\langle E\rangle_{\text{lattice}} = \omega\langle E_n\rangle$$

$$\langle E_n\rangle = \frac{\mu_0}{2} \langle n(n - 1)\rangle$$

where E_n is the energy of a cell containing n spheres with $n(n - 1)/2$ pair interactions. A corollary to this theorem is that the mean value of the total covolume is the same in the lattice system as in the non-lattice system. The process of translating the N spheres to their respective cell centers does not alter the mean value of the total covolume. It is this isomorphic property that makes this lattice model so valuable for treating polymer-polymer interactions. The simplest representation of a polymer molecule is that of a spherical particle of uniform (and very low) monomer density. Thus, when two polymer domains overlap the number of intermolecular monomer-monomer interactions will be proprotional to the covolume.

The utilization of this model will enable us to predict the affects of polymer concentration on chain dimensions.

Phase Transition Behavior of the Isolated Polymer Chain

I. C. Sanchez

A mean field theory of chain dimensions has been formulated which is very similar to the van der Waals theory of a fluid. In the limit of infinite chain length, the chain undergoes a Landau type second-order phase transition. At low temperatures the chain is in a condensed state and the mean square gyration radius $\langle S^2\rangle$ varies $r^{2/3}$ where r is proportional to chain length. At high temperatures the chain is in a gas-like or coil state where $\langle S^2\rangle$ varies as $r^{6/5}$. In the condensed state fluctuations in $\langle S^2\rangle$ are very small (or order unity) whereas they are very large (of order r) in the coiled state. A characteristic feature of the theory is that ternary and higher order intramolecular interactions are approximated. At high temperatures only binary interactions are important, but at low temperatures many of the higher order terms contribute. An important conclusion of this study is that a polymer chain does not obey ideal chain statistics at the θ temperature. Although the second virial coefficient vanishes at θ, the third virial coefficient does not; its presence is responsible for the perturbation of the chain statistics. For an infinite chain, θ and the second-order phase transition temperature are identical. When generalized to d-dimensions the theory yields at low temperatures, $\langle S^2\rangle^{d/2} \sim r$ for all d, and at high temperatures, $\langle S^2\rangle \sim r^{6/(d+2)}$, and $\langle S^2\rangle \sim r$, $d > 4$.

Dynamics of Polymer Chains

P. H. Verdier and D. E. Kranbuehl

The dynamical behavior of polymer chains is important for two reasons. First, the principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, non-equilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

Second, the processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end-products. A major shortcoming of present theory is its inability to treat chain entanglements in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

We have previously shown that for our simple chain models, self-entanglement effects lengthen the longest relaxation times of the chains by a factor proportional to about the first power of chain length. However, our models differ from polymer chains in solution in (at least) two obvious respects: the chains are constrained to lie upon a lattice, and motion from one configuration to another is accomplished solely by a series of purely local chain motions. Theoretical work carried out elsewhere appeared to predict a much weaker dependence of the lengthening of relaxation times upon chain length than we had found, leading to the suggestion that our results were artifacts arising from special constraints in the local chain motions we had employed. We subsequently obtained results for chains with modified rules of motion free of these constraints, and showed that the suggestion was incorrect. This work has just been published. During the current fiscal year we have carried out a series of studies of the effects upon relaxation behavior of the type of lattice employed. Preliminary results suggest that self-entanglement effects are somewhat weaker on face-centered and body-centered cubic lattices than on the simple cubic lattices employed in our earlier work, though still much stronger than the current theoretical predictions. We expect to complete this work early next year.

Additional work planned for the coming year will proceed along three lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasi-elastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. Second, as a step in the direction of investigating melt properties, we will extend the simulation studies to non-dilute solutions. Finally, in order to shed further light on the question of lattice-dependence of relaxation behavior, we will attempt limited simulation studies of chains not restricted to a lattice.

Characterization of UHMW Polyethylene for Synthetic Implants

H. L. Wagner and J. E. Dillon

The use of synthetic implants, man-made replacements for body parts, is becoming more widespread every year. Currently, 130,000 implants of Ultra-High Molecular Weight Polyethylene (UHMWPE) are used annually for a wide variety of load-bearing orthopedic prostheses such as hip and knee joints. This is increasing not only because of our growing elderly population, but also because such surgery is being performed more frequently on younger people as the outlook for long-term success becomes brighter.

The main objective of this project is the development of new or modified standard methods for characterizing the molecular weight and molecular weight distribution of UHMWPE. These methods will provide industry with a needed capability for monitoring rigorously the raw UHMWPE used in the manufacture of orthopedic implants. This capability is necessary since the above-mentioned molecular parameters strongly influence both the processing conditions used in the manufacture of the implants, as well as the physical properties (wear, creep, stress cracking) of the products. They will also provide a basis for issuing an NBS reference material for the calibration of instruments used for characterizing the molecular parameters of UHMWPE.

Zero Shear Viscosity of UHMWPE

H. L. Wagner and J. E. Dillon

Previous work has established that single point dilute solution viscosity estimates of the molecular weight of UHMWPE, the basis on which the material is currently sold, are inaccurate. This is due primarily to the previously unrecognized shear rate dependence of the viscosity determination, and the lack of a valid relationship between molecular weight and viscosity (Mark-Houwink relation) for these very high molecular weight materials. In order to provide a meaningful characterization of UHMWPE it is first necessary to determine the limiting viscosity number in the limit of zero shear rate. The zero shear viscosity, an unambiguous quantity, can be the foundation of a rapid and convenient test method at finite rates of shear by polymer producers and implant fabricators alike.

For this purpose, a low shear rotating viscometer of the Zimm-Crothers type has been built. In this viscometer the shear stress is fixed by the magnetic interaction of external electromagnets with an aluminum core set in an inner cylinder. The liquid being measured is kept between the fixed outer cylinder and the inner rotating cylinder suspended in the liquid. The rate of rotation is measured by a counter timer triggered by a laser beam. The entire apparatus is suspended in an oil bath kept at a constant temperature.

In the initial experiments it was found that the precision was inadequate for relative viscosities up to about 1.4, the generally recommended limit for such measurements. In addition, apparent shear rate effects were observed with samples which were known to be shear rate independent. These difficulties turned out to be due in part to the wobble of the rotor and were largely overcome by fabricating the stator and rotor out of uniform bore tubing and by careful fitting of the aluminum core, properly weighted, in the rotor.

Measurements in the modified apparatus at 34.5 °C in cyclohexane and toluene with both a 30,000 and a 12 x 10^6 molecular weight polystyrene did not reveal any shear dependence at the low shear rates of the rotational viscometer. The high molecular weight polymer did show some shear rate dependence at the much higher shear rates of a variable shear capillary viscometer in toluene and the data were a smooth continuation of the results in the rotational viscometer. Additional runs will be made on higher molecular weight anionic polystyrenes.

These low temperature results, although few in number were satisfactory enough to encourage us to make measurements at 135 °C. At this temperature, however, we find additional modifications are needed because of dimensional changes which occur on heating.

Fractionation of UHMWPE

H. L. Wagner and J. E. Dillon

To determine the molecular weight distribution of UHMWPE, it is necessary to fractionate the polymer because such high molecular weight polymers cannot yet be characterized by chromatography (GPC). Before the advent of GPC, linear polyethylenes with weight average molecular weights up to a few hundred thousand were frequently fractionated by column elution. However this technique becomes more difficult and less efficient as the molecular weight increases and hence was not chosen for the fractionation of UHMWPE.

Instead, the so called "stir fractionation" technique was used. In this method the UHMWPE whole polymer was first dissolved at 145 °C in tetralin. The temperature of the solution was then lowered gradually with fairly rapid stirring until some polymer separated out on the stirrer. This material which separated first is the highest molecular weight fraction. This was removed and the process was continued by lowering the temperature further, removing fractions until no more polymer precipitated.

A total of 7 fractions were obtained between 104 and 90 °C in the first experiment. Viscosity measurements indicated a 4-fold difference in viscosity number (at the same concentration) between the first and last fractions, indicating that at least some fractionation has been achieved. These fractions will also be measured by light scattering and the results should give us an idea of the fractionation efficiency. At this point, the method looks promising.

Development of a Digital Lock-in Light Scattering Photometer

J. R. Maurey, D. B. Minor, and C. C. Han

A state-of-the-art light scattering photometer has been developed for the purpose of measuring the molecular weight of polymer SRM's and ultra-high molecular weight synthetic implant materials. This photometer utilizes the principle of photon counting and digital lock-in has been tested with the measurement of previously certified SRM's. Although, further tests are still needed, our preliminary measurements have demonstrated an angular range of down to $\theta = 15°$, a dynamic range of over three decades without corrections, long term stability and reproducibility and a good dust rejection ratio.

Standards for Gas Transmission Rate Measurements

J. D. Barnes

The documentation of characterization measurements on the polyester film issued as a Standard Reference Material for oxygen gas transmission rate measurements was completed, and the result is available as NBS Special Publication 260-58, "SRM 1470 - A Polyester Film for Oxygen Gas Transmission Measurements."

We continue to assist Committees D-20 (Plastics) and F-2 (Flexible Barrier Materials) of the ASTM in developing improved standards for characterizing the barrier properties of plastic materials. A new standard method presently being ballotted, for the coulometric determination of oxygen gas transmission rates references SRM 1470 as its primary calibration standard. NBS is leading a task group formed to revise ASTM D1434, which is the classical method for the manometric and volumetric determination of gas transmission properties. Interlaboratory testing has demonstrated that improved standards are needed before this method can be expected to give reliable results. ASTM task groups working with instrumental methods for water vapor and carbon dioxide transmission rates have received assistance in the statistical design and analysis of interlaboratory evaluations. These efforts may well point out needs for new or improved standards in the form of test methods or reference materials.

A new automated permeation measuring facility is being constructed. The new facility uses a manometric measuring technique, but it has been designed for greater sensitivity (achieved by a cleaner vacuum on the downstream side) and safer operation (achieved by automated safety interlocks to guard against adverse effects from film failures during testing) than our previous system. The new facility is designed to operate above 100 °C, thus enabling us to study glassy polymers at temperatures above and below the glass transition.

A laboratory minicomputer is being interfaced to the facility. Computer control will assist in more frequent monitoring of calibration parameters and in more detailed characterization of the operating temperature and pressure in the system. More complex sequences of experiments, which are needed in studies of glass transition and annealing phenomena, can then be carried out. Transient phenomena, including time lags and desorption effects, are easier to study under computer control. On-line data reduction will prove useful in detecting significant effects that occur during the course of experiments. It was necessary to develop some software to interface the computer with an existing MIDAS controller and to verify that vendor-provided laboratory routines could be used in our application. Software modules for driving the completed facility will be written as needed when construction is complete.

The first project to be undertaken using the new automated permeation measuring facility is a remeasurement of the oxygen gas transmission rate of SRM 1470. This project is being undertaken to ascertain the significance of any drifts in the rates that might result from storage.

The permeance of polymer films to gases is very sensitive to the microstructure of the material, and gases of differing molecular diameters should be useful as probes for determining the size distribution of free volume elements. Earlier work has shown that there are useful correlations between molecular sizes, the state of the polymer, and transport coefficients. We expect to explore these correlations in experiments using several different gases and samples whose thermal and mechanical histories have been varied so as to change the state of the material. Data of this kind can be used to test molecularly-based theories of transport in polymers. This work is also expected to provide a basis for characterizing SRM 1470 for its transmission rate with respect to additional gases, thus allowing this SRM to be more useful in improving the state-of-the-art in transmission measurements. These studies may also result in improved industrial quality control techniques for characterizing barrier materials. Helium gas permeates films much more rapidly than does oxygen or carbon dioxide. If a useful correlation can be found between helium transmission rates and the transmission rates of other gases, it may be possible to use helium in rapid testing to establish whether a process is under control.

The manometric method is useful as a primary standard, but it is inconvenient to use for industrial quality control. For this reason we expect to investigate ways of using gas chromatography in permeation measurements. Such methods would also be useful in research where the permeant stream contains more than one component.

There are a number of problems arising from the use of archaic systems of units in reporting the results of molecular transport measurements. We started work on a modernized set of units, consistent with SI, for describing such measurements. Most problems arise from a failure to recognize that the mole is the appropriate unit for characterizing the amount of substance being transported across a barrier. Using moles per second as the starting point, it is possible to construct units for permeabilities, permeances, and matter currents that are more meaningful than those presently being employed. This procedure has already been followed on the certificate for SRM 1470 and in the new standard method of test for coulometric determination of oxygen gas transmission rate.

Improved Materials for Dissolved Oxygen Measuring Devices

J. D. Barnes

During FY 1978 the Office of Ocean Engineering of the National Oceanic and Atmospheric Administration sought technical assistance from the NBS Polymer Science and Standards Division in improving the precision and accuracy of dissolved oxygen (DO) measuring systems using membrane-type polarographic sensors. The request was predicated on the idea that the polymer membranes being employed to separate the electrochemical cell from the solution to be measured were a possible source of drifts and instabilities in the measured DO values. We could not find support for this premise from an analysis of data presently being collected, which emphasizes the performance of the measuring system taken as a whole.

Our studies were confined to mathematical modelling of the transient response of the sensor to step changes in DO levels or applied voltage. The modelling calculations of the membrane layer and the electrolyte layer could be separated from one another. This requires transient experiments that measure time-lags as well as permeances. The membrane layer and the electrolyte layer are each thought of as slabs in which the transport of oxygen to the polarographic electrode can be treated as a diffusion problem involving a bilayered structure. The time-lag of the composite structure is a fairly complicated function of the time-lags of the separate layers, and the permeance of the composite structure is simply the reciprocal of the sums of the reciprocals of the permeances of the separate layers. It should be possible to devise a fitting algorithm that extracts the time-lags and the permeances from transient responses, particularly if experiments can be performed using step changes in voltage as well as step changes in DO level.

These results have implications for the characterization of inhomogeneous polymer films because they demonstrate that the diffusion coefficients and solubilities determined by sorption experiments should be different from those obtained in permeation experiments on such films and that the inhomogenity must be taken into account in resolving these differences. Further modelling efforts are needed to see if these results can be used as a characterization tool for polymer films with a "skin" whose transport properties are different from those in the "core" of the film.

The modelling work done for NOAA is described in NBSIR 79-1740, "The Influence of Polymer Membrane Properties on the Performance of Dissolved Oxygen Sensors." The results of this modelling study show that parallel measurements of sorption-desorption kinetics and permeation kinetics on films with various microstructures may reveal interesting differences in measured values of transport coefficients. We hope to pursue this problem.

More direct answers to the question of whether aging of polymer membranes cause drifts in DO measuring systems should be obtainable from measurements on membrane materials taken by themselves. A survey of membrane materials being used in DO sensors revealed that polyethylene has been the material of choice. This choice affords a strong electrical signal and a reasonably rapid response, but the high permeability of polyethylene may accelerate certain electrochemical aging processes within the electrodes. The issue of suitable materials for this application needs to be pursued more systematically by separating the membrane component from the electrochemical components of the sensor.

ASTM Activities

J. D. Barnes serves as a member of the Executive Committee of ASTM Committee F-2 (Flexible Barrier Materials) and as Chairman of Subcommittee F2.93 (Statistical Matters). This Subcommittee is responsible for the statistical design and evaluation of interlaboratory evaluation programs for test methods involving flexible barrier materials. Current projects within this Subcommittee include analysis of the results of interlaboratory test programs on bond strengths of laminates, water vapor transmission rates, retained solvents, seal strengths for retortable pouches, and oxygen gas transmission of packages. A workshop on interlaboratory testing, co-sponsored by the Statistical Subcommittee of Committee D-20 on Plastics, will be held in February, 1980. These efforts are aimed at improving the quality of the precision and accuracy statements that ASTM requires in all test methods.

Dr. Barnes also serves as the Chairman of Section F 2.30.01, which is responsible for developing test methods for measuring the barrier properties of flexible barrier materials.

The work of Committee F-2 is closely related to that of Committee D-20. Section D20.70.07 on Gas Transmission properties has task groups on the coulometric method for oxygen gas transmission measurements and on the revision of ASTM D1434, Standard Method of Test for Gas Transmission Rate of Films and Sheets. The introduction of SRM 1470 as a calibration standard has been important in assisting these task groups in their work of improving these methods.

Dr. H. L. Wagner is Chairman of Section D20.70.05, Molecular Weight Parameters. The Recommended Practice for the Measurement of Number Average Molecular Weight by Membrane Osmometry has been approved and will be published in next year's Book of ASTM Standards. The Recommended Practice for the Determination of Weight Average Molecular Weight by Light Scattering has been revised and will be submitted for balloting.

CHEMICAL DURABILITY OF POLYMERS IN USE

The growing use of polymeric materials as critical parts in systems vital to national needs such as military aircraft, nuclear reactors, synthetic implants, and solar energy devices demands an improved understanding of the chemical factors controlling the lifetime of such parts. The total economics and safety of many large systems depend on reliable estimates of the lifetime of component materials in actual use. Short-term tests for predicting durability are needed for optimum materials selection, and knowledge of polymer degradation mechanisms is needed to guide the development of protective methods and improve materials performance. This task focuses primarily on polymeric materials used in circumstances where the usual strategy of protective additives is inadequate. For example, effective additives for protection against hydrolytic degradation are not in common use, yet the superior properties of polymers with potential hydrolytic instability make these polymers attractive to designers. Technical activities describe studies of polyester polyurethanes used as elastomers in demanding applications.

Polymers play a major role in solar energy systems which are rapidly growing in importance in the national energy supply. In these devices polymers are exposed to high UV radiation levels but, in many instances, must transmit visible radiation and therefore cannot be protected from photolytically-induced oxidation by the usual methods of opaque coatings or fillers. In spite of this, the economics of the systems demand that the polymers perform satisfactorily for many years. In order to facilitate the implementation of mechanism studies of polymer oxidation, Dr. Brian Dickens spent the period September 1978 to June 1979 as a NATO senior scientist at Le Centre de Recherches sur les Macromolecules, Strasbourg, France. The host scientist was Dr. Jean Marchal who has an international reputation based on his work on radiation-induced polymer oxidation at room temperature.

Technical Activity

Oxidation of Polystyrene in Solution

B. Dickens and J. Marchal[1]

[1]CRM, Strasbourg, France

Polystyrene is much more inert to oxidation than polypropylene or polyethylene. One way of providing a measurable rate of attack is to use a solvent whose free radical derivatives are active enough to attack the polymer. The radiolytically induced oxidation of polystyrene in $CHCl_3$ and CCl_4 have already been studied to some extent at the CRM. These investigations were extended and parallel investigations were conducted with CH_2Cl_2 and C_6H as solvents. The aims were a) to clarify the differences between the effects of chlorinated and non-chlorinated solvents; b) to study the interplay between radical transfer to the solvent by hydrogen abstraction and intramolecular hydrogen abstraction on the polystyrene molecule; and c) to shed some light on the role of RO˙ radicals during the oxidation (RO˙ radicals are formed by the reaction of two $RO_2^{\cdot}$ radicals and can either abstract H or undergo β scission).

The analytical techniques used were gas chromatography, wet chemical analysis, and IR. The amount of ROOH groups formed on the polymer was determined by a calorimetric method developed at CRM. The ROOH groups were then decomposed at room temperature by Cu^{II}/Cu^{I} ions. According to the oxidation mechanism developed at CRM, attack on the secondary hydrogen of PS should give benzaldehyde, whereas a repeated attack on adjacent tertiary hydrogens should give acetophenone (both from β-scission of alkoxyl radicals). Attack of one (isolated) tertiary hydrogen gives a chain scission but no small molecule oxidation products are formed. Benzaldehyde and acetophenone were produced in all solutions studied and were detected by GC measurements. The yields of benzaldehyde and acetophenone after decomposition of the ROOH groups by Cu^{II}/Cu^{I} ions were used to show that more secondary hydrogens than tertiary hydrogens are attacked in polystyrene in chlorinated solvents. If this is corrected for the sec tert ratio of 2:1 in polystyrene, attack in chlorinated solvents is essentially random along the polymer chains. Intramolecular propagation occurs and is much faster for tertiary hydrogens than for secondary hydrogens. The chain length is governed by the concentration of $RO_2^{\cdot}$ radicals (i.e., the rate of initiation) and the probability of transfer to the solvent. At lower rates of initiation more ROOH groups are produced and, in general, more acetophenone than benzaldehyde is formed when the ROOH groups are decomposed by Cu^{II}/Cu^{I} ions. It appears that in this case the kinetic chain lengths are longer and allow more intramolecular propagation to occur.

Intramolecular propagation occurs more in CCl_4 and CH_2Cl_2 than in $CHCl_3$. The H in $CHCl_3$ is notoriously easy to abstract. Those in CH_2Cl_2 are not as active and allow longer chain lengths for the intramolecular propagation. The production of the small molecule oxidation products shows that the alkoxyl radicals, RO˙, produce detrimental chain scissions even at room temperature, and their activity is not confined to hydrogen abstraction as is sometimes believed. Protection of the polymer against oxidation may have to consider these radicals as well as the more widely recognized $RO_2^{\cdot}$ (peroxyl) radicals.

Although the decomposition of ROOH by Cu ions turns out to be less than ideal as an analytical method (because of complexations between Cu ions and RO˙ radicals), the results obtained were substantiated by integrated hydrogen absorptions in IR spectra. ^{13}C NMR measurements may be a better way of measuring the site of attack on the polymer backbone.

The amount of attack on polystyrene when C_6H_{12} is used as solvent is much smaller than in the case of chlorinated solvents. The analytical techniques used were not precise enough to give meaningful measurements on these polymers and a mechanistic comparison of the oxidations in chlorinated and hydrocarbon solvents was not possible.

Chemiluminescence from Oxidizing Polymers

R. E. Florin and Brian Dickens

Polymers emit light weakly during oxidation. This effect has aroused recent interest as a means of monitoring oxidative deterioration of polymers. A widely accepted theory of the effect is that the light is emitted during the termination step of the oxidation chain reaction. Although the quantum yield of light emission is very low, estimated at only one photon per 10^9 terminations, this inefficiency can be overcome by the technique of counting individual photons, which leads to an extremely sensitive method, potentially capable of detecting oxidation at temperatures only a little above those of normal service. In contrast, accelerated aging methods require a long extrapolation from test temperatures to service temperatures, over which the mechanism of degradation can change.

The general objective is to obtain a representative data base for correlating chemiluminescence emission rates with overall oxidation rates for polymers of differing physical and chemical characteristics. The appropriate kinetic parameters are the rates of initiation, propagation and termination. We have devised a method for measuring one of the individual rate constants of the process, that of termination. A photoinitiator is added and the sample is exposed to ultraviolet light to reach a steady-state rate of oxidation. The initiating ultraviolet light is suddenly cut off, and the decay of chemiluminescent light emission recorded. A simple second-order termination, such as can be anticipated in a homogeneous rubbery or glassy polymer, should give a linear plot of inverse square root of emission rate against time, from the slope of which the termination rate constant can be computed. To determine the kinetic chain length and the total amount of oxidation, the initiator consumption rate and the steady-state rate of oxygen absorption will also be needed later. Suitable techniques are already well known in the literature.

To conduct automated chemiluminescence experiments of the type described here, a BASIC and a FORTRAN program have been devised. As many as five counting-rate measurements per second can be taken and transmitted to the computer, and the counting interval can be varied in steps during a run. Counting rates significantly above the dark count have been observed for several materials at temperatures of 30 to 50 °C in trial runs. In many instances the chemiluminescence rate of the material as first examined has been greater than in the same material after a heating cycle. The cause of this change has not yet been determined. Termination-rate measurements on two rubbers and two glasses are planned following this.

Further applications of the procedure are: to measure photoinitiation and termination rates, under severe conditions, of clear polymers without additives such as might be used in solar energy equipment;

oxidation and chemiluminescence accompanying straining and breaking; and inhibitor efficiency measurements. With more sophisticated mathematical analysis, investigation of heterogeneous materials, semi-crystalline polymers, blends, and filled materials, would also be possible.

Hydrolytic Degradation of Polyester Urethane Elastomers

D. W. Brown, R. E. Lowry, and L. E. Smith

In warm, humid environments the physical properties of polyester urethane elastomers deteriorate more rapidly than expected. This has resulted in premature failure of parts in military aircraft. Under the sponsorship of the Office of Naval Research, we are investigating the degradation, with the goal of developing better methods of predicting the lifetime of these materials.

The observed deterioration has been shown to be due to the acid catalyzed hydrolysis of the polyester component. This decreases the molecular weight and causes changes in physical properties, which have been the basis of lifetime estimates[1,2,3]. We found that some polyester urethanes crystallized on aging, perturbing the effect of the decrease in molecular weight and invalidating the lifetime predictions[4]. Consequently, our effort has been to base lifetime estimates on other changes by correlating changes in acidity, A, with changes in the number average molecular weight, M.

Our results for three commercial polyester urethanes show that A and $\bar{M}^{-1}$ increase by equivalent amounts. Their time, t, dependence is given by:

$$A = A_0 e^{kt} \text{ and } \bar{M}^{-1} = \bar{M}_0^{-1} + A_0(e^{kt}-1)$$

where subscripts denote initial values. Here k, the fractional rate of increase in acidity, is a pseudo first order rate constant. At 100% relative humidity k obeys the Arrhenius equation between 35 and 85 °C and is approximately proprotional to relative humidity. The lifetime of a polyester polyurethane should be estimated by determining k, determining A or M near the limit of use, and solving either of the above equations for t[5]. For use under varying conditions k should be weighted for the fraction of time spent under each condition.

The degradation of polyester urethanes can be retarded by the addition of carbodiimides[6]. These materials function by reacting with the acid present in the polymer1. Consequently, the equations above are not valid if carbodiimide is present. We are now trying to develop a method of predicting lifetime in the presence of carbodiimide by following the disappearance of carbodiimide by infrared spectroscopy and the concomitant changes in A and M by titration and gel chromatography respectively.

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Thermal, Oxidative and Hydrolytic Degradation of Polyurethanes by Weight-loss Techniques

J. H. Flynn

This work was undertaken as part of a project whose aim was to determine kinetic mechanisms for the thermal and hydrolytic degradation of polyurethanes and estimate lifetime limits of polyurethane elastomers. Two methylene diphenyl diisocyanate (MDI) polyurethanes, one with polyether, the other with polyester soft segments, have been investigated by constant heating rate thermogravimetry from 10^{-1} to 10^{-4} deg/sec. in vacuum, nitrogen, air, water vapor, and combinations of these atmospheres.

The degradation of the polyether polyurethane was insensitive to the presence of oxygen or water at the high temperatures and fast heating rates typical of commercial TG apparatus. However, at very slow heating rates and temperatures under 200 °C, a low activation energy oxidation reaction was found, precluding the use of high temperature weight-loss techniques for durability prediction in this system. Although water has an effect on the weight-loss of polyester polyurethanes, the kinetics are complex and difficult to interpret. Thus, it appears that thermogravimetric techniques are not a sufficient method of lifetime prediction for polyurethanes, but must be used in conjunction with other types of analysis.

Variable Heating Rate Thermogravimetry

J. H. Flynn

The extrapolation of activation energies from accelerated conditions to service conditions for the purpose of lifetime prediction requires extremely accurate measurements and as modest a temperature range of extrapolation as possible. Weight-loss measurement has been a traditional means of assessing durability as electrobalances are rugged, stable, and accurate.

The kinetics of weight loss of several polymers have been investigated in an apparatus which operates at heating rates in the range from 6 deg/min. to 9 deg/day. The wide range in heating rate results in a broad experimental temperature range within which one is able to accurately calculate parameters and test the constancy of the kinetic process. The slow heating rate experiments reduce the reaction temperatures, thus shortening the length of extrapolation and improving the accuracy of lifetime prediction.

Polystyrene has been investigated in air between 120 and 300 °C and a commercial poly(methyl methacrylate) in nitrogen between 180 and 350 °C. Both of these polymers exhibit uncomplicated kinetic spectra over the entire weight-loss and temperature ranges lending credence to the use of weight-loss techniques for the prediction of their durability.

MIGRATION AND THE DURABILITY OF PLASTICS IN USE

All plastic items found in commerce have low molecular weight substances incorporated in them, either as a result of their method of manufacture or from the purposeful incorporation of additives to produce or maintain desirable properties. In use, these substances inevitably diffuse through the polymer to some extent and may eventually migrate out of the polymer.

The consequences of migration are two-fold. First, if the migrating substance is a stabilizing or property enhancing additive, the plastic is left with poorer properties or increased vulnerability to degradation and failure. This is a major failure mode of plastics and programs concerned with polymer durability must explicitly address the possibilities of additive migration. Second, the migrating substance becomes a contaminant of the general environment or, in the case of plastic packaging materials, a contaminant of the material being contained and so questions are raised about the toxicological consequences of such migration. Contamination of food from food packaging materials is regulated by the federal government through the Food and Drug Administration and the control of migrating substances presents an enormous challenge to the scientific basis of regulations.

The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case by case basis, either for selection of materials for optimum durability or for regulation of food and environmental contamination. General material models capable of predicting migration under a variety of service conditions are needed to organize polymer-additive combinations into classes for consideration. The development of these material models is the overall objective of work done in this task.

The technical activities that contribute to this task include (1) the experimental measurement of additive migration by several methods, (2) the compilation of critically evaluated data from this laboratory and the literature, (3) mathematical modeling and empirical correlation of diffusion data for analysis of data and rapid estimation of migration, and (4) fundamental theoretical studies of polymer behavior that can provide truly general predictive models.

Technical Activity

Solvent Extraction Methods of Migration Measurement

S. S. Chang, W. J. Pummer, J. R. Maurey, and L. E. Smith

Following the organization of a radiotracer laboratory and a brief exploratory study on the migration of oligomers and other additives of plastics into solvents, a systemmatic program of measuring the migration behavior of small molecules across the polymer/environment interface was undertaken this year. This program is sponsored by the Indirect Food Additive Program of the Bureau of Foods, Food and Drug Administration, and is aimed at developing methods for the more efficient and reasonable regulation of packaging materials in food contact use.

The first phase of the study has been concentrated on polyolefins. During the current year, both linear and branched polyethylene samples were prepared from the stocks of well characterized Standard Reference Materials 1475 and 1476. The additives studied are two ^{14}C-labeled paraffinic hydrocarbons, n-$C_{18}H_{38}$ and n-$C_{32}H_{66}$. The radioactive tracer technique was used in the study for its high sensitivities in being able to detect the presence of nanogram quantities. Qualitatively, the diffusion coefficients for smaller oligomer molecules are greater than the larger molecules as expected from their molecular sizes. Diffusion coefficients are also larger in the branched, less crystalline, samples. Studies now in progress include the modification of individual samples by thermal treatment to achieve variations in crystallinity, and the study of ethylene-propylene copolymers to achieve varied degree of branching as well as crystallinity. Polar antioxidants are also being studied in low and high density polyethylene.

Different solvents were used in the migration studies, including low molecular weight hydrocarbons, the entire composition range of ethanol-water mixtures, food oils, and pure triglycerides. Depending upon the nature of the solvent and the polymer, severe swelling or absorption of solvent may occur. The migration of the additive or oligomer molecules is greatly enhanced by the swelling of the polymer. The simultaneous swelling of the polymer by the solvent and the enhancement of the movement of the migrant produce an apparent non-Fickian behavior of the migration. In a pre-swollen polymer, e.g., polymers presaturated with n-$C_{18}H_{38}$ for the study of exchanging n-$C_{18}H_{38}$ with the surroundings, the diffusion is Fickian. In solvents where the solubility of the migrant is limited, equilibrium partitioning may be reached and the final concentrations can be calculated or estimated from the saturation solubilities. It is also possible under these conditions to measure the uptake of the migrant by the polymer from the solvent phase.

The studies involving food oils and triglycerides as solvents are used to find suitable simulating solvents for food oils. It is found that either triglycerides such as trioctanoin or even ethanol could be considered as food oil simulating solvents for oligomer migration from polyolefins.

Measurement of Migration in Polymers by Inverse Gas Chromatography

G. A. Senich

Inverse phase gas chromatography (IGC) provides a convenient experimental approach for the determination of fundamental material constants which can be used to estimate the extent of migration of low molecular weight materials from polymers into the surroundings. The technique of IGC differs from conventional vapor phase chromatography in that the material of interest, a polymer of negligible vapor pressure, is employed as a stationary phase which sorbs various volatile organic species, often referred to as probes. Processes of solution, adsorption, and diffusion can be studied in relation to various morphological characteristics of polymers such as the degree of crystallinity both above and below glass transition and melting temperatures. The experiment involves injecting a pulse of the volatile solvent into a stream of flowing carrier gas which sweeps the injected substances through a column containing the polymer of interest. At low rates of carrier gas flow the vapor or probe reaches a steady-state distribution between the vapor and polymer phase and the thermodynamics of polymer-solvent or polymer-migrant interaction yield an upper bound to the amount of migration expected. At high carrier gas flow rates the equilibrium state is not approached and the kinetics of polymersolvent interactions can be determined. The diffusion constant of the probe in the polymer can be determined at low probe concentrations and used to estimate the extent of migration over the time period of interest.

A laboratory to carry out IGC studies has been established over the past year. Preliminary IGC results on NBS SRM polyethylene and alkane systems are comparable to literature data. Further studies of the thermodynamic interactions and diffusion behavior of a series of alkane probes with common polyolefins are in progress. These results will be compared with the findings of migration studies conducted by the radioactive tracer method and employed to test and refine models for migration of small molecules in polymers.

Measurement of Antioxidant Migration by Fluorimetry

F. W. Wang

The migration of antioxidants from polymers is being studied by two types of experiments: extraction experiments and concentration profile experiments. In an extraction experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a limited amount of well stirred solvent. Then, the amount of the antioxidant extracted by the solvent is determined at various times by fluorimetry. In a concentration profile experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a large volume of well stirred solvent. The antioxidant concentration profile along the direction normal to the larger surfaces of the sheet is then determined at various times by microfluorimetry, after the sheet is sectioned with a microtome to expose the profile. Comparison of results from the two different measurement methods on the same additive-polymer system will give information on the effects of the extracting solvent on the diffusion and the concentration dependence of the diffusion constant.

Three of the antioxidants which we have examined show room temperature fluorescence sufficiently intense that their migration from polymers may be conveniently studied by fluorimetry. They are N,N'-di-β-naphthyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine (DPPD), and 3-t-butyl-4-hydroxyanisole. We have focused our efforts on the extraction of DPPD from low-density polyethylene. To date, we have developed a procedure to measure the extraction of DPPD from low-density polyethylene. This procedure involves the purification of DPPD, the preparation of polyethylene films which have uniform thickness of about 0.02 cm, and contain DPPD uniformly distributed and undegraded by the preparation, the construction of an extraction device equipped with a cell for making fluorescence measurements without exposing the solution to oxygen, and the preparation of an analytical working curve relating DPPD concentration to fluorescence intensity. This procedure will be used to determine the migration of DPPD from low-density polyethylene to heptane and to ethanol. Concurrently, in collaboration with Dr. R. A. Velapoldi, Center for Analytical Chemistry, we are developing the procedures to perform concentration profile experiments with the use of a microfluorimeter.

A Critical Compilation of Data on the Diffusion of Additives in Polymers

J. H. Flynn

The immediate objective of this project is the compilation of a reliable data base for the prediction of the durability of polymers containing protective additives. With support from the Office of Standard Reference Data, a comprehensive compilation is expected to be ready for publication by the end of FY80.

The scope of the data compilation will be limited to polyolefin polymers. These include high and low density polyethylenes, isotactic and atactic polypropylenes, polyisobutylene, and poly(4-methyl pentene). Carbon-containing migrants -- organics and compounds containing organic radicals -- will be included. Thus far, diffusion constants as a function of temperature and activation energies of diffusion have been computed and compiled for over 200 polymer-migrant combinations. The data compilation is being accompanied with critical annotation giving information on the physical and chemical properties of the migrants and polymers, experimental methods employed, models assumed for the calculation of kinetic parameters, etc.

Thus, the results will serve not only as a data source, but also as a resource from which empirical relationships for estimating diffusion coefficients in polyolefins may be developed and from which sufficient information will be available to test theoretical models for diffusion mechanisms.

An Empirical Formula for Diffusion Coefficients in Polyolefins

F. L. McCrackin

The diffusion coefficients of many materials in polyolefins were fit to the formula

$$D = PM^F$$

where M depends only on the diffusing material and P and F depend only on the polyolefin. The values of M have been tabulated for 21 materials and values of P and F have been tabulated for 7 polyolefins. Diffusion coefficients calculated by this equation agree in general with the measured values within a factor of two, while the measured diffusion coefficients cover four orders of magnitude. The diffusing materials vary from low molecular weight gases to complex antioxidants with molecular weights of several hundred.

While this formula does not predict accurate values for diffusion coefficients, it yields useful estimates when no other means are available. It will also provide a starting point for more comprehensive expressions which will contain parameters with some physical significance to provide a greater predictive capability.

Self Diffusion in Molten Polyethylene

D. H. Reneker, A. Peterlin, and R. Blinc

Measurements of the self diffusion coefficient of molten polyethylene made by a magnetic field gradient nuclear magnetic resonance method were compared with recently reported measurements made by infrared analysis of the change in concentration with time near a boundary between polyethylene and perdeutero-polyethylene. The NMR measurements yield values for the diffusion coefficients which are several times higher than those obtained from the concentration measurement. Further, the values from NMR do not depend upon M_w^2 where M_w is molecular weight.

Analysis of the NMR method indicates that since the nuclear magnetization decays exponentially with a time constant which is approximately proportional to $1/M_w^2$ the NMR result depends most upon the diffusion of material in the low molecular weight tail of the molecular weight distribution. Analysis of the behavior of a polymer with the Schulz distribution indicates that the diffusion coefficient measured by NMR does not depend upon the molecular weight of the sample but is a function of the breadth of the molecular weight distribution. Data from NMR measurements on three well characterized samples with narrow molecular weight distributions show a lower diffusion coefficient for the sample with $M_w = 32{,}000$ which had the narrowest molecular weight distribution and a higher diffusion coefficient for samples with $M_w = 120{,}000$ and 13,600, both of which had a broader molecular weight distribution.

Extraction of Additives from Plastics

F. L. McCrackin

Physical models of the diffusion of additives in polymers are needed to provide a basis for the efficient regulation of plastics used in food contact regulations. The rate of diffusion of an additive from a plastic in contact with a liquid is often increased by simultaneous diffusion of the liquid in the plastic, that is, by extraction by the liquid. The diffusion coefficient of the additive depends on both the concentrations of the additive and liquid in the plastic, and the diffusion coefficient of the liquid also depends on the concentrations of both the additive and liquid. This diffusion problem can not be solved analytically, but its solution is required for the modeling of extraction of additives from plastics by foods, as well as for the interpretation of experimental studies of solvent extraction of additives from plastics.

A numerical finite difference method has been developed to solve the diffusion equation for extraction, and a computer program was written. Some initial migration curves have been obtained. The calculated migration curves will first be qualitatively compared with the experimental extraction curves. Later, they will be fit to experimental extraction curves and the results applied to the problem of extraction from plastics containers in use.

Type II Diffusion in Glasses

A. Peterlin

The description of this type of diffusion was applied to spheres and films. The analysis of the experimental observations is in perfect agreement with the predictions of the theory which assumes a constant velocity of the propagation of the glass-gel boundary with the gradual formation of a steady state concentration profile in the glass in front of the boundary. This formation yields a square root of time term in the weight gain while the constant propagation velocity of the glass-gel boundary yields a time proportional term which reflects the linear increase of the swollen gel fraction with time. The geometry of the sphere drastically modifies the time dependence of the weight gain. Together with Professor Sarti, Naples (Italy), one has tried to explain the propagation of the glass-gel boundary by the nucleation effect of the crazing caused by the expansion pressure of the polymer in equilibrium with the diffusant.

Moisture Absorption and Desorption Effects in Epoxy Matrix Composites

R. J. Rubin

The following conclusions stem from a literature survey of moisture absorption and desorption effects in epoxy matrix composites:

(1) There does not appear to be a significant dependence of durability or performance simply on diffusion coefficients of the epoxy matrix. That is, transient effects associated with diffusion do not appear to be generally important from the point of view of durability although they may be important in accelerated tests. The typical period of exposure of composites to a humid use environment is of sufficiently long duration that the solubility of water in the epoxy matrix is a more dominant parameter.

(2) Absorption and desorption of water associated with ambient variations in the relative humidity is accompanied by dimensional changes in the epoxy matrix and stresses at the epoxy-fiber interface.

(3) Depending upon the nature of the reinforcing fibers, absorbed moisture can concentrate (and attack chemically) the epoxy-fiber interface.

(4) Combination of the stress variations mentioned in (2) with or without chemical attack of the interface mentioned in (3) can result in fatigue-like failure of the composite.

Theoretical methods of attacking the problem of moisture effects in composite failure have been explored. Harlow and Phoenix[1] have made an initial attempt to apply the chain-of-bundles probability model in studying the failure of composite materials, but these authors do not seem to have paid attention to the possibility that the properties of the epoxy matrix, through its absorbed water content, might play a demonstrable role in the model. The emphasis of Harlow and Phoenix lies heavily on the statistical aspects of the problem. Additional useful physical information appears to be available in acoustic emission studies of fiber composite materials[2],[3]. This information should provide additional physical inputs to any chain-of-bundles failure model of composites.

References:

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Statistical Thermodynamics of Polymer Solutions

I. C. Sanchez

The lattice fluid theory of solutions has been used to calculate heats and volumes of mixing, lower critical solution temperatures, and the enthalpic and entropic components of the chemical potential. Results of these calculations have been compared with literature data on several polyisobutylene solutions. In most instances agreement with experiment is favorable and comparable to that obtained with the Flory equation of state theory. Several insights into polymer solution behavior have been obtained and include: (1) differences in equation of state properties of the pure components make an unfavorable entropic contribution to the chemical potential that becomes large and dominant as the gas-liquid critical temperature of the solvent is approached; (2) limited miscibility of nonpolar polymer solutions at low and high temperatures is a manifestation of a polymer solution's small combinatorial entropy; and (3) negative heats of mixing in nonpolar polymer solutions are caused by the solvent's tendency to contract when polymer is added.

Theory of Interfacial Tension

C. I. Poser[1] and I. C. Sanchez

[1] Guest Worker

A general interfacial tension theory for n-component liquid mixtures of arbitrary molecular weight has been formulated. The theory is based on the lattice fluid model and the so-called "gradient approximation." In the gradient approximation the free energy of a non-uniform fluid is expressed as a sum of a term dependent only on the local density and a square gradient term. The theory has been applied to liquid-vapor interfaces of organic liquids, polymer melts, binary liquid mixtures, and polymer solutions. Currently under study are liquid-liquid interfaces in paritally miscible liquids and polymer solutions as well as polymer-polymer interfaces.

Surprisingly accurate predictions have been obtained for pure fluids. For non-polar low molecular weight liquids, the surface tension can be calculated from the triple point to 0.7 of the gas-liquid critical temperature with an error of less than 5% with no adjustable parameters. The theory is somewhat less accurate for polymer melts because it tends to overestimate the surface entropy.

For two-component systems, the lattice fluid theory requires two mixture interaction parameters. These parameters are difficult to determine for polymer solutions and polymer-polymer systems. As a first approximation, we have used the geometric mean approximation to calculate surface tensions for binary systems, except in cases where sufficient data were available to refine the mixture parameters. For low-molecular weight liquid mixtures consisting of non-polar or slightly polar components, the geometric mean rule yields liquid-vapor interfacial tensions as a function of composition which lie within 5% of the experimental data. The theory also correctly predicts the direction of the deviation from ideal behavior. Comparisons of polymer solution surface tensions (calculated using the geometric mean rule) with experiment are hindered by the scarcity of available data. The results obtained are qualitatively correct and in good agreement with experiment for two systems (PDMS-toluene, PIB-heptane). For liquid-liquid systems, the geometric mean approximation must be relaxed. Preliminary studies on such systems are encouraging. For polymer-polymer interfaces, excellent agreement with experimental values can be obtained with reasonable values of the mixing parameters.

Transient Phenomena in the Orientation of the Rigid Spheroids in the Jet Flow

A. Peterlin

In the jet flow the orientation of the rigid spheroids is a one-dimensional problem. Its time dependence can be expressed by a sum of terms exponentially dependent on λ_{2_p} Dt where the λ_{2_p} are the eigenvalues of the spacial distribution function of the symmetry axis of the spheroids. The time dependent averages of $\cos^2\theta$ and $\cos^4\theta$ determine the intrinsic optical birefringence and the light scattering of such a suspension.

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE

Current trends are to use polymeric materials in applications where long term performance in the use environment without adverse deterioration of mechanical properties is critically important. An example is the increasing use of plastics and composites in automobiles to achieve lighter weight, more fuel efficient, vehicles. The lack of adequate test methods and data for evaluating long term mechanical performance may result in overdesign which not only leads to more expensive items, but also limits potential weight savings. The NBS has established joint programs on mechanical durability with other federal agencies which are fostering the use of polymeric materials in applications with implications in areas of national concern - health, safety and energy. A joint program with the Department of Transportation concerns the reuse of polyethylene shipping containers for hazardous materials transportation. The program addresses questions about long-term mechanical integrity, especially with ladings which may be even mild stress cracking agents. As part of the National Heart Program, the NIH supports development of accelerated test methods for the fatigue life of biocompatible elastomers which are used as bladders in circulatory assist devices. The Department of Energy supports development of methods to evaluate high temperature, chemically inert, elastomers which are used as seals in geothermal energy production. In all of the above applications, there exists a need for test methods and standards to ascertain the physical limits of polymeric materials in various use environments. Evaluation and control of materials parameters which affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life and environment.

The objectives of the task are to identify and analyze the principal failure mechanisms in polyethylene and elastomers under mechanical stress in the use environment. An integral part of these objectives is to determine relationships between microstructure, mechanical properties, and mechanisms at the molecular level which affect mechanical durability. To reach the objectives requires an interdisciplinary approach combining competences in mechanical properties measurements, fracture mechanics, continuum mechanics, chemistry and physics of molecular processes, spectroscopic techniques of infrared, Raman and nuclear magnetic resonance, x-ray scattering, and electron and optical microscopy. This year we have developed the capability for time resolved x-ray diffraction which shows promise for investigating relationships between microstructure and mechanical properties.

Technical Activity

Spectroscopic Investigations of Failure Mechanisms in Mechanically Deformed Polyethylene

B. M. Fanconi, J. P. Colson, and K. L. DeVries[1]
[1]University of Utah

Knowledge of the molecular mechanisms associated with deformation and fracture in polymers provides the basis for predicting long term performance from short time tests as well as insights into how the molecular composition may be changed to improve performance.

The molecular mechanisms associated with mechanical deformation and fracture in polyethylene are elucidated through comparisons between Fourier transform infrared (FTIR) spectra of undeformed and fractured specimens. Small variations in the concentrations of carbon-carbon double bonds, methyl groups, and carbonyl groups result from rupture of carbon-carbon backbone bonds and subsequent free radical reactions. These concentration changes can be detected in difference spectra obtained through subtraction of the digital FTIR data. The detectability of small concentration variations is enhanced by the superior sensitivity of the FTIR method over conventional dispersive infrared spectroscopy.

The difficulties inherent in comparing spectra of unoriented (undrawn) and oriented polyethylene which plagued previous infrared studies of deformed and fractured polymers have been overcome by preparing specimens for infrared analyses by casting films of the drawn and fractured material, or of the reference polyethylene from solution or the melt. The most apparent discrepancy between our results and those reported previously involves the direction of the change in the number of carbonyl groups. We find that the number of carbonyl groups decreases during fracture rather than increases as determined previously. This result was obtained in films of fractured polyethylene which had been prepared by melt casting as well as solution casting. On specimens taken from regions of deformed polyethylene which did not include the fracture surface we find that the decrease in the number of carbonyl groups is less than when the specimens include the fracture surfaces.

We propose that the decrease in carbonyl groups in fractured polyethylene samples result from preferential backbone bond rupture occurring near carbonyl groups. Subsequent chemical reactions produce low molecular weight ketones which are volatilized during preparation of the films for infrared analysis. Experiments are in progress to substantiate these results on drawn polyethylenes to determine whether a relationship exists between level of deformation and decrease in the number of carbonyl groups.

Mechanical Durability of Polyethylene Shipping Containers

J. M. Crissman, L. J. Zapas, and G. M. Martin

This report summarizes research in the area of performance of polymeric materials used in the manufacture of large shipping containers for hazardous materials transport, work supported by the U.S. Department of Transportation Office of Hazardous Materials Operations. A primary goal of this work has been the development of test methods for evaluating stress-crack resistance of ethylene plastics and degree of crosslinking in rotational molded polyethylene containers.

During the past year, studies concerned with stress-crack behavior were expanded to include a variety of biaxial deformation histories such as equibiaxial under inflation, bottle inflation, and bent strip geometries. One important result of this work is the observation that each type of deformation examined, including earlier work on uniaxial creep, yields essentially the same information with regard to stress-crack behavior. On the basis of preliminary data, a new test method employing bent strip geometry has been proposed for evaluating the stress-crack resistance of ethylene plastics. The new test has several advantages over the most common test in current use in that the bend geometry is well defined and controlled and the specimen is subjected to a constant applied load. A test of this type also has the advantage that it can be controlled in such a manner as to optimize testing time.

Also during the past year a wholly new area of study was initiated which is concerned with cross-linkable polyethylenes for rotational molding. This class of materials is now entering the marketplace in the form of large rotationally molded containers for the transport of hazardous materials. The rotational molding of cross-linkable polyethylene represents a different approach to container fabrication than that employed with conventional polyethylenes. For cross-linkable polyethylenes, the physical properties of the final product are highly contingent upon the processing, in particular the cross-linking step. Properties such as impact strength, fracture toughness, and stress-crack resistance are expected to depend rather critically upon the extent of cross-linking. Since the degree of cross-linking clearly represents a key parameter in determining performance, test methods need to be developed which can directly correlate the two. Three types of tests are currently under investigation: stress-crack resistance, swell ratio, and high temperature tensile modulus.

Stress-crack resistance as a function of the degree of cross-linking is currently under investigation, but the work is not yet far enough along to report on here.

A swell ratio test based on dimensional changes alone has been examined for a number of polyethylene samples having widely different degrees of cross-linking and compared to the swell ratio as determined by the conventional ASTM method. A high degree of linear correlation has been established between the two methods and it has been found that both methods yield the same information. The primary advantage of the method based on dimensional changes is that it requires only half the time to perform.

Measurements of the tensile modulus at high temperature carried out on specimens of cross-linked polyethylene having widely different degrees of cross-linking reveal that this method is rather insensitive to the degree of cross-linking achieved and appears impractical as a test method.

Physical Testing of Polymers for Use in Circulatory Assist Devices

R. W. Penn, G. B. McKenna, G. W. Bullman, and F. A. Khoury

This report presents results obtained during the past year in a research program on Physical Testing of Polymers for Use in Circulatory Assist Devices carried out at the National Bureau of Standards with the support of the National Heart, Lung, and Blood Institute of the National Institutes of Health. The main objectives of the program are to develop test procedures for evaluating candidate materials for use in circulatory assist devices (CAD).

The initial phase of our program had been limited by the unavailability of suitable test samples of biocompatible elastomers. To compensate for the lack of biocompatible elastomer samples, we used the standard butyl rubber for samples and we prepared and distributed this material to other investigators engaged in the Physical Testing program. We recently have received several square feet of "Hexsyn" biocompatible polyolefin rubber from Dr. McMillin of Monsanto Research Corporation and a small quantity of "Biomer" polyurethane from Dr. John Kardos of Washington University. Also, we have received approximately thirty square feet of "Avcothane" urethane-silicone copolymer which we have distributed to the other investigators.

Testing of all of these materials has been initiated. We have completed preliminary stress-strain testing of all of the materials. Creep to failure tests are proceeding in both uniaxial and biaxial loading. Uniaxial fatigue tests using sinusoidal loading of the two carbon black filled elastomers have shown a dependence of sample lifetime on frequency such that they fail after the same number of stress cycles. This contradicts the notion of stress dependent additive damage. The number of cycles to failure is independent of frequency over the frequency range studied (from approximately 0.1Hz. to approximately 10^{-3}Hz.). It will be of interest to check this result for the elastomers not filled with carbon black.

Two biaxial fatigue test machines with six testing stations each have been assembled. These devices use pressure controlled pulses of air to inflate circular discs of the test materials at a rate of 3Hz.

The pulses are controlled by motor-driven reciprocating spool valves. One of the machines is mounted in a thermostatic bath suitable for testing at temperatures up to about 60 °C. The other is maintained at room temperature. Means have been found to prevent the evaporation of the saline solution in which the samples are immersed and thus to permit constant pressure amplitude testing over periods of several months.

Studies of the fracture surfaces of failed specimens are continuing. The carbon black filled butyl and polyolefin rubbers appear to fail by a crack growth mechanism. The cracks appear to initiate in the interior of the rubber samples, probably at carbon black aggregates. Failure of the butyl rubber samples is detected when a small crack grows through the sample thickness. The polyolefin rubbers fail by a much more rapidly growing crack which extends most of the way across the specimen.

Examination of the urethane-silicone elastomer under the optical microscope clearly reveals that the structure of these membranes is not homogeneous. It has been established that lenticular regions (which exhibit an essentially circular profile when viewed along the membrane normal and which have an elliptical profile when viewed parallel to the plane of the membrane) occur throughout the new test membranes. The diameter of these lenticular regions varies from a few micrometers to several dozen micrometers. The existence of the regions points to the occurrence of phase separation on a gross scale during the casting of the membranes. It is still not clear whether mechanical failure in these membranes occurs preferentially at interphase boundaries.

Fundamental Aspects of the Crystallization, the Fine Structure, and the Deformation and Orientation of Polymers

F. A. Khoury and L. H. Bolz

Activity in this broad category has been limited to two areas. Our efforts have been primarily devoted during the past year to a study of the habits exhibited by chain-folded polyethylene crystals grown from dilute solutions at elevated temperatures from poor solvents (see Section 2 for summary of results). A main initial objective of this investigation was to seek appropriate solvents, from which polyethylene crystals can be grown at temperatures which approach, and if possible overlap, the temperature range (~ 118 °C - 130 °C) in which the polymer can be crystallized isothermally from the molten state. There have been numerous studies on the habits of solution grown polyethylene crystals in the past. There is, however, relatively little knowledge on the nature of crystals grown above ~ 100 °C. Our original premise, which current results bear out, was that such crystals would serve as useful models for crystal lamellae grown from the melt. The latter lamellae are usually organized in spherulitic arrays and are consequently much less accessible or amenable to the determination of their lateral growth habits (lateral faceting), their conformations (hollow pyramidal, tent-like, or variously curved), and various details of the molecular organization in them (e.g., fold staggering, tilt of chain stems relative to fold surface). The determination of these features, and others, is essential not only to an understanding of the relationships between mechanisms of crystallization and fine structure at the molecular level, but also to the determination of aspects of the mechanisms of polymer deformation and orientation.

As part of an on-going study of the stress cracking characteristics of polyethylene (Crissman and Zapas) we have recently started an investigation of the morphological changes caused in sheets of the polymer when they are subjected to equibiaxial stresses. Information derived from this study will also have a bearing on aspects of the mechanisms of deformation and orientation which underlie compressive stressing as well as biaxial orientation processes used in the manufacture of polyethylene products (e.g., films, containers). Some initial results are summarized:

The Habits of Polyethylene Crystals Grown from Dilute Solutions in Poor Solvents:

Linear polyethylene fractions (M.wt. 11400-100500) and ultra high molecular weight polyethylene (UHMWPE, M.wt. $\sim 4.5 \times 10^6$) have been crystallized from 0.01% solutions in the range 95 °C - 115 °C. Heptyl acetate, heptyl acetate/xylene mixtures, and dodecanol were among the solvents used. Not unexpectedly all the lamellar crystals grown in that temperature range exhibited preferential growth parallel to the b-axis, and at the lower temperatures the lamellae exhibited $\{110\}$ and (200) lateral faceting. In addition, the axial ratio B/A* increased with increasing crystallization temperature. Interestingly, however, we have encountered instances in which the lateral habits of the lamellae tended to become less well defined the higher the crystallization temperature. In particular, crystal lamellae of the lowest molecular weight fraction (M.wt. = 11400) grown at 115 °C from dodecanol exhibited a lenticular lateral profile (axial ratio 5-6). Although these lamellae were bound at opposite tips by $\{110\}$ facets the long lateral edges of the crystals were distinctly curved. Whether this later feature is associated with the manifestation of isothermal thickening during the growth of the crystals remains to be determined. A main feature of interest in these crystals is that the chain stems are tilted (34°) relative to the fold surfaces and that the sense of tilt is the same throughout each lamella although there are indications that the magnitude of the tilt may be smaller in the outer lateral regions of the crystals. This later feature suggests that these crystals may possess, in the as-grown state, a slightly S-shaped cross-section when viewed along the b-axis. Evidence that the constituent lamellae in banded polyethylene spherulites grown from the melt possess an S-shaped cross-section has been recently reported in the literature. Details of the stem tilt in these lamellae are difficult to establish. Our observations on the lenticular crystals grown from dodecanol suggest that the stems in lamellae in spherulites may also all be tilted in the same direction relative to the surfaces of the lamellae.

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*Axial ratio B/A = length of lamella parallel to b-axis/length of lamellae parallel to a-axis.

Equibiaxial Deformation of Polyethylene:

A study of the morphological changes which occur when sheets of polyethylene are subjected to equibiaxial deformation has been started. Replicas have been made of the surfaces of sheets which were subjected to overall strains of up to 10%. Examination of the replicas under the optical microscope revealed cracks in the regions of maximum strain (polar region of bubble), which cracks were bridged by fibrils. The lengths of the cracks varied. The most dominant crack (which exhibited a meandering path) was 0.1 mm long and ∿ 20 μm wide. Most cracks were of the order of 50 μm long or less. In addition to these clearly distinguishable cracks, available evidence indicates the occurrence of preferential small scale deformation at interspherulite boundaries in the regions of maximum strain. These observations clearly emphasize the lack of homogeneous biaxial deformation under equibiaxial stressing even at strains of 10%.

Characterization of Polymeric Solids by 13C Nuclear Magnetic Resonance

D. L. VanderHart and S. J. Kryder

NMR has traditionally been used to probe the spectral density of molecular motions in polymers. Relaxation times have been used to infer such information. The ability to resolve individual carbon resonances by means of magic angle sample spinning (MASS) in polymer systems has opened up possibilities for measuring relaxation times for each of the carbon sites, thereby gaining information about backbone motions as opposed to sidechain motions. Such distinctions are necessary if one wishes to interpret these motions as being relevant to a macroscopic property such as modulus.

The ^{13}C methods offer advantages over proton methods, particularly in that the observed ^{13}C relaxation time is the superposition of the relaxation times of individual carbons in the sample. Proton relaxation, on the other hand, is usually the result of locally averaged relaxation since the proton spins strongly couple to one another and do not relax individually.

The rotating frame ^{13}C relaxation time, $T_{1\rho}^{C}$, is the easiest relaxation time to measure in polymers; furthermore, if $T_{1\rho}^{C}$ is determined by molecular motion, it will give information about the spectral density of motions in the mid-kilohertz range, an important range for dissipating impact energy. Work done in our laboratory this year has led to a much better understanding of when $T_{1\rho}^{C}$ can be interpreted in terms of molecular motion and when it should not be interpreted this way. It has also led to insights into ways of optimizing experimental parameters for obtaining information about molecular motion.

Investigation of Ultimate Resolution in Solid Polymers by Magic Angle Sample Spinning:

Experimentally, it is found that at 15 MHz frequency for ^{13}C nuclei, crystalline substances and polymers in particular, have linewidths ranging from 2-20 Hz. Furthermore, materials with less order and more molecular motion, e.g., glassy polymers, exhibit linewidths typically in the range of 30-100 Hz. It is clear that the utility of the MASS technique will often be related to one's ability to resolve resonances. For example, if one wishes to evaluate cross-link density in a polyolefin, and if the cross-link involves a tetrahedrally bonded carbon, then the width of the backbone resonances which are also tetrahedral carbons is critical since a wide, intense backbone resonance will very likely obscure a weak resonance close by.

Furthermore, through this work and the work of others, it is becoming clear that chemical shifts observed in MASS experiments are often sensitive to conformational differences. Thus, it was found that the non-crystalline resonance of linear polyethylene is shifted from its crystalline resonance because of the non-zero average gauche content of a non-crystalline chain.

Other effects on linewidth have also been investigated such as the effects of molecular motion and off-resonance proton decoupling. The relative importance of various linebroadening mechanisms varies from sample to sample, especially for polymers. Only if molecular motion is an important linebroadening mechanism will resolution improve at higher magnetic fields. Otherwise, it may even deteriorate. Even so, much remains to be understood about resolution, and from the latest results, it looks like the largest contribution to linewidth is chemical shift dispersion. If this is true, it is possible that improved resolution could be obtained by modifying sample preparation techniques. Nevertheless, it is safe to say that resolution in solids will not be as good as resolution in liquids, in fact, resolution will probably be worse by one to two orders of magnitude. This is an important perspective to have gained in using the ^{13}C MASS technique for studying polymers. For example, this severely limits aspirations for studying tacticity in the solid state.

Orientation and mobility of the non-crystalline regions of linear polyethylene (LPE) and their relationship to modulus:

Non-spinning ^{13}C spectra of chemically simple materials like linear polyethylene allow one to get information about orientation. Furthermore, selection of resonances based on molecular mobility allow one to distinguish crystalline from non-crystalline (NC) material. In particular, the orientation in the NC region was studied as a function of annealing in a cold drawn sample of LPE. The change in spectral features accompanying the decrease in modulus (the latter measured by John Crissman on similar samples) suggested that the number of tie chains decreased with increased annealing temperature.

Infrared Vibrational Analysis of Conformational Disorder in Crystalline Polyethylene

D. H. Reneker, J. Mazur, and J. P. Colson

The infrared spectrum of polyethylene in which 5% of the carbon atoms are doubly deuterated contains bands which are attributed to trans-trans (tt) and trans-gauche (tg) dihedral angle sequences. Experimental observations show that even in crystalline polyethylene there are tg sequences and that the number of sequences as measured by the intensity of the infrared bond increases in the temperature range between 60 and 120 °C.

The tg sequences are presumed to be in folds and other crystalline defects such as point dislocations. Calculations of the conformations of such defects show that the crystalline constraints result in dihedral angles which vary over a wide range of values centered around trans and around gauche. Calculations of the vibrational spectrum for different fold and defect conformations show that the tt band is essentially unaffected by the variations in the dihedral angles which adjoin the tt pair. However, the tg band is considerably broadened since its characteristic frequency is shown to depend on the conformation of the dihedral angles which adjoin it.

The determination of an appropriate baseline for measuring the area under the tg and tt bands is a source of considerable uncertainty. Two choices for the baseline were examined. Both of them showed that the tg intensity increased with temperature. One choice, a baseline fitted to the minima and shoulders of the spectrum resulted in a baseline position and shape that varied with temperature. The other choice established a temperature independent baseline by extrapolating to low temperature the parameters in the temperature dependent baselines. This second choice resulted in a ratio of the area under the tg band which is commensurate with the number of tg sequences expected from x-ray and Raman measurements of the number of folds and point dislocations in the sample.

Investigation of Disorder in Polymethylene Chains

J. Mazur and B. Fanconi

Recent work on Raman active longitudinal acoustic modes (LAM) in n-alkanes and polyethylene has demonstrated that these vibrations could be used to determine aspects of the chain conformation of polymethylene chains including the energy difference between gauche and trans conformations. To fully utilize vibrational analyses of LAM for this purpose we have determined the effect of chain disorder on the frequencies and have substantiated the validity of a previously proposed method of calculating vibrational intensities from normal coordinate displacements.

We have calculated the Raman spectra of liquid n-alkanes in the LAM frequency range. These theoretical spectra have been used to determine the energy difference between gauche and trans rotational isomers in polymethylenes from analysis of melt phase n-alkane spectra.

In the course of these investigations we have elucidated a previously unresolved aspect of the Raman spectra of n-alkanes by showing that the anomalous band profiles observed in the LAM spectra of some n-alkanes result from Fermi-type resonance between LAM and transverse acoustic modes, the latter of which have little Raman intensity in the absence of this resonance. Our calculations have yielded both the frequency shifts and intensity profiles resulting from these interactions. The intensity calculations were carried out using a method previously developed for LAM intensities of disordered chains. Our analysis provided a means of testing the intensity calculation method and the excellent agreement found indicated that the method is reasonable.

Transport Properties of Drawn Low Density PE

R. Russo, F. de Candia, V. Vittoria[1], and A. Peterlin

[1]Naples, Italy

The drawing reduces the sorption and much more the zero concentration diffusivity, but increases the concentration dependence of the diffusivity. Annealing reduces these effects of drawing drastically and brings the transport properties of the sample almost back to the values before drawing. If, however, the annealing is performed with fixed ends the annealed material upon standing at room temperature returns, as far as the transport properties are concerned, back to the values before the annealing. Such an effect can be explained by slow crystallization of the tie molecules which became partially relaxed during the annealing but as a consequence of the fixation of the ends of the sample could not pull back the blocks they are anchored in toward their initial position. After crystallization they form long-range axial connectors which are the main cause of the high axial elastic modulus. If the annealing is performed with free ends, the sample shrinks as a consequence of the contraction of tie molecules. After the shrinkage connects the blocks over a much shorter distance they do not, even after partial crystallization, act as long-range connectors.

Permeation Performance of Polyethylenes Used in Containers for Hazardous Materials Transportation

J. C. Phillips

This project is concerned with developing test methods to be used by the Department of Transportation in formulating regulations concerning the barrier properties of polyethylene shipping containers. Efforts for the current year are concerned with determining the range of applicability of the permachor concept of predicting permeation behavior.

Weight loss determinations were performed at t = 50 °C for a n-carboxylic ester series and a n-alcohol series. The ester series consisted of ethyl acetate, butyl acetate, and amyl acetate. The alcohol series consisted of methyl, ethyl, propyl, butyl, hexyl, and octyl alcohols. In addition, weight loss determinations were done for n-heptane and n-hexadecane (cetane). Two PE bottle types were used in these studies, $\rho = 0.92$ g/cm^3 and $\rho = 0.940$ g/cm^3.

The ester and alcohol series showed a decreasing dependence of weight loss on increasing PE density at a given time. The low density bottle, $\rho = 0.920$ g/cm^3, showed a very large time dependence in weight loss while in the high density bottle, $\rho = 0.940$ g/cm^3, the time dependence was comparatively much smaller.

The weight loss for the ester series decreases from ethyl acetate to butyl acetate to amyl acetate with the first two members showing a slower decrease compared to the third member. The same relative weight loss behavior was observed in both density bottles and the loss rate for each member of the series appeared to be constant.

The weight loss for the alcohol series decreased from methyl to ethyl to propyl and increased to butyl to hexyl and subsequently decreased to octyl. The loss rates seemed constant for methyl through butyl, but appeared to show a large time dependence for hexyl and octyl. The same general behavior for each member of the series was observed for each density bottle, but the time dependence of the loss rate in the high density bottle appeared to have shifted to longer times compared to the low density bottle.

The weight loss and loss rate for the ester and alcohol series do not show a parallel behavior to that of the n-alkanes for the range of chain lengths investigated. The results do suggest that at large chain lengths there may be a better correspondence. These results further suggest that polarity and association effects for the early members of a homologous series greatly influence the relative behavior of the series to that of the n-alkanes and, therefore, compounds any quantitative correlations.

Optical Method of the Measurement of Transport Properties of Strained Polymer Samples

J. Phillips, A. Peterlin, and F. Waters

An IR cell apparatus was designed and constructed for the purpose of determining transport and mechanical properties of transparent polymer films. The transport properties were measured from IR intensity changes of ethyl acetate vapor at the carbonyl frequency where the absorbence of the polymer was small or negligible. The mechanical properties of the film were determined simultaneously by using a load cell. The polymer, LDPE and PVF$_2$, were chosen to show the applicability of the IR cell to measuring conventional and nonconventional diffusion properties. The transport and mechanical properties of these polymers were extensively investigated in ethyl acetate vapor at t = 30 °C over a wide pressure and elongation range.

The results for PE/ethyl acetate showed that sorption and desorption were conventional and the diffusivity was approximately independent of the concentration of the vapor. The transport properties also showed a morphological transition at about $\varepsilon = 0.10$ for diffusivity and permeability while sorption increased continuously with strain to an apparent limiting value. The stress relaxation at vapor pressure, p, and cyclic sorption/desorption experiments showed an increasing difference between stress relaxation at p = 0 which indicated that structural changes were occurring as a function of time.

Polyvinylidene fluoride which has a T_g -38 °C showed non-conventional or Type II behavior above a transition vapor pressure, p^*, and conventional behavior below p^*. On the imposition of a uniaxial tensile strain, transport properties and mechanical relaxation are enhanced and the transition pressure of ethyl acetate decreases. These results indicate that Type II behavior for PVF_2/ethyl acetate at a temperature above the glass transition temperature of the system depends on the pressure of ethyl acetate vapor as well as the strain level of PVF_2.

The IR technique is inherently limited to polymer/vapor systems in which the polymer has a high transparency in a region of the spectrum where the vapor has a strong absorption peak. In order for the absorbence to be correctly translated to actual concentrations, $c_v(t)$, corrections for changes in film thickness due to swelling and strain should be considered and properly applied.

Non-Linear Viscoelastic Behavior of Polymeric Materials

G. B. McKenna, L. J. Zapas, and E. A. Kearsley

Project objectives are to characterize the viscoelastic behavior of polymeric materials using non-linear viscoelastic constitutive theory. Methods are developed to determine strain-energy functions, time dependent strain potential derivatives, and material response specific deformations such as two-step deformations and cyclic loading.

Part of this project is concerned with characterization of the extensional creep and stress relaxation behavior of carbon black filled rubber. We are using a modified form of the BKZ theory which accounts for the "damage" which occurs to the elastomer upon loading and unloading of the material in order to account for the accelerated creep and stress relaxation behavior observed in cyclic loading. This work will bear directly on the problem of failure of filled elastomers under fatigue loading conditions to the extent that we can describe the damage due to cycling using a constitutive equation and to the extent that a failure envelope describes the behavior of the filled elastomer. Experiments have been initiated to characterize the creep and stress relaxation behavior of the material and to obtain a failure envelope for the material. Cyclic creep, stress relaxation and failure behavior will also be characterized.

During the last year we substantiated a prediction made by the BKZ theory through experiments on both poly(methyl methacrylate) (PMMA) and a concentrated solution of poly(isobutylene) in cetane. The BKZ theory predicts that in a two step torsional stress relaxation history where the second step deformation, γ_2, is half of the first step deformation, γ, (i.e., $\gamma_2 = \frac{1}{2} \gamma_1$), then the second step normal stress response is predicted to be independent of the duration of the first step and equal to the response in a single step history at a deformation of $\gamma = \gamma_2$.

Also, during last year, we determined the time dependent strain potential derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_1$ for PMMA tubes. The results of this work indicate that $\partial W/\partial I_1$ is a negative at short times and becomes positive at high strains and long times. Such behavior is unusual and bears directly on the concept of using a shift in the mechanical relaxation spectrum to characterize the non-linear viscoelastic behavior of polymeric glasses. Work during the coming year will be undertaken using solid cylinders of PMMA rather than tubes to assure that the result is not an artifact of torsional measurements on a tube without applying an internal pressure.

Experience with various rubbery polymers has shown that the strain-energy function (from which elastic behavior can be determined) can be measured from experiments on pure shear. Our recent work has shown that this function can also be measured from torsion data or from combined data from simple extension and biaxial extension. These methods are considerably simpler than the conventional methods of measuring strain-energy. The method has been successfully applied to natural rubber (peroxide vulcanized), high molecular weight poly(isobutylene), and to butyl rubber. The two parameter Martin, Roth and Stiehler equation for characterizing a rubber has been adapted to characterize the strain-energy function in this way, also.

In the coming year, the application of these ideas to a viscoelastic material will be examined. It is hoped that the method will lead to simplified methods of measuring extensional viscosity. Extensional viscosity is an important parameter in the technology of polymer processing and is ordinarily an extremely trying measurement.

Acoustic Emission of Crazing Polymers

A. Peterlin, R. Green, and J. Smith

Glass-bead epoxy resin composites and PMMA (commercial grade) were strained in an Instron Tensile Tester. Water and aceton induce crazing. Some acoustic emission was detected which was caused by the microcracking of the sample under the sharp dents of the grips. The Kaiser effect was also observed. The frequency spectrum of the acoustic emission by the growing crazes is probably so far below the response frequency of the sensor that the amplitude is not sufficiently above the background noise to be detected. Hence, only a small number of emissions could be registered. The method would permit a destructionless testing of the polymer specimen and of its load and deformation history if one can perform the experiment in a less noisy environment.

Elastic Modulus and Strength of Crystalline Polymers

A. Peterlin

The basic idea of the theory of both effects starts from morphological considerations. The existence of almost fully extended chains connecting the nearly rigid crystals through the much softer amorphous matrix is responsible for the high elastic modulus. The presence of the defects of the regular morphology causes the sample to fail. The situation is particularly simple in the fibrous structure when the axially oriented microfibrils with a great many tie molecules connecting the crystal blocks yield a high elastic modulus, up to 70 GPa in highly drawn linear polyethylene with E_c = 240 GPa (elastic modulus of the crystal in the chair direction). The defects of the microfibrillar structure are the ends of the microfibrils where the axial connection by taut tie molecules is drastically interrupted. Under the tensile load, the strain in such defects is many times higher than in the bulk sample, thus leading to microcrack nucleation and adjacent microfibril rupture. The effect is enhanced by a high elastic modulus to the microfibril. Consequently in a highly drawn sample the strain to break decreases with increasing draw ratio. In spite of the increase of the modulus the strength remains practically constant or increases much more slowly than the axial elastic modulus. The rupture of chains detectable by ESR is an effect which occurs during the straining of the sample although it does not determine the tensile strength.

Durability of Paper

J. C. Smith, E. E. Toth, and E. L. Graminski

The durability of paper is an important consideration in currency applications where replacement of worn out currency is a costly operation. The Bureau of Engraving and Printing supports work at NBS to characterize those aspects of the morphology of paper networks which affect durability with the objectives of improving durability and to achieve this improvement by replacing the presently used cotton and linen pulp with a less expensive pulp made from blended wood fibers.

Before these objectives can be realized, however, it is necessary to have an improved understanding of the relationship between the structure of paper, the morphology of the fibers, the processing conditions and the mechanical and physical properties of the paper and its components. Over the past several years studies on the bondability of pulp fibers at the National Bureau of Standards have helped to provide some of this background information.

Parameters for characterizing interfiber bond strength have been obtained from tensile tests on a low-density openweb handsheet prepared from the pulp to be evaluated. The force-elongation curve for a specimen from this handsheet contains numerous force drops, each drop caused by the breakage of a bond between fibers constituting the handsheet network. The relative number of bonds per unit area is characterized by the average elongation between bond breaks. The bond strength is characterized by an average of the force-drop magnitudes, by an average of the energy losses resulting from bond break, or by a characteristic elongation indicative of the stretch in the network needed to cause a break. These bonding parameters are being evaluated for handsheets of various areal densities, made from several different pulps that were subjected to various beating treatments. The morphologies of the handsheets and the constituent pulp fibers are being examined by optical and scanning electron microscopy.

Since the microstructure of the fiber network is influenced by the manner in which water is bound to the fibers, a part of this project is concerned with the characterization of water in pulps. Pulp fibers, especially chemical pulp fibers, are not suitable for paper manufacture as produced by a pulp mill. In order to make paper having suitable properties, it is necessary to subject the fibers to mechanical action. Mechanical action, such as beating or refining, causes fibers to imbibe water and to become more flexible. The more flexible a fiber becomes, the better it can conform with another fiber under pressure, which is the hallmark of interfiber bond formation. Fiber flexibility is also a factor in the formation of other physical properties essential to the paper conversion industry.

Part of the water imbibed by the pulp fibers is bound to the cellulose while the remaining water is considered to be free water. It is believed that the free water is most effective for fiber flexibility. As fibers are treated increasingly by mechanical action and imbibe more and more water, there is a question of whether the water sequentially imbibed is totally free water. There is the possibility that increased mechanical action can result in a decline in crystallinity and at some point the incremental imbibed water will be a combination of bound and free water.

The total water imbibed by a fiber can be measured by several methods, but the most frequently used method is by the solute exclusion principle. Weight specimens of fiber and excess water are added to known quantities of solutions of high molecular weight material such as dextran, with a molecular weight of 2×10^6. The large dextran molecules cannot migrate into the cellulose fibers and thus the dilution of the dextran solution occurs by the water exterior of the fibers. The concentration of the dextran solution is measured accurately by polarimetry. The difference between the total water in the specimen and the amount of water which diluted the dextran is the water imbibed by the fibers. The water imbibed by the fibers is known as the fiber saturation point.

Water, bound to cellulose, does not freeze at temperatues up to 223 K, and this has been a means for measuring bound water. A method was developed for measuring bound water in pulps by means of differential scanning calorimetry. Weighed specimens of fiber and water were hermetically sealed then frozen. The amount of ice in each specimen was determined calorimetically and the total amount of water in each specimen was determined by drying the specimen to constant weight. The difference between the total water and the amount of ice in each specimen is equal to the amount of water bound to the cellulose.

Bound water and the fiber saturation point was determined for two beaten and unbeaten wood pulps and virgin cotton. The results indicate that beating has no effect on the crystallinity of wood pulps, but a significant effect on the crystallinity of cotton. Additionally, most of the imbibed water in beaten cotton pulp appears to be contained in the shortest fiber fraction. The longest fiber fraction in beaten cotton appears to imbibe considerably less water.

This large difference in the behavior of wood and cotton pulp during the mechanical action process apparently results in a significant difference in the microstructure of rag and wood pulp fiber. This difference in microstructure may be the reason for the large difference in mechanical properties of cotton and wood pulp papers.

Configurations of Polymer Chains

R. J. Rubin

Configurations of Polymer Chains Interacting with Plane Interfaces--Treatment in Terms of a Random Flight or Diffusion Equation:

An isolated polymer chain in solution near a surface or between parallel surfaces will adopt various configurations depending upon the temperature and affinity of the links for the surface. A number of years ago, Rubin[1] and DiMarzio and Rubin[2] analyzed lattice models of the foregoing systems. In the absence of the complicating effects of interaction with surfaces, configurations of long chain molecules can be modeled by a random flight or diffusion equation. However, it is known from the lattice models that if the energy of attraction between links of the polymer chain and the surface are sufficiently high then there is a discontinuous collapse of the chain on the surface at a critical energy. The description of such discontinuous behavior within the framework of a diffusion equation appears to present technical difficulties. deGennes[3] and Lèpine and Caillè[4] have proposed a method of dealing with this problem in which the attractive (or repulsive) interactions of segments of the chain with a surface are treated in terms of a mixed boundary condition at the surface, i.e., $\ell\frac{\partial p}{\partial x} + mp = 0$ where p is the solution of the diffusion equation. I have investigated some of the ramifications of this approach and have calculated several quantities which appeared to be difficult to calculate within the framework of the lattice model:

1) the distribution function of the span of an adsorbed chain molecule at a plane solution surface in a direction normal to the surface, i.e., the distribution function of the thickness of the adsorbed molecule layer.

2) the distribution of the segments of a polymer chain confined between two parallel solution surfaces as a function of energy of interaction and chain length.

These calculations are in the process of being outlined in a paper for publication in the Journal of Chemical Physics.

Internal Configurations of Span Constrained Random Walks:

The spans of a random walk on a simple cubic lattice are the sides of the smallest rectangular box with sides parallel to the coordinate axes that entirely contains the random walk. The position of a random walker after N steps and constrained by a set of spans S is considered. In one dimension, if $S^2 >> N$, the random walker tends to be located at the extremities of the span while in the contrary case the random walker is most likely to be found half-way between the extremities. In higher dimensions the position of the random walker in the direction of the largest span tends to lie at the span extremities while the position in the direction of the smallest span tends to be in the middle.

These calculations, performed in collaboration with G. H. Weiss of the National Institutes of Health, have been summarized in a paper which has been accepted for publication in the Journal of Statistical Physics.

Additional calculations are planned for other properties of span-constrained random walks including the statistics of occupancy within the rectangular box and the expected number of points visited.

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Polymeric Sealants for Geothermal Energy

E. A. Kearsley

The Department of Energy envisions that within a matter of decades the exploitation of geothermal energy resources will be making a substantial contribution to our national energy needs. However, in order for this to be accomplished, it is necessary to stimulate several associated technologies. The Division of Geothermal Energy of DoE has accordingly requested help in developing tests of polymeric materials to screen likely candidates for use as geothermal sealants. Since there are many forms of seals used in the drilling and production of geothermal wells and down-hole environments vary considerably among the different well locations, it is not possible to specify reasonable requirements for geothermal sealants in general. The most interesting and energetically important wells are potentially those with ambient down-hole temperatures greater than 260 °C and with strongly corrosive reducing (rather than oxidizing) atmospheres. The sealant materials should perform (frequently this means maintaining large elastic stresses for fixed deformations) under these demanding conditions for time periods ranging from hours for well-drilling sealants to months or years for production seals. Current technology for such seals is largely based on developments for the petroleum industry and is, consequently, adapted to lower temperatures and less corrosive, chemically different, conditions.

The program in the Polymer Science and Standards Division is currently beginning a survey of the needs and uses of sealants in the geothermal industry in order to understand the actual requirements for usage which a geothermal sealant material should meet. Concurrently, an experimental program is being designed to determine what features of the geothermal environment dominate the lifetime of sealants. Initially, materials will be subjected to various environments for periods of time and then tested for mechanical properties at laboratory conditions. Concepts such as time-temperature superposition and additivity of damage (Bailey's criterion) will be tested for their usefulness in estimating the performance of materials at extrapolated conditions from this laboratory data. Eventually, mechanical properties measurements at test conditions will be made. The aim of this program is to contribute to the development of industry-accepted screening tests for geothermal polymer sealants.

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS

The objective of this research is to contribute to dental health care through development of better performing materials and test methodology and standards appropriate thereto. Materials research and techniques are pursued with the goal of developing adhesive composite restorative materials of greater durability and wear resistance, and improved base metal alloy alternatives to the costly gold alloy prostheses. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials and for defining the interactions that occur thereon.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense Medical R&D Command. Medical materials research is guided by close interaction with the National Heart, Lung, and Blood Institute and the ASTM F4 Committee (Medical and Surgical Materials and Devices).

Technical Activity

Development of Adhesive Bonding Techniques

G. M. Brauer, R. L. Bowen[1], J. M. Antonucci, D. W. Misral, J. S. Stansbury, E. E. Toth, and J. M. Cassel

[1] Research Associate

A dentally applicable technique which established and maintained adhesive bonding would not only offer an important means for reducing the dental caries that is encouraged by percolation of fluids and bacteria at restoration margins but would afford a means of changing the mode of cavity preparation so as to reduce sound tooth structure destruction. Strong mechanical bonding of acrylic resins to enamel surfaces can be obtained through acid etching of such surfaces but such treatment is not applicable to the surfaces of dentin, the other major component of teeth. Such bonding has also not been entirely satisfactory in the caries-preventive application of pit and fissure sealants to the occlusal enamel surfaces of children's teeth.

A number of investigative routes to the development of adhesion to dentin are being followed. These include: synthesis of multi-functional methacrylate monomers that contain groups that can react with either the organic or inorganic portion of dentin; evaluation of cyanoacrylate-based systems; examination of urethane monomers that contain polymerizable methacrylates and residual isocyanates; synthesis and evaluation of multi-functional adhesion-promoting surface active amine accelerators;

determination of techniques by which the polymerization shrinkage and resultant gap formation between restoration and cavity wall can be eliminated and investigation of tooth surface cleansing techniques and mordant treatments.

Initially, the bonding of cyanoacrylates to dentin or bone, a somewhat similar mineralized tissue, is very promising. However, the hydrolysis as the bonded specimens are aged or thermally cycled in water is extensive and debonding occurs rapidly. Attempts to slow down this deleterious effect of water have not been successful. Formulations containing various urethane-methacrylates and polymerizable diluents have developed initial bond strengths to dentin that are less than that attainable with cyanoacrylate and therefore are not satisfactory. Several surface-active amines when adsorbed to a powdered hydroxyapatite surface appear to be more reactive in the adsorbed state than when in solution and need further examination for their adhesion promoting ability. A number of isotonic, buffered acid solutions have been shown to remove the adhesion-inhibiting smeared layer produced at the surface of cut dentin and to do so without pulpal irritation. An isotonic ferric chloride mordanting solution has been found to form a modified dentin surface in less than 30 seconds and moderately improve adhesive bonding to composite resins.

Dental Composite, Resin, Sealant, and Cement Chemistry and Development

G. M. Brauer, J. M. Antonucci, J. M. Cassel, R. L. Bowen[1], H. Argentar[1], and D. W. Misra[1]

[1] Research Asociate

Early work in this laboratory resulted in a major breakthrough in the application of dental resin systems to restorative dental practice. Such materials constitute about one-fourth of all restorations placed per year. Because they are more durable than the silicate cements they replaced, considerable savings to the public is being accrued. However, deficiencies in the currently used commercial materials include: an ill-defined color stability problem; a high viscosity which requires dilution with lower viscosity compatible monomers for ease of application; insufficient storage stability except under ideal conditions; interfacial bonding of filler to resin that is inadequate for stress bearing applications; and a lack of capability for adhesive bonding to the tooth surface. Current efforts are directed toward providing solutions to these areas.

The approach to developing improved color stability involves synthesis and characterization of monomer systems: which are polymerizable at room temperature within the required time span for dental application; which employ minimal amounts of amine accelerators -- a source of color instability; which have a more hydrophobic character as a result of incorporating fluorine-containing monomers and should therefore be more stain resistant; which may use the eutectic mixture of crystalline methacrylate monomers as a means for eliminating color-prone impurities. Since some discoloration may originate in reactions with residual double bonds in the monomers, efforts are made to quantify such unsaturation. Such analysis is fairly straightforward in the resin matrix alone but difficult in the glass or quartz filler-reinforced composite. Infrared and Raman spectroscopy as well as differential scanning calorimetry are being applied to this problem. One route we are pursuing as a means of reducing residual unsaturation is to synthesize "prepolymer" monomers, e.g., oligomers or polymers which have reactive functional groups capable of generating further polymerization.

The influence of the type of viscosity-reducing methacrylate monomers diluent on the extent of marginal gap between composite restoration and cavity wall is being explored. Water sorbing diluents as well as those that can produce extensively cross-linked systems are being examined. A correlation is being sought between gap formation (and marginal leakage as determined with radioactive techniques) and properties of the monomer solution (e.g., viscosity, surface tension), and of the cured system (e.g., strength, indentation and recovery, and coefficient of thermal expansion).

To reduce tooth pulp toxicity response to the accelerator in dental composite restorations we are developing amine accelerators which generically should be less toxic and/or which are more efficient accelerators, and hence are required in lower concentrations for the polymerization. Two recently synthesized, very favorable amines for both toxicity and accelerating efficiency are N,N-dimethylaminophenethanol and N,N-dimethylaminophenylacetic acid. Efficiency of experimental amines is evaluated by measuring the speed of polymerization reactions as well as the minimal concentration of amine required to achieve polymerization at infinite time. A semi-automatic viscosity-measuring device to determine the state of polymerization has been designed and used in this work.

To determine specifically which components of a dental composite system, e.g., monomer, initiator, accelerator, inhibitor, U.V. absorber, etc., contribute most significantly to the tooth pulp response, collaborative projects have been initiated with the University of Florida and the Navy Medical Research Institute in Bethesda. A first phase result, based on pulp responses in primate teeth, did not indicate significant irritation with any one individual ingredient. Tests are now under way on combinations.

Wear Resistance and Mechanical Properties

G. B. McKenna, J. E. McKinney, W. Wu, and J. M. Cassel

An immediate objective of this effort is to demonstrate that data can be obtained with an accelerated laboratory test that will predict the durability of composite restorative materials when they are used in stress bearing situations. Such a test procedure would eliminate the need for very costly clinical trials that are now required. A second principal objective is to define the mechanism of the wear process that occurs clinically and to determine the physical test procedures and the data that will enable a correlation to be made between the physical-mechanical properties of the composite system and its durability. This correlation will serve to expedite development of more durable, stress resistant composite systems.

The third version of the wear apparatus was essentially completed during FY79. The new version determines the wear track length by counting revolutions rather than determining the product of an assumed angular velocity and time interval. By using "depth" measurements on flat brass discs that are not contacted by a wear pin, we have determined that in over 40,000 revolutions the experimental uncertainty itself will not exceed 0.5 mm. Measurements made at ten positions around a circular wear track in both amalgam and composites indicate there are inhomogeneous regions in specimens as we have prepared them. One factor which appears may influence the results with amalgam is the force applied in condensing the amalgam disc specimens. Results to date indicate we may be able to employ synthetic durapatite pins as substitutes for those we derived by careful and tedious grinding of human tooth enamel.

An effort has been initiated to determine the relationship, if any, between wear resistance and the fatigue behavior of composite systems. The approach utilizes the concept of damage accumulation that has been elucidated by others working the Polymer Science and Standards Division on mechanical properties of polymers. By cycling materials to various fractions of their lifetime and then conducting wear measurements on the fatigued samples, the effect of the state of damage on wear rate is explored.

A second approach being taken to correlate the mechanical properties of dental composites with wear behavior is the study of the resistance of these materials to crack propagation. The study of fracture toughness and fatigue crack propagation along with the fatigue/wear investigations should enable us to determine the contribution of these parameters to the wear of dental composites.

Because the BIS-GMA system commonly used in commercial dental composites is extremely brittle, a factor which should work to reduce their wear resistance, we have initiated efforts to develop methods for toughening the system by incorporating elastomeric components.

Dental Alloy Ceramic and Implant Research

J. A. Tesk, R. P. Whitlock[1], E. E. Parry[1], C. P. Mabie[1], R. M. Waterstrat[1], and D. L. Menis[1]

[1] Research Associate

Despite the difficulties encountered in handling dental gold alloy alternatives, 25% of all porcelain veneered crowns are now constructed of Ni-based alloys. This investigation is designed to determine the characteristics of base metal casting alloys and associated bonding porcelains in relation to the feasibility of their use in cast crowns and fixed partial dentures; to determine the effects of fabrication techniques on the clinical serviceability of the restorations; to explore the overall problem of bonding dental ceramic materials to metal substrates; and to fabricating these porcelain/metal restorations.

The goal is also to determine new or improved methods and techniques for fabrication of prostheses from dental alloys and veneering materials; development of new alloys and veneering materials in consideration of those needs and the need for reliable sources of raw materials; investigate new approaches for manufacture of dental porcelain and the incorporation of fluorescing agents into porcelain; examine opportunities for modification of operative techniques involving subperiosteal implants through changes in materials and material properties employed and conduct feasibility study for stress analysis-aided improvement in implant design, and implement experimental studies for improvement of mechanical properties and material handling characteristics of methacrylate resin based bone cement with possible applications for dental implant, as well as orthopedic procedures.

Porcelain Fused to Base Metal Alloys

R. P. Whitlock[1], J. A. Tesk, and E. E. Parry[1]

[1] Research Associate

The characterization of ceramic materials available for bonding to dental casting alloys has progressed quite well. The measurement of dimensional change resulting from thermal cycling has been completed for nearly all ceramic specimens. The degree of expansion/contraction of the ceramic materials relative to the same properties in the substrate alloys during recommended firing schedules must be compatible in order to minimize the build-up of excessive stress in the materials which could result in brittle fracture of the porcelain in the completed restoration. Interfacial stress can be increased markedly through a "mismatch" of these properties. The data collected thus far indentify considerable variation in the expansion/contraction characteristics among different manufacturers' ceramic products. Further, these changes appear to be linked directly to the thermal history of the specimen, i.e., the number of firing cycles to which the material is exposed during fabrication processes. Generally, it would appear on early examination of the data that the expansion coefficient (α) increases with repeated thermal cycling. However, this phenomenon does not manifest the same way for all materials. Further observations suggest that qualitative and/or quantitative changes in crystallinity of the ceramic materials may develop as a function of thermal history. Early results from x-ray diffraction analyses indicate that, indeed, crystal patterns are different in these specimens. Further study in this area is under way at this time to ascertain the extent of crystalline conversion that is occurring and to correlate these differences with changes in the refractory nature of the materials. These observations may have major operational significance inasmuch as some ceramic materials, apparently, can withstand more (repeated) exposure to high temperatures during laboratory fabrication processes without showing appreciable changes in either a or phase structure.

The ability of ceramic powders to "wet" substructure alloy surfaces during the fusion process is a critical element in promoting chemical and mechanical interaction at the interface which is necessary for accomplishing optimum bonding of the materials. Analyses of particle size distributions among the various porcelain manufacturers' products have been completed and the data are being examined. Some differences in this regard have been found to exist among the products examined. Specific combinations of alloys and bonding porcelains have been fused together and are presently being analyzed via void (no contact) formation at the interface for completeness of "wetting." Variations in alloy surface preparation, preconditioning of the substrate (oxidation) and (opaque) porcelain application techniques are being evaluated to ascertain the effects of these variables on the wetting process. Preliminary analysis of the data collected in this phase of the investigation would suggest that 1) variations in porcelain alloy combinations influence the area of contact between the materials after fusion, and 2) different techniques used for applying (opaque) porcelain powders to the alloy substrate may alter the completeness of the "wetting" process. Knowledge gained from the foregoing experiments should assist greatly in more appropriate selection or matching of compatible alloy/porcelain combinations as well as fabrication techniques.

Corrosion, Base Metal Alloys

J. A. Tesk

The extent to which pitting corrosion might be predicted in a clinical situation for a given alloy of a given composition and microstructure is of importance for at least two reasons: 1) the greater the degree of pit formation, the more the tendency for plaque formation with its accompanying undesired organic acid release, and 2) the pit formation process must of itself release ions to the surrounding medium that may be deleterious in one way or another. Availability at NBS of extensive expertise and instrumentation in the area of corrosion and alloy microstructure determination and the presence on the staff of a guest worker from the University of Düsseldorf for a year with a strong interest in this area allowed an immediate attack on this phase of our base metal alloy effort.

Three Ni-Cr alloys representing typical materials of this kind have been investigated. These materials not only consist of different chemical compositions but their microstructures which were observed by light micrographs and SEM exhibit major differences. One appears to be almost single phase with only a few precipitates within the grain whereas the other two show a eutectic constituent in the microstructure. Anodic polarization curves of as cast and fire-cycled samples were generated and breakdown potentials determined in artificial saliva solution adjusted to pH 3.2. This preliminary work points toward a lower *in vitro* corrosion resistance in a Be-containing alloy with a eutectic constituent in its microstructure.

New Dental Ceramic Directions

C. P. Mabie[1] and D. L. Menis[1]

[1] Research Associate

Porcelain frits have been developed which fuse at lower temperatures than current commercially available porcelains. These were prepared by the calcination of gelatinous precipitates and have fusion temperatures in the range 900 to 930 °C. Thermal expansion coefficients of these porcelains, which determine matching of the porcelain to gold alloy or base-metal substrates, are near those of commercial porcelains fusing at higher temperatures.

To strengthen porcelains, quartz and alumina grains and glass fibers are being dispersed into the gels. Attempts are being made to fabricate micacaeous porcelains that are stronger and more machinable. Emphasis is being placed, also, on development of porcelains with small working-range temperatures so that interfacial stresses, which often result in porcelain-to-metal bond failures, can be relaxed.

Investigation of new investments for the casting of base-metal alloys continues. The objectives are to develop investments that are less susceptible to mold reactions and in which most of the dimensional compensation can be obtained thermally. Zirconium phosphate and aluminum phosphate bonded investments, with flint refractory grains, are to be studied. Investments more suitable for the especially routine titanium alloys are being investigated.

Irradiation Effects from Neutron Activated Dental Materials

J. A. Tesk

As a result of the very limited information available in the literature, calculations have been made to estimate the effects of secondary radiation from gold crowns receiving neutron irradiation. Gold is the only element examined to date and was chosen because of its high neutron activation cross section, relatively short half life (2.7 days), and its extensive use as a dental restorative material. Estimates on γ and β radiation doses delivered to soft tissue were made for single crowns and a mouth full of crowns. A 50 REM neutron exposure was assumed as this is clearly a sublethal exposure. The results are that a single gold crown is likely to provide an additional 2 REM γ dose to local tissue and six or more adjacent crowns provide an additional dose between 3 and 5 REM. It is estimated that the local tissue can receive a β dose of at least 25 REM following a 50 REM neutron dose.

It has been calculated that temporary shielding of local tissues from maximum energy β radiation from gold is possible by using 0.40 cm of ordinary mouth guard material. The use of higher density materials decreases the thickness of shielding required according to the relationship $t\rho = 0.40$, where t is the thickness and ρ the density. However, for subgingival restorations, shielding is virtually impossible.

Dental Implants

J. A. Tesk

No viable dental implant exists except for what has become known as the subperiosteal implant. This implant, while particularly well suited for older edentulous patients who have suffered severe loss of bone to the extent that the use of conventional dentures is ineffective, might find greater usage if the lengthy operative procedures could be reduced. Simplification of the procedure via development of a heat treatable, biocompatible alloy system which could be formed to fit the bone while in the dead soft condition is being considered. The time required to wax, invest, cast, clean, polish, and transport the implant might be eliminated and the total time for a one-day procedure reduced from 12-13 hours to 3-5 hours.

Much of the current interest in dental implants centers around theoretical analysis to provide a more clear understanding of the effects of stress on bone with anticipation that implants may be more effectively designed by individuals armed with such knowledge. Much fundamental information of these stress effects is not yet available. Efforts to collaborate with the University of Illinois in developing extended studies of stress in oral tissue using finite element techniques are being finalized.

Clincal and Laboratory Investigation of Dental Amalgams

N. W. Rupp[1], G. C. Paffenbarger[1], and R. M. Waterstrat[1]

[1]Research Associate

Amalgam restorations account for 70% of all restorations currently placed. The reasons for their progressive deterioration are not as well understood as is desired. Seven-year-old amalgam restorations are being observed for margin integrity, tarnish, corrosion, and change in contour. These clinical observations corroborate laboratory results which show that amalgams having high creep values tend to "grow" or extrude out of the cavity. This growth is not necessarily caused by repeated loading of the tooth but, as observed earlier, the amalgam expands as a result of continuous changes in phases within the amalgam. As these phase changes take place, forces are generated which cause expansion; however, amalgams having low creep values are restrained in their dimensional changes by the cavity walls.

Recently it has been observed that alloys which do not contain zinc have very little expansion even when unrestricted as compared to those which contain zinc. This raises questions concerning the role of zinc in these silver alloys. Specifically, does zinc facilitate phase changes? If so, can zinc be removed from all alloys, thus reducing the phase changes and, consequently, the forces which might result in unwanted expansion of the amalgam restorations?

Also, we observed that the creep values of certain amalgams are increased by an increase in mercury content; other amalgams were not as sensitive to this increase in mercury content. Nonetheless, amalgams should be mixed and inserted so that the restoration will have the lowest possible mercury content. Even the recently-introduced alloys that use approximately 45% mercury in the original mix should have only 39-41% remaining in the restoration.

It now appears that the elimination of the weak and corrosion-prone tin-mercury phase does not always produce a more durable amalgam, and claims for such an effect have apparently been exaggerated. Some other factors must be partly responsible for the demonstrated clinical superiority of the copper-containing amalgams. Resistance to creep and corrosion are certainly desirable characteristics, but it is not clear how these can best be achieved. Recent experiments showed that small amounts of manganese dissolved in the conventional silver-tin alloys produce amalgams with a sharply reduced creep and that the maximum reduction in creep may be achieved without sacrificing essential corrosion resistance. This is accomplished by optimizing the ratio of the copper and manganese contents so that the manganese content is minimized. The manganese not only tends to eliminate the tin-mercury phase, but it also seems to inhibit the formation of other phases. We are hopeful that this will help to prevent gradual breakdown of the margins and occlusal surfaces and prolong the useful life of the restoration.

Dental Enamel Chemistry and Preventive Dental Treatments

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[1]Research Associate

The objective of this project is to develop and apply fundamental information on the solubility and crystallographic structure of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with 1) development of physicochemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated into tooth enamel, and 2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid etch bonding treatments and improved topical fluoride procedures.

Crystallographic research is utilized to provide a sound structural basis for understanding the chemical properties of the calcium phosphates in tooth, bone, dental calculus, and those that are formed or used in dental therapy. The chemical reactivities of calcium phosphates are structure dependent; this program continues to be the major source of structural information on these compounds for the National Institute of Dental Research. Recently a new project was commenced that is capable of providing powerful insight into the mechanism of growth of tooth and bone crystallites. This mechanism, which involves interlayering of enamel mineral with another calcium phosphate, was shown to be valid for crystals grown in vitro. If this proves valid for enamel mineral in vivo, it will be a major step forward in understanding both the role of fluoride in preventing caries and the mechanism that causes enamel mineral to incorporate impurities, e.g., carbonate, that affect its resistance to caries. An ultra-micro technique is being used to study the effects of demineralizing environments on the composition of solutions within incipient carious lesions in human enamel. The objective is to gain an increased understanding of the events that control lesion formation. This in vitro study has produced, for the first time, information on pH changes within enamel and membrane potentials across the enamel surface when the specimen is undergoing demineralizing processes.

The effectiveness of an experimental topical fluoridation procedure has been examined in an animal study in collaboration with the National Institute of Dental Research. The procedure consists of a pretreatment with a calcium phosphate solution capable of forming the crystalline compound $CaHPO_4 \cdot 2H_2O$ in the enamel. This is followed by a fluoride treatment to convert the newly-formed salt into an insoluble form of tooth enamel. The new procedure resulted in significantly higher fluoride uptakes compared to conventional sodium fluoride or stannous fluoride treatments. Animals that received the new treatment procedure also had the lowest mean caries scores, but this result was not highly significant from a statistical point of view. Further studies of the new procedure were carried out in cooperation with the School of Dentistry, Taiwan

University. A single application of the commercial topical acidulated phosphate fluoride solution (APF), preceded by a treatment with the $CaHPO_4 \cdot 2H_2O$-forming solution, yielded a mean fluoride uptake of approximately 2000 ppm when measured three months after treatment. The mean fluoride uptake from a single APF treatment control experiment was only 100 ppm and was not statistically significant. It appears that, under clinical conditions, the new topical fluoridation procedure produces fluoride uptakes that are much greater than have been obtained by fluoride agents presently in use. This procedure could prove to be a major step forward in fluoride therapy.

Phosphoric acid etchants are now in frequent use for pit and fissure sealants, cementing of orthodontic brackets, and repair of incisal edges. It previously had been shown that partial saturation of the etching solution with calcium and phosphate would reduce the loss of mineral in the initial stage of etching. It remained to be shown, however, that the new etching procedure would produce enamel surfaces to which plastic would adhere. Laboratory tests have now shown that the new solutions were at least as good as the ones in use and do not cause potentially harmful loss of enamel. The new procedure warrants clinical evaluation.

Dental and Medical Materials Standards

J. M. Cassel, G. M. Brauer, J. A. Tesk, and N. W. Rupp[1]

[1] Research Associate

Active participation from Task Force level to the role of Subcommittee Chairman, occurs in development of dental standards through ANSI MD 156 and ISO TC 106, Dental Materials and Services. Development of medical implant standards is assisted by serving in roles of Polymeric Materials Chairman and Task Force leadership in the efforts of ASTM F4, Medical and Surgical Materials and Devices, and as Chairman, USA TAG ISO TC 150, Surgical Implants.

Molecular Weight Dependence of Polymer Adsorption on Solid Surfaces

W. H. Grant and R. E. Dehl

The adsorption of polymer molecules on solid surfaces is being investigated for both theoretical and practical reasons. The nature of the interaction of large molecules with surfaces is relevant to the problem of adhesion faced in medical cardiovascular implant application, dental plaque accumulation, and in securing plastic coatings to surfaces in a multitude of end uses. This interaction also has an important role in the strength and stability of polymer composite materials. It is fundamentally important to understand the changes which occur in the conformation of a long-chain molecule when it interacts with a surface. The number of points of attachments at the surface and the distribution of adsorbed segments, loops, and tails are all relevant to the stability and integrity of the polymer-substrate interface.

Previous work at NBS and elsewhere has provided significant insight into the understanding of this problem. However, recent theoretical and experimental studies by a group from the Agricultural University in The Netherlands is casting doubt on some of the accepted precepts about polymer adsorption. For example, it has been commonly believed that the adsorption of macromolecules is an irreversible process. According to the recently developed theory, however, polymer molecules are not necessarily adsorbed irreversibly, but desorption always occurs by the displacement of short chains by longer ones in the supernatant solution. Phenomena such as the rounded shape of the adsorption isotherm, the dependency of the adsorbance on the solution concentration, and the absence of desorption upon dilution are explained in the current theory by polydispersity of the polymer.

The predictions of the displacement theory are currently being tested by the use of radiolabeled polystyrene fractions having narrow molecular weight distributions. To date, studies have involved only one radiolabeled component in a binary mixture, which has left ambiguities in the interpretation of results. Future studies will involve the use of two different radiolabeled species, with a different nuclear tag on each species. In this way, the adsorption and displacement behavior of the different molecular weight species will be examined in detail.

Other Division Activities

Invited Talks

"Synthesis of Polyfluorinated Polymethacrylates for Dental Applications"
IADR & AADR 57th General Session and Annual Session,
New Orleans, Louisiana
J. M. Antonucci
March 1979

"Composite Restorative Materials"
15th Annual Meeting Brazilian Dental Materials Group,
Florianopolis, Brazil
Dr. R. L. Bowen
July 1979

"Effect of Diluent on the Properties of BIS-GMA Based Composites"
IADR & AADR 57th General Session and Annual Session,
New Orleans, Louisiana
G. M. Brauer
March 1979

"New Amine Accelerators for Dental Composites"
ACS Meeting
G. M. Brauer
September 1978

"Two Types of Pyroelectricity in a Copolymer at Vinylidene Fluoride & Tetrafluroethylene"
International Workshop on Electric Charges in Dielectrics, Kyoto, Japan
M. G. Broadhurst
October 1978

"Piezoelectric Polymer Transducers"
NBS Conference Room - Science and Technology Attaches visit
M. G. Broadhurst
May 1979

"Piezoelectric Polymers"
18th Annual Meeting of the Plastics Institute of America
United English Center, New York, New York
M. G. Broadhurst
April 1979

"Piezoelectricity & Pyroelectricity in PVDF - A Model"
(CEIDP) Pocono, Pennsylvania
M. G. Broadhurst & G. T. Davis
October 1978

"Basis of Piezoelectricity in PVDF"
Univ. of Tokyo (Japan)
M. G. Broadhurst
October, 1978

"Polyvinylidene Fluoride Viewed as a Polycrystalline Ferroelectric Material"
Kyoto, Japan
M. G. Broadhurst
October 1978

"Electrical Properties of Polymers"
Waseda University, Japan
M. G. Broadhurst
October 1978

"Basis of Piezoelectricity in PVDF"
Kyoto University, Japan
M. G. Broadhurst
October 1978

"Current Developments in Piezoelectric Polymer Research and Applications"
Bell Labs, Murray Hill, New Jersey
M. G. Broadhurst
August 1979

"Piezo- & Pyroelectricity in Polymers" Part of 1979 Summer Institute in Polymer Science and Technology, University of New York, New Paltz, New York
M. G. Broadhurst
June 1979

"Cooperative Molecular Rotations in a Ferroelectric Polymer"
NBS Colloquim on Mathematical Modeling in Science and Engineering, NBS
M. G. Broadhurst
August 1979

"NBS Pyroelectric and Piezoelectric Polymer R & D: I. Structure Activity and Use"
National Bureau of Standards, Washington, D. C.
M. G. Broadhurst
January 1979

"Some Aspects of Poling PVDF"
Army Research Office Workshop on Piezoelectricity,
Dover, New Jersey
M. G. Broadhurst
January 1979

"Piezoelectric Polymers"
Video taped for future file on WDVM-TV, Steve Gendel, interviewer
M. G. Broadhurst
July 1979

"Kinetics of Hydrolytic Aging of Polyester Polyurethane Elastomers"
ACS National Meeting, Washington, D. C.
D. W. Brown
September 1979

"Mechanisms of Action of Fluoride in Prevention of Dental Caries"
ACS/Japan Chemical Congress, Honolulu, Hawaii
W. E. Brown
April 1979

"A Testing Program for Porous Polymer Tapes"
EPRI - Seminar on Solid Dielectric Materials,
Monterey, California
A. J. Bur
January 1979

"Lifetime Behavior of Polyethylene Sheets Under Inflation in the Presence of Stress-Cracking Agent"
American Chemical Society, Washington, D. C.
J. M. Crissman
September 1979

"Static Fatigue of Polyethylene in Uniaxial Creep in the Presence of Stress-Cracking Agents and Solvent"
American Chemical Society, Washington, D. C.
J. M. Crissman
September 1978

"Progress Report on Mechanical Properties Studies Relevant to the Performance of Plastic Packaging for Hazardous Materials Transportation"
Public Meeting on Polyethylene Packagings held at the Department of Transportation, Washington, D. C.
J. M. Crissman
July 1979

"Piezo- & Pyroelectric Polymers - Mechanisms & Application"
Gordon Research Conference, Program on Polymers,
New London, New Hampshire
G. T. Davis
July 1979

"Poling of PVDF at High Electric Fields"
CEIDP - Pocono, Pennsylvania
G. T. Davis
October 1978

"Charging of Polymer by High Electric Fields"
Conference on Electrical Insulation and Dielectric Phenomenon,
Pocono, Pennsylvania (CEIDP)
A. S. DeReggi, M. G. Broadhurst
October 1978

"Research in the Polymer Science and Standards Division"
Solar Energy Research Institute, Golden, Colorado
R. K. Eby, L. E. Smith and B. M. Fanconi
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
Washington State University, Pullman, Washington
R. K. Eby
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
University of Washington, Seattle, Washington
R. K. Eby
October 1978

"Order-Disorder Transitions in Polytetrafluoroethylene"
University of Tennessee, Knoxville, Tennessee
R. K. Eby
February 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Proctor and Gamble Corporate Central Research Laboratories, Cincinnati, Ohio
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
March 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
General Motors Research Laboratory, Warren, Michigan
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
June 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Boeing Research Laboratory, Renton, Washington
R. K. Eby, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
June 1979

"Dynamic Measurement of Nip Pressures"
10th Annual Symposium on Paper Properties & Technology,
Oxford, Ohio
S. Edelman
May 1979

"The Adsorption of Human Serum Albumin and Gamma Globulin on Hydrophobic and Hydrophilic Surfaces"
Joint Meeting of the Japanese Chemical Society and the American Chemical Society,
Honolulu, Hawaii
Warren Grant
April 1979

"Temperature & Molecular Weight Dependence of Polymer Dimensions in Solution"
IBM Laboratories, San Jose, California
C. C. Han
January 1979

"Some Nonlinear Effects in Polymer Testing"
Subcommittee on Geothermal Seals of ASTM, Committee D11.36,
Minneapolis, Minnesota
E. A. Kearsley
June 1979

"Dental Investments"
Wilford Hall USAF Medical Center, Lockland AFB,
San Antonio, Texas
C. P. Mabie

"The Crystal Structure of $Pb_8K_2(PO_4)_6$: An Apatite Without Hexed Anions"
American Crystallographic Assoc. Meeting, Honolulu, Hawaii
Dr. Mathai Mathew
March 1979

"Measurement of Molecular Weight Distribution by Recycle Size Exclusion Chromatography"
ACS National Meeting, Washington, D. C.
F. L. McCrackin
September 1979

"Time Dependent Failure Behavior of Glassy and Semi-Crystalline Polymers"
IBM, San Jose Research Laboratories, San Jose, California
G. B. McKenna
January 1979

"Time Dependent Failure of PMMA and Polyethylene"
Naval Research Laboratories, Chemistry Division Seminar, Washington, D. C.
G. B. McKenna
February 1979

"Development of Fiber Reinforced Polymer Composites for Orthopedic Applications"
3M Corporate Research Center, St. Paul, Minnesota
G. B. McKenna
June 1979

"Time Dependent Processes in Polymeric Materials - Viscoelasticity and Failure"
University of Minnesota, Department of Chemical Engineering, Minneapolis, Minnesota
G. B. McKenna
June 1979

"Low Temperature Dielectric Loss Characterization of Polypropolene"
(CEIDP) Pocono, Pennsylvania
F. I. Mopsik
November 1978

"Physical Testing of Polymers for Use in Circulatory Assist Devices"
Second Annual Contractors Meeting, Devices and Technology Branch, NIH, Bethesda, Maryland
R. W. Penn
December 1978

"A Defect Which Transports a Polymer Chain Along the Molecular Axis"
Universität für Makromolekulare Chemie der Albert Ludwigs Universität, Freiburg, West Germany
D. H. Reneker
September 1978

"A Defect Which Transports a Polymer Chain Along the Molecular Axis"
Universität Ulm, Ulm, West Germany
D. H. Reneker
September 1978

"Diffusion in Polymers"
Josef Stefan Institute, Ljubljana, Yugoslavia
D. H. Reneker
October 1978

"Localized Defects in Polyethylene and the Use of Infrared Absorption to Measure the Number of Trans-gauche Bond Pairs"
Instituto di Chimica del Politecnio, Milano, Italy
D. H. Reneker
October 1978

"Nuclear Magnetic Resonance Line Shape, Relaxation and Self-Diffusion of Polyethylene in the Melt"
American Physical Society Meeting, Chicago, Illinois
D. H. Reneker
March 1979

"Overview of Technical Activities of the Polymer Science and Standards Division of the National Bureau of Standards"
Picatinny Arsenal, Army Armament R & D Command, Dover, New Jersey
D. H. Reneker, M. G. Broadhurst, L. E. Smith, and B. M. Fanconi
May 1979

"Research in the Polymer Science and Standards Division of the National Bureau of Standards"
Lawrence Livermore Laboratory, Livermore, California
D. H. Reneker, M. G. Broadhurst, and B. M. Fanconi
July 1979

"Transport of a Polymer Chain in a Crystal Lattice in the Axial Direction"
IUPAC 26th International Symposium on Macromolecules, Mainz, West Germany
D. H. Reneker
September 1979

"Detecting and Monitoring Deterioration in Bearings Using Piezoelectric Polymer"
Symposium on Detection Diagnosis & Prognosis System Applications, San Antonio, Texas
S. Roth
November 1978

Discussant at Winter Gordon Conference on Polymers
Santa Barbara, California
R. J. Rubin
January 1979

"Enzyme-enzyme Interactions, Diffusion, and Steady-State Kinetics"
American Physical Society Meeting, Chicago, IL
R. J. Rubin
March 1979

"Effect of Enzyme-Enzyme Interactions on Steady-State Enzyme Kinetics: Some Exact Results in a Lattice-Fluid Model"
International Symposium on Mathematical Topics in Biology, Kyoto, Japan
R. J. Rubin
September 1978

"Effect of Enzyme-Enzyme Interactions on Steady-State Enzyme Kinetics: Some Exact Results in a Lattice-Fluid Model"
Seminar, Physics Department, Waseda University, Tokyo, Japan
R. J. Rubin
September 1978

"Selection and Use of Dental Materials"
U. S. Air Force, Andrews AFB, Maryland
Dr. N. W. Rupp
May 1979

"Dental Materials - Their Selection - 1979"
College of Dentistry, Ohio State University, Columbus, Ohio
Dr. N. W. Rupp
June 1979

"Statistical Thermodynamics of Polymer & Oligomeric Mixtures"
Gordon Research Conference on Polymers, Santa Barbara, California
I. C. Sanchez
January 1979

"Statistical Thermodynamics of Polymer Solutions"
E. I. duPont de Nemours, Wilmington, Delaware
I. C. Sanchez
May 1979

"Statistical Thermodynamics of Bulk and Surface Properties of Polymer Mixtures"
Joint US/Japan Conference on Multi-component Polymers,
Kyoto University, Japan
I. C. Sanchez
December 1978

"High Resolution Solid State ^{13}C NMR in Polymers"
Chemistry Department Seminar, University of Maryland,
College Park, Maryland
D. L. VanderHart
November 1978

"High Resolution ^{13}C NMR of Solid Polymers"
Chemical Society of Washington, Topical Session, NIH,
Bethesda, Maryland
D. L. VanderHart
February 1979

"Spin-Spin and Spin-Lattice Contributions to ^{13}C Rotating Frame Relaxation and Linewidths in Polymers"
Gordon Research Conference on Magnetic Resonance,
Wolfsboro, New Hampshire
D. L. VanderHart, William L. Earl, & A. N. Garroway

"Expectations for Resolution in High Resolution ^{13}C NMR of Solids: Particularly Polymers"
21st Annual Rocky Mountain Conference on Analytical Chemistry,
Denver, Colorado
D. L. VanderHart
July 1979

"^{13}C NMR Studies of Semicrystalline Polymers: Polyethylene and Cellulose"
Sixth Annual Meeting of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Pennsylvania
D. L. VanderHart
September 1979

Publications and Patents

"Molecular Weight & Temperature Dependence of Polymer Dimensions in Solution"
A. Ziya Akcasu and Charles C. Han
Macromolecules, 12, 276-280 (1979)

"Mechanical and Transport Properties of Drawn Low-Density Polyethylene"
L. Araimo, F. deCandia, V. Vittoria, and A. Peterlin
J. Poly. Sci. (Phys. Edition), 16, 2087-2103 (1978)

"Performance of Plastic Packaging for Hazardous Materials Transportation"
J. D. Barnes, G. M. Martin, and F. L. McCrackin
Report # DOT/MTB/DHMO - 77/5

"Critical Review of Vibrational Data & Force Field Constants for Polyethylene"
John Barnes and Bruno Fanconi
J. Physical and Chemical Reference Data, 7, 1309-1321 (1978)

"The Influence of Polymer Membrane Properties on the Performance of Dissolved Oxygen Sensors"
John D. Barnes
NBSIR 79-1740

"SRM 1470: Polyester Film for Oxygen Gas Transmission Measurements"
John D. Barnes and Gordon M. Martin
NBS Special Publication, 260-58 (1979)

"Adhesive Bonding of Various Materials to Hard Tooth Tissues XVIII: Synthesis of a Polyfunctional Surface-active Comonomer"
R. L. Bowen
J. Dent. Res. 58(3): 1101-1107 (Mar. 1979)

"Adhesive Bonding of Various Materials to Hard Tooth Tissues--Solubility of Dentinal Smear Layer in Dilute Acid Buffers"
R. L. Bowen
International Dental Journal, 28(2): 97-107 (1978)

"Effects of Mechanical Environment on Bone Healing"
G. W. Bradley, G. B. McKenna, H. K. Dunn, A. U. Daniels, and W. O. Stratton
J. Bone and Joint Surgery, in press

"Durability of the Bond Between Mineralized Tissues and Potential Adhesives"
G. M. Brauer
ACS Symposium Series, No. 95, Durability of Macromolecular Materials, R. K. Eby, Editor (April 1979)

"Properties of Sealants Containing Bis-GMA and Various Diluents"
G. M. Brauer
J. Dent. Res. 57(4): 597-607 (April 1978)

"Formation of a New Crystal Form (α_p) of PVDF Under Electric Field"
D. Naegele, D. Y. Yoon, and M. G. Broadhurst
Macromolecules, 11, 1292 (1978)

"On the Calculation of Piezoelectricity and Pyroelectricity in Polyvinylidene Fluoride"
M. G. Broadhurst, G. T. Davis, J. E. McKinney, and R. E. Collins
1978 Annual Report on CEIDP
National Academy of Science, Washington, D. C., p. 85 (1978)

"Piezoelectricity & Pyroelectricity in Poly(vinylidene Fluoride) - A Model"
M. G. Broadhurst, G. T. Davis, J. E. McKinney, and R. E. Collins
Journal of Applied Physics, 49, 4992 (1978)

"Piezo- & Pyroelectric Properties of Electrets"
M. G. Broadhurst and G. T. Davis
Book Chapter - Topics in Modern Physics - Electrets,
Ed. G. M. Sessler, Pub. Springer-Verlag

"Ferroelectric Polarization in Polymers"
M. G. Broadhurst and G. T. Davis
1979 Annual Report GEIDP

"Piezo- & Pyroelectric Applications of Plastics"
M. G. Broadhurst, S. Edelman, and G. T. Davis
American Chemical Society Proceedings of 176 Annual Meeting - 1979

"The Radiation-Induced Copolymerization of Tetrafluoroethylene & Styrene at High Pressure"
Daniel W. Brown and Robert E. Lowry
J. Poly. Sci., Polymer Chemistry Edition, 17, 759-768 (1979)

"Molecular Weight Standards from Sulfonation of Polystyrene"
Daniel W. Brown and Robert E. Lowry
J. Poly. Sci., Polymer Chemistry Edition, 17, 1039-1046 (1979)

"Crystallinity in Hydrolytically Aged Polyester Polyurethane Elastomers"
Daniel W. Brown, Robert E. Lowry, and Leslie E. Smith
Durability of Macromolecular Materials, p. 145-153, Chapter 10, 1979

"Interlayering of Crystalline Octacalcium Phosphate and Hydroxylapatite"
W. E. Brown, L. W. Schroeder, and J. S. Ferris
J. Phys. Chem., 83, 1385 (1979)

Session V, General Comment: Third International Symposium on Tooth Enamel, General Comments
W. E. Brown
J. Dent. Res., Special Issue B (March 1979)

"Pyrolysis Gas Chromatography of Some Fluorine-Containing Polymers"
Constantin N. Cascaval and Roland E. Florin
J. Fluorine Chemistry, 13, 65-70 (1979)

"Lifetime Behavior of Polyethylene Bars in Uniaxial Extension in Various Chemical Environments"
J. M. Crissman
Symposium on the Durability of Macromolecular Materials, ACS Symposium Series, Vol 95, 289 (1979)

"Stress Strain-Time Diagrams, Including Failure Envelopes, for High Density Polyethylenes of Different Molecular Weight"
J. M. Crissman
Symposium on the Durability of Macromolecular Materials, ACS Symposium Series, Vol. 95, 301 (1979)

"Poling of PVDF at High Electric Fields"
G. T. Davis
1978 Annual Report of Conference on Electrical Insulation & Dielectric Phenomena
National Academy of Science, Washington, D. C., p. 75 (1978)

"Experiences in Developing an Automated Factor-Jump Method of Thermogravimetry"
Brian Dickens
Thermochimica Acta, 29, 87-113 (1979)

"Computer Program to Implement Automated Factor-Jump Thermogravimetry"
Brian Dickens
Thermochimica Acta, 29, 57-85 (1979)

"Automation of Factor-Jump Thermogravimetry for Active Computer Control"
Brian Dickens
Thermochimica Acta, 29, 41-56 (1979)

"Evaluation of Commercial and Newly-synthesized Amine Accelerators for Dental Composites"
Dianne M. Dulik
J. Dent. Res. 58(4), 1308-1316 (April 1979)

"Observations in Solid Polyethylene by ^{13}C NMR with Magic Angle Sample Spinning"
William L. Earl and D. L. VanderHart
Macromolecules, 12 (1979)

Durability of Macromolecular Materials
R. K. Eby, Editor
ACS Symposium Series 95, ACS, Washington, D. C. (1979)

"Energetics of Methyl Branches in Hydrocarbon Crystals"
B. L. Farmer and R. K. Eby
Polymer, 20, 363-366 (1979)

"Free Radicals in Stretched Vinylidene Chloride Copolymer"
Roland E. Florin
J. Poly. Sci., Polymer Physics Edition, 16, 1877 (1978)

"Application of New Kinetic Techniques to the Lifetime Prediction of Polymers from Weight-Loss Data"
Joseph H. Flynn and Brian Dickens
Durability of Macromolecular Materials, p. 97-115, Chapter 7, 1979

"Concentration Dependence of the Diffusion Coefficient of Polystyrene at Theta-Condition"
Charles C. Han
Polymer, 20, 259-262 (1979)

"Diffusion Coefficients of the 45S and 50S States of the Large Ribosomal Subunit of E. Coli by Quasielastic Light Scattering"
Charles C. Han, I. N. Serdyuk, and Hyuk Yu
J. Res. of the NBS, 84, 1-8 (1979)

"Molecular Weight & Polydispersity Measurements of Polystyrene by Quasielastic Light Scattering"
Charles C. Han and Frank L. McCrackin
Polymer, 20, 427-432 (1979)

"Differential Scanning Calorimetry Studies of Some Analogs for the Lipid Component of Biological Membranes"
J. T. Joseph, Albert Hybl, and Joseph H. Flynn
Chemistry and Physics of Lipids, 22, 239-243 (1978)

"Some Methods of Measurement of an Elastic Strain Energy Function of the Valanis-Landel Type"
E. A. Kearsley
To be published in Journal of Rheology (1979)

"Some Non-Linear Effects in Polymer Testing"
E. A. Kearsley
To be published in Proceedings of ASTM Committee D11.36 (Geothermal Seals)

"Fabrication of Piezoelectric Polymer Film"
J. M. Kenney and S. C. Roth
NBS J. of Research (Sept. 1978)

"Aspects and Implications of the Diversity in the Habits Exhibited by Polymer Crystals Grown from Solution"
F. Khoury and L. H. Bolz
Proceedings IUPAC 26th International Symposium on Macromolecules (1979)

"Substitution in Barium-Fluoride Apatite: The Crystal Structures of $Ba_{10}(PO_4)_6F_2$, $Ba_6La_2Na_2(PO_4)_6F_2$ and $Ba_4Nd_3Na_3(PO_4)_6F_2$"
M. Mathew, I. Mayer, B. Dickens, and L. W. Schroeder
J. Solid State Chem., 28, 79-95 (1979)

"Crystal Structure of a Struvite Analogue, $MgKPO_4 \cdot 6H_2O$"
M. Mathew and L. W. Schroeder
Acta Cryst., <u>B35</u>, 11-13 (1979)

"Raman Intensities of Longitudinal Acoustic Modes"
J. Mazur and B. Fanconi
J. Chem. Phys. (accepted for publication)

"Monte Carlo Calculations of the Number of Ways to Pack Nonoverlapping Rods on a Square Lattice"
Frank L. McCrackin
J. Chem. Phys., <u>69</u>, 5419-5423 (1978)

"The Normal Stress Response in Non-Linear Viscoelastic Materials - Some Experimental Findings"
G. B. McKenna and L. J. Zapas
Submitted to J. Rheology April 1979

"Degradation Resistance of Some Candidate Composite Biomaterials"
G. B. McKenna, G. W. Bradley, H. K. Dunn, and W. O. Statton
J. Biomed. Matls. Res., in press

"Time Dependent Failure Behavior of Poly(methyl Methacrylate) and Polyethylene"
G. B. McKenna and R. W. Penn
Submitted to Polymer, August 1979

"Surface Area of Dental Enamel, Bone, and Hydroxyapatite: Chemisorption from Solution"
D. N. Misra, R. L. Bowen, and G. J. Mattamal
Calcif. Tiss. Res., <u>26</u>, 139-142 (1978)

"The Dielectric Loss of Polypropylene Films and Polypropylene Laminates at Cryogenic Temperatures"
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NBSIR 79-1735

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Seminars for Staff and Guests

Professor C. Macosko
"Rubber Elasticity in Model Silicone Networks"
10/2/78

Professor R. Byron Pipes
"Fracture of Composite Materials"
10/5/78

Dr. J. H. Mason
"A Review of Electrical Discharges in Insulating Materials"
10/20/78

Dr. Philip Geil
"Amorphous Polyethylene"
10/24/78

Professor Guilio Sarti
"A Physical Interpretation for Case II Transport Solvent Induced Stresses and Crazing Kinetics"
11/3/78

Yasuo Suzuoki
"Thermally Stimulated Currents in Polymers"
11/7/78

Professor Kichinoske Yahagi
"Relation Between Dielectric Breakdown and Morphological Structure in Polyethylene"
11/8/78

James O'Reilly
"Enthalpic Retardation Times of Polymer Near the Glass Transition Temperature"
11/16/78

Dr. D. Richter
"Study of the Segmental Diffusion of Polymers in Solution Using Neutron Spin Echo Spectroscopy"
11/27/78

Dr. Vidomir Markoviç
"Use of Radiation for Crosslinking - Introduction Radiation Technology in the Polymer Field"
12/6/78

Dr. W. E. Brown
"Calcium Phosphates: Gibbs, Gibbs-Duhem and Galvani"
12/14/78

Dr. Martin G. Broadhurst
"NBS Pyroelectric and Piezoelectric Polymer R & D: I. Structure Activity and Use"
1/4/79

Dr. M. G. Broadhurst
"NBS Pyroelectric and Piezoelectric Polymer R & D: II. Improper Ferroelectricity, Space Charge Effects, and Devices"
1/11/79

Dr. Takeji Hashimoto
"Small Angle X-ray Scattering of Block Copolymers"
1/31/79

Professor Georgio Ronca
"Dynamics of Swollen Rubbers: Mechanical and Optical Factors"
2/7/79

Dr. James O'Malley
"X-ray Photoelectron Spectroscopy of Polymer Surfaces"
2/16/79

Dr. D. L. VanderHart
"High Resolution ^{13}C NMR in Solid Polymers: Polyethylene"
2/27/79

Dr. Robert Snyder
"C-H Stretching Vibrations and the Structure of Polymethylene Chains"
3/29/79

Professor Bernard Coleman
"On Theories of Melt Fracture of Polymers"
3/30/79

Kent B. Abbas
"Thermal Degradation of Polyvinylchloride"
4/10/79

Dr. Claude Y. P. Quivoron
"Recent Developments on the Use of Polymer Materials in Liquid Chromatography"
4/25/79

Professor E. L. Thomas
"A Reassessment of Dark Field Microscopy Evidence for Order in Amorphous Polymers"
5/2/79

Dr. Frank L. McCrackin and Herman L. Wagner
"Measurement of Molecular Weight Distribution by Recycle Size Exclusion Chromatography"
5/3/79

Dr. Richard Gaylord
"Who is P. G. deGennes and why is he saying those things about polymers?"
Subtitle: "Simplified derivations of some of the deGennes scaling formulas"
5/8/79

Prof. Seymour Gilbert
"Physical Chemical Aspects of Migration in Polymers"
5/14/79

Dr. David Dollimore
"The Optimum Flocculation Conditions for Concentrated Suspensions of Powdered Materials"
5/24/79

Dr. Alan English
"Molecular Motions Observable in Solid Polymers with Multiple Pulse NMR"
5/25/79

Professor Aubrey Jenkins
"Polymerization Initiated by Titanium Amides"
5/29/79

Dr. Mustapha Benmouna
"Temperature Effect on the Dynamic Structure Factor of Polymer Solutions"
5/29/79

Dr. R. Koningsveld
"Thermodynamic Aspects of Polymer Compatibility"
6/5/79

F. Micheron
"Thermodynamical Model of PVF_2 and New Data"
6/6/79

Dr. Alan Berens
"Transport of Gases and Vapors in Rigid Polyvinylchloride"
6/13/79

Professor Andrew Keller
"Radiation and the Crystal Lattice of Polyethylene and N-Paraffins"
6/25/79

Dr. Bernard Lotz
"Structure of Synthetic Polypeptides, Models of Transmembrane Channels"
7/6/79

Dr. Leonard L. Katan
"Migration in Plastics"
7/20/79

Dr. Leszek Jarecki
"Formation of Ultra-High Modulus PE by Ultra-Drawing at Elevated Temperatures and/or Hydrostatic Pressures"
7/23/79

Prof. A. Ziya Akcasu
"Concentration and Temperature Effect on the Apparent Diffusion Coefficient of Polymers in Solution"
8/2/79

Linda K. Nicholson
"A New Neutron Scattering Technique for Observing Polymer Solution Dynamics"
8/8/79

Dr. M. Daoud
"An Introduction to Scaling in Polymers"
8/9/79

Dr. M. Daoud
"Vulcanization and Critical Exponents"
8/10/79

Prof. George Summerfield
"Combined X-ray and Neutron Scattering Applied to Polyethylene"
8/13/79

Dr. Gerhard Wegner
"Crystallization of Copolymers"
8/17/79

Dr. Ernest A. Boucher
"Polymer Transformation Reactions in Solution"
8/21/79

Dr. Manfred Schmidt
"Information of Polymer Branching and Polydispersity from Combined Integrated and Dynamic Light Scattering"
8/23/79

Dr. Terence Cosgrove
"Polymer Adsorption from NMR, Neutron Scattering and Light Scattering Measurements"
8/24/79

Professor Hiroyuki Tadokoro
"Structure and Properties of Crystalline Polymers"
9/5/79

Professor Bruce Eichinger
"Characterization of Random Networks"
9/14/79

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SC.16 Hook-up Wire Insulation
SC.17 Thermal Capability
SC.94 Editorial
SC.91 International Standards
SC.96 Federal Standards

ASTM D-11 Rubber and Rubber-Like Materials
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ASTM Plastics D-20
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SC.19 Film and Sheeting
SC.70 Measurement Techniques
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SC.04 Size Exclusion Chromatography
SC.05 Molecular Weight Parameters (Chairman)

ASTM D-27
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ISO TC 150 Implants for Surgery
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METAL SCIENCE AND STANDARDS DIVISION

METAL SCIENCE AND STANDARDS DIVISION

R. Mehrabian, Chief
H. C. Burnett, Assistant to the Chief
D. E. Harrison, Secretary

The mission of the Division is to provide data, measurement methods, standards and reference materials, concepts and information on the fundamental aspects of processing, structure and physical properties of metals to industry, government agencies and scientific organizations. The program of the Division involves studies of the phase transformations of metals and alloys during metallurgical processing and of the resulting structure and properties in order to foster their safe, efficient, and economical utilization to meet our national needs within the larger framework of the materials cycle. Competences are developed and maintained in the general areas of process metallurgy, phase diagrams and phase stability, quantitative microstructural characterization including non-destructive evaluation, properties including friction, wear, and the application of metals as synthetic orthopedic implants. The Division also makes a significant contribution as a national resource of metallurgical information through its Diffusion Data Center and Alloy Data Center. It provides consultation and assistance to other government agencies and standards organizations in the development of necessary test methods and standards.

The competences available in the Division are applied to research problems in the areas of atomic, electronic, and magnetic structures; defects, interfaces, and microstructures; phase stability and phase transformations; and the modelling of metallurgical processes. The program is designed to help us meet our future national needs for materials, which will depend in large measure on our response to forces which are now well recognized. Some of these are classical laws of supply and demand; others include such national problems as energy, environment, productivity, and such international problems as materials availability from third world nations. For example, our Division, in addition to being involved in theoretical and experimental studies of phase stability, has a joint effort with the American Society for Metals to provide critically evaluated phase diagrams to the metallurgical community. Advancement in the understanding of phase diagrams and the development of predictive models for phase stability are essential in the development of new alloys for our future needs. These could include stronger and lighter alloys for the transportation industry to improve energy cost, new alloys specifically designed to exploit the beneficial effects of innovative new processes such as those referred to as rapid solidification processes, and alloys which would permit substitution of scarce or unavailable elemental constituents.

The detailed programmatic content of the Division that follows is described in the four task areas: metallurgical processing; metallurgical chemistry, structure, and property characterization; and wear and implant alloy durability. The technical activities under the various tasks are closely interrelated and address the overall mission of the Division to meet our present and future societal needs for metals. The central purpose of these scientific activities is to probe the relationships among processing conditions, the internal structure of metals and their properties and performance; so that the resulting knowledge can be used to efficiently produce, shape, and otherwise process metals so as to control their properties and achieve the desired reliable and durable performance in the finished product. Results of our scientific findings on the effect of metallurgical processing conditions on microstructure and properties are communicated to the metallurgical community through the organization and sponsorship of conferences and meetings on various subjects such as acoustic emission, synthetic implant retrieval, alloy phase formation, solidification, wear, and re-refined oils; technical publications; active participation of Division members in various national and international committees; lectures and personal contacts. Critical data compilations are being developed and delivered to users concerned with alloy properties, diffusion, and phase diagram information. Standard reference materials are being produced for electron microscope calibration, electron microprobe analysis, and electrical conductivity. Contributions are made to NBS programs in nondestructive evaluation, recycled oil and materials, and artificial implants. Active productive interactions with other groups at NBS are another feature of this program in areas such as surface analysis, wear, microstructural characterization, acoustic emission, and phase diagrams. Computer graphics methods incorporating phase diagram predictive techniques and thermodynamic data are being developed in collaboration with the Applied Mathematics Division of the National Engineering Laboratory.

The available competences in the Division have recently been strengthened and expanded by: the appointment of a process metallurgist as the new Division Chief in July, 1979, a successful budget initiative in the area of metallic wear which will be fully implemented in FY80, a new competence initiative within the National Bureau of Standards to develop research programs at the Synchrotron Light Source at Brookhaven National Laboratory with the main materials expertise to reside within the Metal Science and Standards Division, and the development of a transformation science budget initiative for FY81. The latter is used below as an example of envisioned expansion of an existing competence within the Division.

The transformation science budget initiative is aimed at improving our national productivity in the field of metals processing. It is composed of two interrelated programs; rapid solidification processing and fundamental studies on the rheological behavior of partially solidified alloys subjected to vigorous agitation, and the effect of process variables on the microstructure and properties of cast or forged components made from partially solid initial materials. Emphasis in this initiative would be placed on enhancing our limited fundamental understanding of the liquid-solid transformations involved. Mathematical and physical process models would be developed to establish the interrelationships between process variables such as composition, pressure, temperature, time, etc., and microstructures and properties. The proposed program would be based on and expand our existing world-reknowned competence in the field of solidification within the metallurgical processing task of the Division. In the past year the alloy solidification program has been expanded through a project sponsored by DARPA aimed at extending current solidification theory to high liquid-solid interface velocities encountered during rapid solidification of metal powders and filaments and to surface modifications of conventionally processed components subjected to directed high energy sources such as a laser or an electron beam. There is a common underlying competence for this initiative throughout the Division's four tasks. For example, on-line nondestructive methods would be needed for the control of these innovative processing techniques, the phase stability activity would address the design of specific new alloys to exploit the benefits of rapid solidification, while the significantly altered surface compositions and microstructures would require fundamental studies in friction and wear. National and international recognition of this competence within the Division is evident by the participation of its members as chairman of the AIME Solidification Committee, Chairman of AIME Alloy Phase Committee, Chairman of the Second International Conference on Rapid Solidification Processing, memberships in three NMAB committees on rapid solidification and powder metallurgy, board membership of international journals on diffusion and crystal growth, membership in the US-USSR subcommittee on Electro-Slag Remelting, and membership in several ASTM committees including the chairmanship of the ASTM Committee B-6 on Die-Cast Metals and Alloys, and the Chairmanship of the ASTM Committee E-42 on Surface Analysis.

METALLURGICAL PROCESSING FOR ALLOY DURABILITY

The properties of alloys depend on their compositions and microstructures, which in turn depend on their processing history. Thus, the durability and performance of alloy components depend strongly on the solidification processes, transformations, diffusion and other kinetic changes which the alloys undergo during preparation and use. The objective of the present task is to develop data and understanding concerning the transformations and kinetic processes in alloys which influence final alloy compositions and microstructures. With new types of advanced materials, such as metallic glasses, and with the rising importance of materials with controlled compositions, such as achieved in protective alloy diffusion coatings, the understanding of the mechanisms governing these processes is increasingly important.

During the past year, a new program on kinetic effects arising during rapid alloy solidification was initiated. Rapid solidification can be used to produce alloy powders which show unusual homogeneity and also can yield amorphous alloy structures, i.e., metallic glasses. In this task, basic aspects of metallic glass formation, the effect of solidification velocity on the stable and unstable phases formed, and conditions for maintaining interface stability in order to promote alloy homogeneity are being investigated. Applications of rapid solidification technology include formation of new types of alloys with special properties unattainable by conventional means, unique surface modification techniques and improvements in powder metallurgy products. A budget initiative in this area was successfully developed for FY 81. Task members are organizing an international conference on rapid solidification processing to be held in March 1980.

In other significant accomplishments, the onset of convection caused by simultaneous concentration and temperature gradients during directional solidification of alloys was analyzed and predicted. Since interface velocities and surface tension effects are important in many solidification and transformation processes, work to improve methods of measuring these has been undertaken. Techniques are being developed to provide Auger measurements of surface impurities and highly accurate surface tension measurements simultaneously on the same metal sample. Division members serve as chairman of the AIME Solidification Committee, on the boards of international journals on diffusion and crystal growth and on several ASTM and NMAB committees on alloy processing, including the chairmanship of ASTM Committee B-6 on Die-Cast Metals and Alloys.

Initial steps have been taken to automate our diffusion data files. Analyses are being made of diffusion data in brasses and bronzes to complete a review on mass transport in copper systems. The initial volume in this series, which was published last year in cooperation with the International Copper Research Association, has already sold out its first printing. Kinetic calculations were made of the effect of vacancy binding on the diffusion of non-equilibrium vacancies. Significant effects on alloy segregation and on swelling caused by void growth in irradiated nuclear-reactor alloys were found.

The technical activities described in this task are rapid solidification, alloy solidification, interface velocity measurements, surface tension measurements, diffusion in metals data and diffusion kinetics.

Technical Activity

Rapid Solidification

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

In the past twenty years many processes have been invented which subject liquid alloys to cooling rates ranging up to 10^{10} K/s. Exciting new materials as well as improved traditional material have been produced in the form of powders, ribbons, filaments, and surface layers. Examples of new materials are metallic glasses and new metastable phases. Improved traditional materials have been solidified with the absence of unwanted phases and reduced or completely eliminated microsegregation. A broad class of experimental results on rapidly solidified materials is extremely difficult to understand based on a simple application of existing theory. It is, therefore, important to extend current solidification theory to high velocities.

This project, begun in April 1979, has initially focused on three topics: a) microsegregation as influenced by the shape stability of the freezing interface, b) metastable reaction sequences in multicomponent systems, and c) glass formation by rapid cooling of eutectic alloys. Brief summaries of progress in these areas are reported below.

(a) Microsegregation and Stability at the Solidification Interface

During freezing of alloys instabilities can occur in which a smooth solidification front (separating solid from liquid) becomes wavy and eventually breaks down into a broad dendritic zone of coexisting solid and liquid. As a result of the breakdown, the various chemical components segregate between solid and liquid and when the alloys are finally solid the segregation pattern is frozen in. For conventional solidification the smooth solidification front can be maintained by solidifying slowly, maintaining a high temperature gradient. Under extremely rapid solidification another region of stability has been predicted which is independent of temperature gradient. Calculations of the stability-instability demarcation have been carried out for Al-Cu alloys. For large velocities, the absolute stability criterion of Mullins and Sekerka is a good approximation to c_∞^*, viz.

$$c_\infty^* \cong k^2 T_M \Gamma V/[(k-1)mD] = 1.9\ (10^{-3})V$$

for Al-Cu alloys, where T_M is the melting point and Γ is the ratio of the solid-liquid surface tension and latent heat of fusion per unit volume. In this equation D is the liquid diffusion coefficient, m is the liquidus slope, k is the distribution coefficient ($m<0$ if $k>1$), V is in cm/s and c_∞ is in w/o Cu.

(b) Metastable Reaction Sequences in Multicomponent Systems

In a one component system, the molar free energies of the phases can be used to rank the phases in a hierarchy of stability. Reactions that convert a phase to one with a higher free energy are forbidden. It has long been known that no such ranking of individual phases is possible for multicomponent systems and indeed there is experimental confirmation of theoretically predicted instances (because free energy is reduced) in which stable phases dissolve in metastable ones. The exploration of the kinds of hierarchies that follow from the requirement that the free energy of the entire system can not increase has led to the discovery of a rule that may be practical and lends itself to the graphing on phase diagrams of lines or hyper-surfaces where the order in the hierarchy of two stable or metastable states is altered. An exploration of the kinds of thermodynamic information needed and the various practical methods of obtaining these is being explored.

(c) Glass Formation by Rapid Cooling of Eutectic Systems

Eutectic systems are multicomponent systems in which liquid remains the equilibrium phase to low temperatures because no solid with the same composition is stable. Because of the stability of liquid at low temperatures these systems have been prime candidates for glass formers by rapid solidification. The theory and practice of how rapidly one needs to solidify has focused on the nucleation of the solid phase as the difficult step in crystallization. In some systems theory is clearly at odds with experiment.

We have focused instead on the growth problem. There are two aspects being explored: 1) the thermodynamic question for each system of the existence of a solid phase with the same composition as the liquid which at some temperature below the eutectic becomes stable relative to the liquid, 2) systems in which such a phase does not exist can only crystallize into mixtures of crystals of differing composition. The diffusional sorting of the components is a relatively well understood slow step which may govern the crystallization rate. These ideas have led to a series of predictions for such systems which are being explored experimentally.

For this purpose, experimental methods designed to solidify eutectic alloys at known velocities up to 10 cm/s and temperature gradients of 200 K/cm (cooling rate = 2000 K/cm) are being developed. This cooling rate should be sufficient to form metallic glass in a few model alloys (e.g., Pd-Si-Cu). Two methods are being pursued: 1) Rapid Directional Solidification using the quenching of thin (<1mm) alloy filled tubes in liquid Ga at controlled speeds, and 2) Electron Beam Surface Melting. Both of these methods should permit quantitative determination of solidification conditions which can be correlated to alloy microstructure (e.g., eutectic spacing or glass formation).

Alloy Solidification: Solutal Convection

S. R. Coriell, W. J. Boettinger, and F. S. Biancaniello

This research is directed toward an understanding of solutal convection caused by the simultaneous concentration and temperature gradients present during the directional solidification of alloys. Included in this study is investigation of the effects of convection on the microstructure and chemical homogeneity of directionally solidified alloys and of the conditions under which undesirable effects can be eliminated. The chemical uniformity and distribution of phases produced during the solidification of alloys controls essential properties and performance such as fracture and corrosion.

In the theoretical part of this research, the onset of coupled convective and constitutional interfacial instabilities during the directional solidification of a single phase binary alloy at constant velocity vertically upwards (positive z-direction) is treated by a linear stability analysis. We consider a system for which the temperature gradient alone would cause a negative density gradient and the solute gradient alone would cause a positive density gradient. The temperature and concentration fields are coupled through the hydrodynamic equations. Because the usual solidification boundary conditions are used at the solid-liquid interface, the hydrodynamic and interfacial stability phenomena are also coupled. Specific calculations were made for physical properties appropriate to the solidification of lead containing tin. Results indicate that the stability-instability criterion can differ substantially from the criterion of a net neutral density gradient. For a temperature gradient in the liquid of 200 K/cm and for velocities in the range 1-40 μm/s, a convective-like long wavelength instability occurs at a critical concentration that increases with velocity; whereas for $V>40$ μm/s, the concentration at which instability occurs decreases as velocity is increased and the values of concentration and wavelength at the onset of instability correspond to the predictions of previous morphological stability theory which neglected density changes and convection. Application of a vertical static magnetic field increases the critical concentration for convective instabilities but a field of a tesla is needed to cause an order of magnitude change.

The occurrence of solutal convection and its effects on the microstructure and macrosegregation of directionally solidified alloys, particularly off-eutectics, also has been investigated. During plane front solidification the concentration of less dense solute is increased in the liquid near the solid-liquid interface and there is the possibility of solutal convection. In this year's research, the effect of solute gradient induced convection on the macrosegregation of Pb-rich Pb-Sn off-eutectic alloys during vertical solidification is determined experimentally as a function of composition and growth rate. In many cases macrosegregation is sufficiently great to prevent the plane front solidification of the alloy. The transition from dendritic to composite structure is found to occur when the composition of the solid is close enough to the eutectic composition to satisfy a stability criterion based on G/V (temperature gradient/growth rate).

Interface Velocity Measurements

R. L. Parker

It is well known that a key variable in solidification processing is the position and rate of motion of the solid-liquid interface. Yet these quantities are difficult to measure in opaque systems such as solidifying metals. We have used an ultrasonic technique for in situ real-time measurement of the position and motion of the interface in the directional solidification of a low-melting metal (tin), and this technique should be applicable to many metals, alloys, and other opaque materials processed by the metals industry and the semiconductor industry.

The technique utilizes the fact that a solid-liquid interface, because of the differences in density and sound velocity of the two phases, should act like a flaw to an incident ultrasonic beam, reflecting a small but non-zero percentage of the incident energy. Thus the interface should be able to be detected by modern ultrasonic flaw detection equipment. The equipment uses a piezoelectric transducer which generates the pulse and which receives the echo from the flaw. The transducer must be well coupled to the liquid (or solid) metal using an appropriate couplant. A standard pulser-receiver apparatus gives an oscilloscope display of the out-going pulse and the return echo. With a knowledge of the velocity of sound in the medium, the distance to the interface is read directly off the screen, and as the interface moves, its velocity is obtained.

This technique has potential advantages for application to industrial solidification processes, since it provides in situ real-time nondestructive measurements. In particular, it could supply readings to an operator or control system without significantly disturbing the melt. In further work on this technique we will explore the types of solidification problems to which it can be applied, and the consequent knowledge and control of the solidification structures thus obtained. An example might be continuous casting of alloy ingots where the size and shape of the "mushy" zone during solidification affect the microstructure and properties of the final ingot.

Surface Tensions and Their Variations with Temperature and Impurities

S. C. Hardy and S. R. Coriell

The liquid-vapor surface tensions of many metals and semiconductors are not well known and the temperature and concentration variations of the surface tensions are even less certain. This is probably due in most cases to the presence of unknown and uncontrolled surface active impurities which may alter the surface tensions in complex ways. The objective of this project is to obtain reliable surface tension data by controlling and characterizing these impurities. This seems to be a feasible goal because of the present availability of materials of very high purity and the development of instruments and techniques such as Auger spectroscopy which can be used, at least in the case of low vapor pressure materials, to analyze directly the chemical constituents at the liquid-vapor interface.

In the past year we have measured the surface tension of gallium of nominally 99.9999% purity over a wide temperature range using a sessile drop technique in which the liquid drop rests in a shallow quartz cup in order to assure a circular cross section. The gallium drops were contained in an ion-pumped vacuum system operating at vacuum levels around 10^{-9} torr. Above 200 °C the surface tension decreases linearly with temperature with a slope of -0.068 mJ/m^2 °C. Below 200 °C there is significant curvature which is probably due to a surface active impurity which is not being desorbed. Moreover, this low temperature behavior depends on the previous high temperature treatment of the drop in a way which suggests the gallium is being contaminated by some component of the quartz cup. This matter is being investigated at present.

In addition, we have started measurements of the concentration of impurities on a liquid gallium surface using an Auger spectrometer. Initial results show oxygen and carbon persist in significant concentrations even with heating to 350 °C.

Diffusion in Metals Data

D. B. Butrymowicz, J. R. Manning, and M. E. Read

Information about diffusion in metals and alloys is important in many areas of science and technology. Industrial processes such as heat treatments, use of protective coatings, sintering, welding, and gas/metal interactions all depend on an understanding of, and quantitative data for, diffusion. The NBS Diffusion in Metals Data Center provides a central source where data from the technical literature involving diffusion and related kinetic reactions are collected, analyzed, and compared. Critical reviews are published and inquiries from the technical community for data on particular alloy systems are answered. More than 22,000 papers reporting diffusion data now are on file. These references are classified according to the alloys on which they contain data for ready retrival. In order to handle this information efficiently, initial steps have been taken to computerize the bibliographic and classification data in these files.

In the past year, the first printing of the 322-page volume Diffusion Rate Data and Mass Transport Phenomena in Copper Systems was sold out. The monograph was published by the International Copper Research Association (INCRA) as part of the current activity. This handbook contains critically-evaluated data for a considerable number of copper alloys. Funding for the publication was provided by the trade association. To provide for a comprehensive collection of handbook data on these technologically important alloys, new funding was granted by INCRA for a second volume.

Analyses are now being made of data not only for such large classes of alloys as the brasses and bronzes but also of those elements crucial to the smelting and refining processes of copper itself. Emphasis is also being given to evaluation of transport phenomena related to the durability of copper and copper base alloys. The attack and subsequent degradation of these cast and wrought alloys through oxidation, sulfidation, etc., is one special concern of the second treatise.

Metals are frequently exposed to environments which change their physical and chemical characteristics because of reactions between the metal surface and the environment. Thus, the science and technology of surface preparation to improve metal properties has gained much importance during the last decade. The bulk of these efforts have been directed toward the modification of the surface through coatings. It is with this in mind that the Data Center initiated an activity related to high-temperature protective coatings on metals. A collection of diffusion data in such systems was initiated this past year. Alloy systems containing the critical metal chromium are of direct interest to the present activity.

A joint project with the Alloy Data Center on the compilation and critical evaluation of data for candidate hydrogen storage materials resulted in the publication in Hydrogen Energy Systems, Volume 4 (1978) of "Numerical Physical Property Data for Metal Hydrides Utilized for Hydrogen Storage," by members of both data centers. The three primary materials, FeTi, $LaNi_5$, and Mg_2Ni, were covered for eighteen possible physical and chemical properties, including reaction rates, diffusion coefficients, and other kinetic properties. Other materials, $CuMg_2$, $LaCo_5$, and MgH_2, have also been evaluated, with data sheets for all being sent to Lawrence Livermore Laboratory, where an on-line data base for these materials is being established.

In another cooperative project, the Diffusion in Metals Data Center is compiling a bibliography on selected titanium binary and ternary alloys to assist the Alloy Data Center in determination of the best phase diagram for a Ti-Al-Nb-Ta-Mo (6-2-1-0.8) alloy. Thus far, several primary data-base searches have been done. They are being scanned, requisitioned, and classified.

Diffusion Kinetics

J. R. Manning

The effective driving force for diffusion in alloys can be greatly changed by defect binding and defect fluxes. Changes in driving forces for atom diffusion produced by binding of vacancies in vacancy pairs have been calculated. In addition, the effect of vacancy-impurity binding on the atom flux originating from non-equilibrium vacancy concentrations in irradiated alloys has been investigated. Significant segregation can be produced by these non-equilibrium vacancy fluxes. It is found that modifications of the diffusion driving forces by binding effects often are large enough to change the sign of the resulting alloy segregation. This result can be applied to control diffusion and segregation in nuclear reactor alloys.

Descriptions of the driving forces were obtained first in terms of effective atom jump frequencies and applied to situations where diffusion occurs in the presence of electric fields. These fields and accompanying alloy segregation effects are important in electric energy applications, materials processing and electronic technology. The approach using effective jump frequencies allows the complex atom motions in the presence of electric fields to be related directly to well-established diffusion correlation factor calculations. As a consequence, the correlation factor values, whose magnitudes have been measured and calculated in several important limiting cases, can be used to calculate effective vacancy binding effects on atom drift velocities in electric fields.

A similar method was used to calculate the effect of binding on the redistribution of material in irradiated alloys. This redistribution comes from diffusion of the vacancy and interstitial defects toward surfaces and internal voids. The swelling of reactor alloys caused by void growth limits reactor alloy durability. The growth of voids in turn is strongly influenced by alloy segregation at void surfaces and trapping of defects by impurities. Driving force differences leading to the observed segregation were calculated from effective jump frequency equations. In addition, binding conditions which would cause a reversal in the sign of the alloy segregation gradient were determined from these equations. These results for alloy segregation produced by non-equilibrium vacancy concentrations can be related to the segregation effects which occur when there are other driving forces, such as those produced by an electric field.

ALLOY PROPERTIES SCIENCE FOR STRUCTURE CHARACTERIZATION

The objectives of this task are to develop methods and standards for the quantitative microstructural characterization of alloys to optimize performance and to provide measurement methods, standards, and data relating microscopic and submicroscopic structure to critical engineering properties of alloys. Because of the increasing industrial emphasis on quality control and automated processing, the technical emphasis of this task is centered on the application of metal science techniques to microstructural characterization methods. Thus there are subtasks using x-ray, eddy current, magnetic particle, positron annihilation, acoustic emission, and ultrasonic methods.

During the past year, task expertise in x-rays has helped make available NBS access to the new synchrontron being built at Brookhaven National Laboratories. CMS expertise in this field resides in this task and a prototype instrument has already been built for carrying out real-time x-radiography at Brookhaven.

An automated x-ray system for nondestructive evaluation of surface residual stresses has also been designed this year. This equipment will be employed to improve measurement methods for surface residual stresses.

In the area of electromagnetic NDE, a new theoretical model needed by ASTM E07.03 for magnetic particle testing was developed to describe magnetic leakage fields and their relation to the formation of particle indications on the much used ASTM magnetic particle test ring. This model points the way to providing a quantitative standard practice for transferring observations on the ASTM test ring to results on actual parts.

In the areas of acoustic emission and ultrasonic characterization, a new computerized facility has been configured and is being put together to permit high speed ultrasonic and acoustic emission data acquisition and processing. With the capability of communication with remote computing facilities for the purpose of transferring data or utilizing software. This will permit acoustic emission and ultrasonic studies of such important metallurgical phenomena as ductile versus brittle mechanisms for microcracking, martensitic phase transformations, texturing, and secondary phase characterization. Our theoretical efforts in modelling acoustic emission in a plate and in developing an experimental multichannel system for analyzing the tensor character of the acoustic emission source will bring two guest workers from the United Kingdom Atomic Energy Research Establishment, Harwell, to work with us in the next year. Experimental work is beginning on acoustic emission from indentation induced cracks in embrittled plates.

A new program supported by NASA in ultrasonic characterization of soft spots in aluminum is also beginning. Initial work in this problem, which has already caused some national concern, will involve the participation of Prof. R. Green of Johns Hopkins University. Longer range activities in this area will center on providing better characterization methods of critical microstructural parameters and their relationship to aluminum processing so that more meaningful specifications can be provided by the government and other purchasers of aluminum alloys.

Technical activities described in this task are:

Application of Synchrotron Radiation to Materials Science
Real-Time Radiographic System Performance Standards
X-ray Residual Stress Evaluation in the Interior of Materials
X-ray Diffraction Studies
Electromagnetic and Submicroscopic NDE
Acoustic Emission
Ultrasonic Materials Characterization
Scanning Electron Microscopy

Application of Synchrotron Radiation to Materials Science

M. Kuriyama, W. J. Boettinger, and H. E. Burdette

NBS and other scientific laboratories now have been invited to develop research programs at the National Synchrotron Light Source, when it goes into operation at the Brookhaven National Laboratory in 1981. Hard radiation down to as short as 0.5Å will be produced from accelerated orbiting electrons in a storage ring operated at 2.5 Gev. Synchrotron radiation produces a spectrum of photons that is highly collimated, very intense, continuous in energy, and linearly polarized. These unique properties offer tremendous opportunities for advancing materials science with the following three major advantages over laboratory x-ray sources: (1) the approximately ten-fold increase in photon flux permits, for the first time, real-time in situ studies on materials transformations, (2) the tuneability of available radiation for a desired energy permits determination of the phases of crystallographic reflections, thereby resolving important structural ambiguities. It also permits, via the elemental tuneability, the study of materials whose structure deviates greatly from the periodicity locally, and (3) inelastic scattering could be employed for the first time as a practical tool to study materials properties and phase transitions via electronic properties of individual atoms and molecules in condensed matter. Among many problems aiming at the ultimate goal in materials science, which would be the formulation and verification of discrete atomistic theory for rates of phase transformation and structure stability, we have placed an emphasis at the initial phase on the development of dynamic in situ measurement capability to obtain an advanced knowledge in kinetics of microstructural transformations. To achieve this, we have started developing real-time topography with x-ray image magnification[1]. The prototype instrument has been completed in our laboratory, awaiting a test at the synchrotron radiation facility at the Cornell University. In addition, we have performed an experiment concerning the polarization rotation effect in materials using synchrotron radiation at the Stanford University[2].

[1] W. J. Boettinger, H. E. Burdette, and M. Kuriyama, Rev. Sci. Instr. 50, 26-30 (1979).

[2] G. G. Cohen and M. Kuriyama, Phys. Rev. Letters, 40 957-960 (1978); to be published in Phys. Rev. B, (1980).

Real-Time Radiographic System Performance Standards

M. Kuriyama, W. J. Boettinger, and H. E. Burdette

This is one of the Division's activities relating to the NBS NDE program. This year's objective of this specific activity is to remedy the confused situation in industry caused by the lack of performance standards for real-time radiographic systems. Before proposing the industrial resolution standards for radiographic diagnosis, the current needs in industry demands the reevaluation of "radiography."

Currently the characteristics of a real-time radiographic system are described by individual laboratories for their own convenience. The resolution claimed to be attained by one laboratory using a single isolated small object does not necessarily provide the desired resolution for other laboratories which, for example, deal with a collection of such small objects distributed in materials. In addition to resolution, there are two other important factors for characterizing radiographic systems: speed of obtaining diagnostic results and contrast (or detectability) of objects. There has not been a unified theoretical basis for standards which can cover these three factors. The need of such standards requires a possible unified method to describe the fundamental characteristics of any real-time radiographic system. The feasibility of this method is demonstrated using an actual x-ray source for a radiographic system.

The resolution of real-time radiographic systems is often considered to be dominated by the resolution of viewing detectors. This is true, if only one can prepare either a mathematical point source or a truly parallel beam. In real-time radiography, detectors, unlike films, cannot be placed in direct contact with or very close to object materials. Thus the divergence of the beam, or exactly speaking, the apparent source size cannot be ignored. The resolution of any radiographic (or x-ray optical) system is intimately related not only to optical slit and detector systems but also to the characteristics of x-ray sources. It is, therefore, best to evaluate the quality of radiographic systems including the radiation source as they are in use. The method proposed is based on the following theoretical consideration. The source emits radiation non-uniformly; the radiation from a point of the source has a different angular distribution (divergence) from radiation emitted from different points. This non-uniform property, including different degrees of divergence, is represented by $I_S(x)$, where x indicates a point in the source. The objective in evaluating the quality of optical systems is to determine such an expanded quantity $I_S(x)$ for the overall system as accurately as possible. For real radiographic systems, this quantity $I_S(x)$ obviously includes the effects due to the slit systems before and viewing detectors (image intensifiers, films, or counters) after the object.

Among many possible ways, we choose the two simplest modes of the evaluation of $I_S(x)$. We use as an object a plate which consists of two regions of different thicknesses. In mode I, this Heaviside object is set at a stationary position and the intensity profile is obtained as a function of position. In mode II, the object is moving at a constant speed, while the intensity is recorded at a fixed position in space as a function of time.

We have obtained an actual intensity distribution observed from our radiographic system. Using a mini-computer on site, we can differentiate the observed intensity to obtain $I_S(x)$ and further to obtain the Fourier transform of $I_S(x)$, which is the modulation transfer function (or more exactly the optical transfer function.) Also, one can obtain the minimum detectable image from this measurement. The details of the application of this method including reproducibility, reliability, and easiness have been documented in the past year. This technique also provides simultaneous information on the detectability of objects and the measure of speed required for diagnosis.

X-ray Residual Stress Evaluation in the Interior of Materials

M. Kuriyama, W. J. Boettinger, and H. E. Burdette

This is another of the Division's activities relating to the NBS NDE program. This year's objective of this specific activity is to respond to an industrial demand for the evaluation of residual stresses in the interior of industrial components, which often cause mechanical failure in industrial products.

One of the nondestructive methods currently used for measurements of residual stresses in industrial materials involves the application of x-ray analysis for stress measurement. X-ray diffraction phenomena are used to determine macroscopic residual stresses in engineering components. The methodology of analysis and its basic principles are well known. Briefly, when materials are under stress, x-rays are diffracted with a Bragg angle which is slightly different from the Bragg angle expected in unstressed materials. The change in the Bragg angle is related to the alteration of atomic interplanar spacings when the crystal lattice of the materials is strained. As a measurement system, the essential part of this x-ray technique is the accurate measurement of lattice constants (or their changes) in materials by use of well-refined Bragg diffractometry. The surface residual stress can be evaluated from the strains measured by x-ray diffractometry using a set of assumptions regarding material elasticity and homogeneity. Although the accuracy obtained by this technique is, in principle, superior to any other methods, an obvious shortcoming lies in its incapability of detecting strains (or stresses) in the interior of bulk materials.

Currently, improved quality control of industrial components demands quantitative information concerning the stress distribution near cracks and residual stress distributions after different types of cold working and heat treating. These demands naturally lead to the necessity of measuring residual strains in the interior of materials. Ordinary Bragg diffractometry will not be sufficient to respond to these demands. There is an entirely different approach to the x-ray evaluation of residual strains although it uses the principles of x-ray diffraction. This approach involves the use of energy dispersive solid state detectors with high energy x-ray photons. The use of solid state detectors has been introduced very effectively in the fields of scanning electron microscopy (microanalysis) and x-ray fluorescence analysis of materials in the past ten years. It is called energy-dispersive spectroscopy. Unlike these successful applications, this technique has not been applied to the residual stress (strain) measurements of materials. Extremely high resolution and accuracy are required for strain measurements in comparison with the other applications. If one can improve the resolution sufficiently and overcome other important technical problems, this new system would be ideal for residual stress measurement in industry; the equipment will be displayed visually and almost instantaneously, and analysis of the data will be made on site by a computer. Also this system, in general, works better for high energy photons. High energy photons also make practical the use of the transmission geometry, since the x-ray absorption coefficient of materials is approximately inversely proportional to the third power of the energy of x-ray.

The use of an energy dispersive system for possible residual stress evaluation was tested in 1973 by Leonard[1], who concluded, however, that this system did not have sufficient accuracy for this purpose. We have proven that his conclusion was premature and it is still too soon to dismiss the possible industrial use of this technique for the evaluation of residual stresses. In doing so, we have proposed[2],[3] a method for determining a strain tensor in predetermined volumes in the interior of a material. One may claim then that the energy resolution of current solid state detectors is not small enough to reduce the resolution for the evaluation of residual strains. It has been known fortunately, that each diffraction profile in the energy spectrum obtained from the solid state detector is very close to a Gaussian. If the mathematical shape is known for a spectral profile, then the claim mentioned above can be circumvented: mathematically filling the observed peaks with Gaussian functions, one can determine the centroids (or peaks) of the profiles far more accurately than the $\Delta E/E$ value stated above would indicate. Indeed, we have proven that one can improve by a factor of 100 in the accuracy of determining the centroid positions. Our result demonstrates that strains of 5×10^{5} can be detected with reliable reproducibility, if_sufficient counting statistics are established, and strains of 3×10^{-4} can be detected even with moderate counting statistics.

In conclusion, an energy dispersive diffraction system has demonstrated its capability as a useful tool for the determination of residual stresses inside materials, when the curve fitting technique is used simultaneously. The present demonstration has been carried out with low energy photons. The use of high energy photons certainly makes more practical the use of these energy dispersive systems for residual stress evaluation. More penetration and increased energy resolution of detectors will improve the resultant accuracy and detectability of strains. Since the energy dispersive system can be made simple and compact, without any delicate moving parts, the system is quite ideal for an industrial use on site, particularly when data are handled by a mini-computer. By no means, has an energy dispersive system such as used here reached the ultimate resolution; further improvements on x-ray optics and detectors should be made, in particular, with high energy photons.

[1] L. Leonard, Franklin Institute Research Lab (Philadelphia) Report F-C3454 July (1973).

[2] M. Kuriyama, W. J. Boettinger, and H. E. Burdette, ASNT National Fall Conference, October, Denver, Colorado, p. 49 (1978).

[3] M. Kuriyama, W. J. Boettinger, and H. E. Burdette, Symposium on Accuracy in Powder Diffraction, National Bureau of Standards, June (1979).

X-ray Diffraction Studies

C. J. Bechtoldt

The use of conventional surface x-ray techniques is an indispensible part of any microstructural characterization effort on metal alloys. Two main research projects are currently being undertaken in this area along with a considerable amount of support service. The processing of titanium-aluminum alloys for durability is hampered by inadequate knowledge of the Ti-Al phase diagram. Many conflicting reports are in the literature as discussed in the Metallurgical Chemistry of Durability Task. Part of the problem is the incomplete characterization of carefully prepared Ti-Al alloys.

Initially, we will carry out phase identification in these alloys by quenching-in the structure and examining the specimen by x-ray diffraction. Measures will also be taken to identify the phases at temperature by high-temperature x-ray diffraction which has not been done before. The room temperature study has the advantage of permitting higher magnification and resolution and sharper lines in the diffraction patterns, but quenching to room temperature carries the risk that the high-temperature phases will not be retained. It has been pointed out in the literature that to settle the controversy between investigators, the observations must be made at high-temperature to avoid any possibility of the phase transformation upon quenching to room temperature.

The second research project concerns development of improved techniques for more accurate measurement of surface residual stresses. An automated x-ray data acquisition system has now been configured and is now out for bid, and some of the newer, more promising techniques will be critically evaluated and compared with the SAE standard method.

Studies have also been made by x-ray diffraction on the texture and precipitations in beryllium used in gyroscopes in cooperation with the Fracture and Deformation Division. No appreciable texture was noted but up to five different precipitates were identified in this grade of beryllium using non-conventional Debye-Scherrer methods.

Studies continued in the principal area of characterization of metals and alloys as used in several other projects in this Division and other activities at the Bureau. This included such problems as the study and identification of phases of compounds resulting from corrosion; the precision measurement of lattice constants; qualitative and quantitative determination of minor and major phases in metal alloys used in research problems; determination of degree in ordering in alloys, determination of grain size, residual stress, nature of twinning, and the orientation of single crystals or large grains in metals or alloys; x-ray diffraction, ordering, and lattice constant studies on Ti-Al alloys as part of this Division's activities in that area.

Most alloys prepared in the Specimen Preparation Laboratory, purchased on the outside or donated are submitted for characterization by x-ray diffraction studies and measurement of the lattice constants where appropriate. These studies include metal carbides and metal phosphites as pure substances or mixtures or with added impurities. These studies include identification of phase present, lattice constants, and grain size. Lattice constants and degree of ordering were studied in Ni_3Al alloys where part of the aluminum was substituted with another metal. X-ray diffraction studies were made on dental amalgams, Cu-Sn phases, and in the $Pd_3(Si-Cu)$ system. Over 80 diffraction patterns were made on paper products or fillers used in paper products.

Electromagnetic and Submicroscopic NDE

L. J. Swartzendruber, R. C. Reno, J. R. Cuthill, and L. H. Bennett

Magnetic particle NDE is a relatively simple and inexpensive, yet effective and rapid method. It has extensive use for both production and field testing of ferromagnetic components. Despite its apparent simplicity, a large number of variables influence the inspection process and need careful control in order to obtain repeatable and reliable results. Obtaining a sound scientific basis for properly controlling these variables is the purpose of this project. For testing particle sensitivity the use of standard test parts has been recommended, and a number of these are currently being included in general specifications for magnetic particle inspection processes. However, the extent to which such test parts evaluate the properties of the particles being used rather than a combination of operator skill, proper magnetization levels, proper particle densities, and other contributing factors, is poorly understood. An evaluation of the importance of the various contributing factors requires the development of a mathematical model to describe the formation of magnetic particle indications. An important step in this development, obtaining a suitable description of the magnetic leakage fields from sample defects and how they influence particle motion, is currently under investigation.

One test part currently under extensive use is in the form of a ring with cylindrical defects. Because of the non-linearity of a ferromagnetic material, an exact description of the leakage fields from the defects in this ring poses formidable mathematical difficulties. However, we have shown experimentally that, to a good approximation, a simple linear dipole model can be used to describe the leakage fields provided that a proper equivalent depth which is less than the true depth, and a proper value for the effective dipole moment per unit length are used.

Using the leakage field description model as described above, a simple model taking into account only leakage field and gravitational forces was investigated. This model showed clearly, in quantitative terms, the importance of particle shape and surface mobility in forming magnetic particle indications. Using the observed leakage field strengths and the known number of defects that form indications on the test ring at various current levels, a detection criterion could be stated in terms of the force experienced by an isolated spherical particle. An extension of this criterion to other situations would be very useful and might allow the calculation of required magnetization levels and detectable defect size, parameters which must not be determined empirically.

The utility of Doppler-broadened position annihilation line shape measurements as an NDE tool is being investigated. Lineshape measurements have been used to study defect behavior in titanium samples which were first cold-worked and then annealed at temperatures ranging up to 850 °C. The lineshape as a function of annealing temperature was used to show that a simple lineshape parameter can be used to reflect changes in the defect structure, including changes that occur well below the recrystallization temperature that are not detected by hardness measurements. Thus measurements of this parameter might be useful in monitoring processes that occur in titanium both prior to and during recovery and recrystallization.

The production of standard metal blocks for the calibration of eddy current test equipment is being investigated. This work is being carried out in cooperation with the Electrical Measurements and Standards Division. Four aluminum alloys have been selected for use in these standards. The Metal Science and Standards Division will supervise the fabrication of the standards. Each standard will be individually calibrated by the Electrical Measurements and Standards Division. Personnel from this task are also serving on the Organization Committee for the joint NBS/ASTM/ASNT/IEEE Eddy Current Symposium to be held September 1979.

Acoustic Emission

J. A. Simmons and R. B. Clough

Acoustic emission (AE) is a relatively new nondestructive testing technique relying on the detection of stress waves emitted during the motion of flaws or from other microstructural changes in a highly stressed region of a structure. This technique has been applied to aerospace, petrochemical, bridge, and power plant structures to monitor structural integrity. It has also been used to detect faulty welds in production lines. In addition, AE has been used for materials research studies on microstructure related properties such as deformation mechanisms, phase transformations, and fracture.

This activity is part of the joint EPRI/NBS program on acoustic emission whose overall objective is to provide the electric power industry with the technical basis for deciding whether or not to incur the costs of flaw monitoring systems based on quantitative analysis of detailed AE signals. Aside from providing theoretical guidance and metallurgical assistance to all tasks of the NBS/EPRI program, the Metal Science and Standards Division contribution to this program may be divided into four parts: (1) to develop the theoretical basis for describing acoustic emission from moving defects; (2) to develop experimental procedures and test methods for obtaining reproducible quantitative acoustic emission signals in structural metals, e.g., pressure vessel steels; (3) to develop data processing techniques to permit analysis of acoustic emission signals from structural flaws; and (4) to assist the technical community in the development of calibration and interpretation standards and procedures in acoustic emission.

Work in the theory of acoustic emission has itself been divided into four parts:

i) Deriving the transfer function formalism
ii) Dealing with the plate geometry
iii) Signal processing and deconvolution
iv) Modelling AE from defect sources.

signal received at a given transducer in terms of a transfer function containing the material geometry and transducer characteristics and a

i) The transfer function formalism which may be summarized by the equation

$$V(\omega) = T_{K\omega}(\omega)\underline{\dot{\sigma}}^{A}_{K\omega}(\omega)$$

allows one to express the voltage frequency response from a given AE signal received at a given transducer in terms of a transfer function containing the material geometry and transducer characteristics and a mean stress drop tensor, $\underline{\dot{\sigma}}^{A}$, associated to the emission event. The transfer function representation is not generally valid, but requires both restrictions and assumptions. However, it appears likely that this formalism may well be valid in many technological important applications.

If one wishes to invert the AE information to find the source stress drop tensor, the transfer function formalism leads to certain important implications. 1) Unlike scalar transfer function problems where inversion information can be obtained directly from power spectra, to find $\underline{\dot{\sigma}}^{A}$ from $V(\omega)$, multiple transducers yielding complex spectra with phase information are generally necessary. Generally, six separate observations are needed to separate the six stress components. 2) Bandpass filtering to eliminate the defect size effect may also be required, which, together with other filtering to eliminate noise, can at best yield band limited information about the source.

ii) In order to be able to experimentally verify new measurement concepts for quantitative acoustic emission, one must have a detailed understanding of elastic wave propagation in a structure on which acoustic emission experiments can be performed. The two geometries for which this is realistically possible are the plate and the tube. The plate geometry was selected and a solution for elastic wave propagation in an isotropic plate has been developed in collaboration with Prof. John Willis of Bath University, England. This solution, based on a new Fourier transform technique, allows one to compute the transient response in an elastic plate due to various stress sources located up to about ten plate thicknesses from the detector. Study of the dipole source characteristics indicate the possibility that in addition to obtaining detailed information about an acoustic emission source whose exact position is known, the depth of some types of technologically important sources may also be determinable. Other theoretical consequences of the plate solution are being studied including calculating the effects of high frequency attenuation due to averaging over transducer faces.

iii) In order to invert the signals received from the transducer to obtain information about the AE source, it is necessary to carry out a numerical deconvolution procedure. A formally similar deconvolution procedure is required to produce a transducer calibration. Because of the high priority associated to this latter need, work was temporarily suspended on the plate solution results to look at deconvolution algorithms. Most of the ordinary algorithms in use today were found to be non-robust, frequently yielding incorrect or ridiculous answers to deconvolution with the type of signal needed for transducer calibration. The problem occurs because of numerical noise amplification produced by deconvolution algorithms. Three new algorithms were developed. One, based on an FFT type algorithm, was supplied to the Mechanical Processes Division where AE transducer calibration is being carried out. The other two require more extensive computer facilities. One of these methods is being explored for signature analysis potential. The third, developed in cooperation with Dr. Diane O'Leary at the University of Maryland, is still being studied. Since there are a great number of fields where deconvolution is used, the importance of these new algorithms extends well beyond acoustic emission.

iv) The theory for acoustic emission from expanding planar dislocation loops has been developed. In an infinite body, only three qualitatively different types of response function are obtained, two for prismatic collapse type of dislocation loop generation (looking at the dislocation from different directions and monitoring different displacements) and one for slip type loops. Typical values for dislocation loops in metals show that a rapidly nucleating loop of 3 μm diameter, for instance, produces displacements of the order of 10^{-13} cm at a distance of 10 cm. Thus it is clear that acoustic emission events for single dislocations are undetectable and that sources approximately 10^{13}-10^{4} times as strong are required.

In order to improve our capabilities in experimental metallic microstructural characterization by acoustic emission methods, Roger Clough, formerly of the Mechanical Processes Division, where most of the transducer calibration work is being carried out, has transferred into this task while Nelson Hsu, in turn, has transferred to the Mechanical Processes Division. The data acquisition system that Dr. Hsu was using has also gone over to the Mechanical Processes Division, and a new completely reconfigured minicomputer based high speed data acquisition and processing facility more appropriate for tests involving complex microstructural emission phenomena is being installed. The laboratory facilities have also been remodeled, and a new facility for ultrasonic characterization of materials has been added.

The need to study real defects as opposed to simpler calibration type sources introduces a number of requirements due to the generally lower signal level of real defects and the tensor nature of the defect signal. The high speed data acquisition system and its associated minicomputer system are now being procured. Low noise preamplifiers are being built to directly mount on the back of well characterized capacitative transducers each of which will be recorded by a separate high speed analog to digital converter (only one A to D converter is currently available). The current A to D converters have only 8 bit resolution with concomitant lack of dynamic range, and we are currently studying means for increasing the dynamic range if needed. The outputs from the analog to digital converters are dumped at very high speed into a remote high speed peripheral making it possible to record multiple emissions in a single test in a laboratory environment separated from the computing facility.

We have chosen to study experimental acoustic emission signals in steel plate specimens, and we are currently studying indentation loading methods under a variety of conditions to select the most promising experimental configurations. Our goal is to study microcracking under controlled conditions where the cracking mechanism will vary from ductile to brittle. While not yet fully evaluated, brittle type cracks have been produced at the surface in the heat-affected zones of welds (both continuous and spot) and in high carbon steel which was given an embrittling heat treatment.

ASTM interaction continues strongly with the vice-chairman of ASTM E7.04 coming from this program. Interaction is also quite active with the Theoretical Physics Division and the Nondestructive Testing Center at the A.E.R.E., Harwell. We expect two visitors next year from Harwell, Dr. H. Wadley, to do experimental work using our new multichannel instrumentation for determining the tensor character of AE sources, and Dr. J. Sinclair, to study our solution for waves in an elastic plate and to convert our computer programs to be usable on the Harwell computer.

Ultrasonic Materials Characterization

J. A. Simmons, D. E. MacDonald, and R. B. Clough

This is a new activity using ultrasonic techniques for nondestructively measuring microstructural material parameters. Ultrasonics as commonly used in pulse echo or imaging systems detects macroscopic discontinuities such as flaws or interfaces in material structures. However, the measurement of ultrasonic attenuation and velocity changes or the study of the absorption and transmission spectra of scattered ultrasonic waves provides a wealth of detail on the mean microstructural properties of metallic materials. These techniques have great potential for measuring texture, porosite, and multiphase distributions, as well as for studying the kinetics of phase transformations both by observing and inducing such transformations.

Work in cooperation with Prof. R. Green of Johns Hopkins University is beginning on ultrasonic characterization for soft spots in aluminum alloys. Due to what appears to be an improper quench procedure, incorrect second phase precipitate distributions have been produced at unknown spots in the fabrication of a variety of high strength aluminum alloy plates used in aerospace applications. In some cases, these spots have their ultimate tensile strength reduced by 70 percent. The first priority question here is to develop a reliable NDE method for detection of these soft spots. Velocity, attenuation, and ultrasonic scattering techniques will be employed and their reliability assessed. Longer term studies are contemplated of the kinetics of the aging process itself leading to better specifications for such alloys in the future.

Work has also been carried out on the application of ultrasonics to residual stress measurements. When the elastic constants of material are changed such as occurs when the material is heated or stressed, the changes in these constants can be induced by precise velocity measurements from which information on the material state can be inferred. This technique has great promise for the measurement of residual stresses and has been used in a number of applications. However, few formulations have taken into account the simultaneous dependence of the velocity on stress and strain such as occurs in thermally stressed materials. This separate dependence on stress and strain has been demonstrated with the aid of a mathematical model used to find the effect of finite strain on the wave velocities. For shear waves with either the propagation direction or the displacement direction parallel to the maximum principal stress, the change in the wave velocity results from nearly equal but opposite contributions from the stress and from the strain dependent moduli.

These findings, for instance, have application to determining the longitudinal force in continuously welded rail. The constrained configuration of the rail results in the development of buckling forces during temperature increases. The absence of any longitudinal strain greatly modifies the balance between the stress and strain contributions to the velocity. This enhanced stress dependence of the velocity may provide a way to nondestructively determine the longitudinal force in continuously welded rail.

The direct stress dependence of the ultrasonic velocity reflects the fact that wave propagation in stressed material is fundamentally different from the stress-free case with the related symmetry. A comparison of wave speeds for materials with isotropic, transversely isotropic, cubic, and tetragonal symmetry and these same materials under tri-axial stress has been made which indicates how to separate the effects of stress and texture. This information can be applied to the problem of determining the residual stresses in unidirectional metal matrix composites.

Scanning Electron Microscopy

D. B. Ballard

The IR-100 award winning SRM 484 magnification standard for scanning electron microscopy has been one of the most successful in the SRM program. A reissue of 250 samples was made available in March of this year at which time there were already 85 units backordered. As of late August, 124 samples have been sold, including several overseas.

The problem of edge seepage and new encapsulating techniques has been tentatively solved. Removal of seepage and contamination can be removed by sputter plasms etching in an argon atmosphere or by stripping a dried cellulose acetate replica. A new procedure for incapsulating the Au-Ni composite consists of mixing tin powders of 1-5 μm and 500 μm size into epoxy resin and centrifuging the casting at 24,000 G for two hours. The required electrical conductivity and surface bonding seems to be satisfactory.

Copies of Draft #3 "Recommended Procedure for Calibration of the Magnification of a SEM Using NBS-SRM-484" have been approved by E-4 ASTM for review by Subcommittee XI (Electron Microscopy).

The SEM laboratory and associated equipment has continued to provide support to NBS personnel who have used the facility for over 850 hours. Several requests for training of new operators have been fulfilled and consulting services have continued. A cooperative student position in this laboratory has been provided that allows back-up operation of the facility when the manager is absent. The SEM facility has been used by the senior researcher to support other research activities at NBS. Some examples of activities this year are as follows.

Thin electrodeposited gold plating is used in industry as decorative coatings, in electronics as a conductive film, and in space for ultraviolet reflective protection. Accurate measurement of thickness less then 1 μm are essential for optimum efficiency and economical use. Using the availability of the SRM-484 (SEM Magnification Standard) and properly prepared cross sections of specimen accurate measurements of thin gold plating coatings were made to 10 percent or better. A paper "Thickness of Gold Coating Measured with a Calibrated SEM" describing the techniques used and results has been written for publication.

A section of the fracture surface that included weld metal from the replacement bridge for the Silver Bridge across the Ohio River was submitted by the Fracture and Deformation Division to ascertain the mode and mechanism of fracture. Fractographs and x-ray spectrograph results were included in the reported analysis. A paper on this investigation is planned.

Urea-formaldehyde foam is used as a thermal insulation in existing housing structures. Under certain conditions of temperature and humidity this material loses its desirable properties. An SEM examination of as-formed and of field and laboratory degraded samples submitted by Structures and Materials Division revealed changes of cell structure. The SEM results will be the basis for an intended report and later publication.

The results obtained from the SEM examination of six different solar panels on details of surface texture, thickness, corrosion products, and degradation mechanisms was incorporated in a paper to be submitted for publication. This information is of particular interest to the paint and solar energy community.

A combined effort within the Metal Science and Standards Division is to redetermine accurately the Titanium-Aluminum Alloy Phase Diagram. The SEM has been used to study the observed phases, results of hardness impressions, x-ray spectro analysis, and fractography of preliminary alloys.

Micrographic studies and minor phase analysis are also planned as part of the Division's effort in the soft spots in aluminum problem.

ALLOY DURABILITY FOR WEAR AND IMPLANT APPLICATIONS

The provision of data and understanding concerning the durability of materials in service is one of the principal technical thrusts in the Center for Materials Science. This task is concerned with the wear durability of alloys and with the application of metals as synthetic implants, principally orthopedic implants.

The wear activities have involved research into the mechanisms of metal wear under dry sliding, abrasive, and solid particle erosive wear. Efforts have continued to develop and improve test methods that address the anti-wear characteristics of oil lubricants with emphasis on re-refined motor oils. A major NBS conference is this area has been organized for Fall 1979. Highlights of the ASTM standardization work in the past year include the development of abrasive wear and erosive wear test methods. The post of vice-chairman of ASTM-G2 on Erosion and Wear will involve many wear standards activities as well as long-range planning for this Committee. NDE activities in the wear condition monitoring of systems have continued with some significant developments in standardization areas. A budget initiative in wear will be implemented in FY80 to develop research into areas of fatigue wear, fracture effects, and environmental aspects of wear. Several staff additions will result from this initiative. We have also agreed to serve as Program chairman for the Third International Wear Conference in 1981.

The projects concerning alloys used in synthetic implants have continued to concentrate on corrosion and the fatigue behavior of several relevant alloys. Two new areas of investigation have started on fretting wear of implant alloys and on the chemistry of metal-organic reaction. Fretting is a potential source of metallic particles in the body; the characteristics of such particles and the potential hazards must be determined. Experiments studying the chemistry of metal reactions in organic solutions that simulate body fluids have begun involving a new staff member. Standardization work in ASTM-F4 has involved a new method for wear testing of implant materials and planning for a major NBS Symposium on Retrieval and Analysis of Implants to be held in 1980. The technical activities in this task (described below) are the mechanisms of metallic wear, wear standardization, wear NDE activities, lubricated wear, and metals used as biological implants.

Technical Activity

Mechanisms of Metallic Wear

A. W. Ruff, L. K. Ives, S. Bushby, and P. Boyer

It is often said that there is little understanding of the influence of materials properties on wear behavior. Indeed, the past development of alloys to resist wear has proceeded mainly on an empirical basis. Thus when improved materials are required or new conditions are encountered, there is little in the way of fundamental knowledge to guide or assist in the development and design process.

The purpose of this project is to improve the understanding of basic wear mechanisms. Particular attention has been focused on the relationship between the microstructure of metals and the wear process. The approach has been to expose carefully prepared specimens to a variety of wear conditions using simple laboratory devices. The specimens and the wear debris are then characterized, principally by means of scanning and transmission electron microscopy. In this way, surface topography, subsurface microstructural changes, and wear debris characteristics can be related to exposure condition. The morphology of wear debris fragments is often found to be a valuable indicator of the wear process. In previous work, copper (99.99 wt.%) was exposed to solid particle erosive wear and the significant processes were determined. During the past year, a study of copper exposed to three body abrasive wear, dry sliding wear, and lubricated sliding wear was carried out. The results of this investigation were reported in a paper delivered at the International Conference on Wear of Materials held in Dearborn, Michigan. Additional findings were presented at the annual meeting of the Electron Microscopy Society of America in San Antonio, Texas. Certain features were found to be characteristic of the different types of wear. For example, the high strain rates associated with particle impact in erosive wear lead to deformation twinning. Twinning was not observed in connection with other types of wear in which the strain rates were much less. Common to many types of wear contact, however, was the transition from a dislocation cell structure to large depths below the surface to a layer of highly misoriented often elongated subgrains. Depending on the contact stress and type of wear, the thickness of this layer was 5 to 10 µm. A large fraction of the plastic strain that occurred was accomodated in this layer. It was also from this layer that wear particles are generated. Plans for next year will include studies of the details of the microstructure that develops within the first few micrometers of the worn surface and on the structure of wear debris fragments. In this way, insight may be gained on the relationship between wear debris particle generation and microstructure. It also appears that the crystallographic orientation texture that develops at worn surfaces can be influenced by contact stress, sliding velocity, and temperature. By studying the orientation textures, information can be obtained on the dynamic processes, for example, local thermally induced recrystallization, by which the textures are produced. An extension of this work to copper alloys of significance in bearing applications as well as certain bcc and hcp metals, probably iron and cobalt, is planned. A new contract from the Office of Naval Research has been received to further extend our studies of wear mechanisms. There the relationship between macroscopic mechanical properties such as strain hardening and ductility with wear performance will be examined for several steels and other metals.

Another phase of this project is concerned with the wear of coatings on metals. Support from the NBS Director's Reserve Fund has permitted starting a new effort. Coatings of all types are widely used in industry to extend the durability of materials with regard to wear and corrosion. Coatings also permit the substitution of materials, in particular, the conservation of strategic metals. Our work has focused on metal coatings and their wear performance. A new wear test facility was designed, constructed, and applied to studies of chromium, nickel, and electron beam melted coatings. The wear tester is computer controlled and the system provides continuous output of wear rate, friction, temperature, load, and speed. Software has been developed to start, control, and terminate the tests according to a variety of criteria. Dry sliding wear studies have shown that electroless nickel coatings can provide significant wear resistance on steels. An electron beam apparatus has been developed (in collaboration with F. Biancaniello) to surface melt and rapidly solidify tool steel and stainless steel specimens. These rapidly solidified layers (coatings) have an extremely fine microstructure and show an increased wear resistance relative to normal thermal treatments of the base materials. Further studies in the mechanisms of wear in rapidly solidified coatings and other materials are planned for next year.

Wear Standardization and NDE Activities

A. W. Ruff, and L. K. Ives

Standardization activities involve the ASTM Committee G-2 on Erosion and Wear as well as the NBS Office of Standard Reference Materials. Work in the G-2 Committee involves the Vice-Chairman post concerned with overall committee work and long-range planning as well as four subcommittees. We are responsible as chairman for the Editorial subcommittee and the Terminology subcommittee. In two technical subcommittees, wear and solid particle erosion work is underway involving project staff on two test methods. The first test method under development is concerned with the abrasive wear of materials. The test employes a rotating rubber-faced wheel to rub loose SiO_2 particles against a specimen and is known as the dry sand/rubber wheel (DS/RW) abrasion test. The DS/RW test addresses a form of wear that is probably one of the most costly and prevalent, being predominant in industries concerned with moving ore, and excavation, to name a few. The ASTM DS/RW task group has reached the final stages of preparing a standard test method. Our contributions have been to the standards writing activity, to round robin test exercises and to improving the test procedure itself. There are several aspects of the test that can lead to serious systematic errors. For this reason, it is deemed necessary to develop one or more standard reference materials to be used as test specimens. We are presently evaluating 1020 steel for this purpose. The second method concerns solid particle erosion testing of materials where a draft standard has been developed and two cycles of round robin measurements are completed. A standard reference material (1020 steel) is being developed in this project for use with the method for the first time. These efforts should lead to a greatly improved measurement capability for wear and erosion and encourage the development of improved wear resistant metals. A new effort has begun in G-2 concerned with reference methods for wear debris analysis. About 10 industrial and government laboratories have indicated that they plan to be involved in this developing activity.

This project is also concerned through the NDE program with the nondestructive monitoring of the operating capability (health) of mechanical systems in which wear is a significant lifelimiting process. This monitoring can take several forms in the field, e.g., measurements of system operating parameters (temperature, speed, pressure, or vaccum, etc.), vibration monitoring of rotating machinery, and the recovery and analysis of wear debris. The Navy Department has led in many of these developments although all such programs now extend throughout the DoD. These methods generally extract the wear debris from oil lubrication systems and provide a nearly continuous measure of wear metal formation rate. The debris method is frequently combined with spectrochemical methods of oil analysis in the diagnosis of system condition, although the two methods are sensitive to wear products in a different way. Debris can also be recovered from non-oil-lubricated systems, e.g., gas turbine engine ducts. Some of these techniques are being applied in the private sector, e.g., several major airlines and truck fleet systems. Relatively little understanding exists of the trends in wear characteristics and in debris generation mechanisms. The project is oriented to assist in these problem areas through method development, the provision of fundamental understanding, and assistance in standardization activities. We are studying wear debris formation mechanisms in steel and copper metals. The emphasis has been on rubbing (adhesive) wear and on abrasive wear. Abrasive wear is a major cause of failure in lubricated systems, generally the result of particulate contamination from outside the system (seal problems) or from recirculation of wear debris particles (filter problems). We have examined the type of wear debris removed from steel surfaces under various abrasive conditions. Particle size and shape distributions have been obtained. In the case of wear of copper (whose alloys form the usual commerical bearing materials), wear debris studies have been combined with surface and subsurface microstructure studies. Findings include the tendency for abrasive particles to fragment and become imbedded in the ductile metal surface. The identification of cutting chip particles in debris collections does not appear to be a satisfactory indicator of system wear mode. In fact, many debris particles are produced by plastic deformation processes during abrasive wear and must be distinguished from normal rubbing wear particles. Plans for next year include the acoustic monitoring of wear systems in order to correlate that information with the debris recovery data.

Lubricated Wear/Recycled Oil Activities

L. K. Ives, A. W. Ruff, K. Ludema, M. Peterson, and P. Boyer

This project is supported by the Recycled Oil Program. Its objectives are to evaluate available laboratory wear bench tests for determination of the consistency and the wear behavior of recycled base lubricating oils and to develop additional laboratory wear bench test procedures that can be used for this purpose. It is necessary to recycle used lubricating oils both for resource conservation purposes and to protect the environment from pollution. Section 383 of the "Energy

Policy and Conservation Act of 1975" directs the National Bureau of Standards to develop test procedures for the determination of substantial equivalency of re-refined used oils with new oils. The intention of this law is to remove present restrictions that constrain the recycling of used oils, including motor oils and a variety of industrial oils. This project is concerned entirely with automotive engine oils. Tests to evaluate the properties of lubricating oils may be categorized as chemical, physical, or performance tests. A wear test is essentially a performance test that is more or less responsive to some or all aspects of the lubricant. The wear test may employ the actual machine for which the lubricant is intended, a single component of the machine, or rubbing elements that bear no particular relationship to the machine. There are several ASTM standard test methods which employ bench wear test machines that can be used for evaluating motor oils. Three different machines known by their specimen geometries are used in the ASTM tests. They are the pin and V-block, the block-on-ring and the 4-ball test machines. All of these machines are widely used in laboratories of companies that produce lubricants or evaluate lubricants for use in their machinery, including the automobile companies.

Each of the test machines mentioned above has been acquired by the Recycled Oil Program for evaluation. Two of these machines, the pin and V-block and block-on-ring machines are being examined by this project. Evaluation of the ASTM Standard Test Methods employing the pin and V-block machine has been completed and other modified procedures carefully examined. It appears that the pin and V-block machine will be of limited applicability with respect to oils.

Evaluation of test procedures using the block-on-ring machine are underway. Due to the inherently greater precision and flexibility of this machine, it may offer some advantages over the pin and V-block machine. In evaluating the significance of bench wear test methods, consideration must be given to the nature of the wear process itself. The closeness of the coupling between bench test results and service performance will depend on the extent to which the wear processes are comparable. Many features of the wear process may be revealed through an examination of the worn surface and the debris fragments that are generated.

A scanning electron microscopy study of worn engine components and bench test specimens has been initiated. The engine components were obtained from the Southwest Research Institute and had been used in oil qualification sequence tests. A similar investigation of wear debris particles is planned. A literature survey of lubricant wear testing has been carried out and an evaluation of literature reports on failure modes in engine components is being conducted. The project plan includes close coupling between actual component metallurgy and wearing conditions with bench test metallurgy and conditions in setting the proper context for examining re-refined base oil consistancy, additive interactions, and impurity effects through wear bench testing.

A fall conference of the Mechanical Failures Prevention Group, jointly sponsored with the Recycled Oil Program, will address many of these issues including oil analysis, wear and fatigue durability, and bench testing methods.

Metals Used As Biological Implants

A. C. Fraker, A. W. Ruff, K. M. Speck, G. J. Mattamal, and
M. A. Imam

The use of metals in the body is increasing steadily. Some applications are in orthopedics, dentistry, and heart pacemaker cases. There are many problems with these applications that require a much better understanding of metals as synthetic implants. The purpose of this project is to study implant metals and relate their properties and reactivity to the requirements for the various uses in the human body. The emphasis of this work falls into five primary areas which are closely interrelated. These are (1) corrosion, (2) corrosion-fatigue, (3) wear and fretting, (4) metal-organic reactions, and (5) standards activities, and are described in the following paragraphs.

Corrosion - Personnel in this project also include Dr. Pei Sung, guest worker from the FDA, Dr. Heiner Weber, a West German dentist who was a guest worker in the NBS Dental and Medical Materials Group, and Jocelyn Orbock, a cooperative student from the College of Notre Dame. The project is studying the chemical reactivity and electrochemical behavior of implant metals, dental amalgams and casting alloys to determine possible metal ion loss to the body environment, and degradation of the metal. Anodic polarization measurements were conducted to provide a means of evaluating materials in terms of their passivity and film breakdown. The effects of coupling different implant metals and various alloying additions were studied with this technique and using scanning electron microscopy. Repassivation studies are underway to establish the kinetics of film formation under various conditions. We participated in an ASTM round robin pitting corrosion test and conducted a number of tests in this regard. Three publications and two talks resulted from these studies.

Corrosion-Fatigue - This is a cooperative program involving Prof. Charles M. Gilmore of the George Washington University. The fatigue life of implant metals is measured under fully reversed torsion conditions in prepared physiological solution at 37 °C. Effects of material microstructure, frequency, and load are considered. Most alloys have been obtained from implant manufacturers for testing and the results have been presented at professional society meetings. This past year, these results were presented in three talks, one publication, and will appear in another publication which is in preparation. Recently, studies have begun on a new improved cobalt-chromium alloy in the forged high-strength condition. Another material being currently studied is a relatively new titanium alloy, Ti-4.5Al-5Mo-1.5Cr (Corona 5). In conjunction with fatigue testing and electron microscopy studies of these metals, an effort is being made to separate the mechanical and chemical factors and to determine mechanisms of corrosion-fatigue under these conditions.

Wear and Fretting - In cooperation with Dr. Ian C. Clark, University of Southern California, a recommended wear test procedure was developed, and it is now in its second subcommittee balloting by the ASTM Committee F4 on Implants. Laboratory apparatus has been designed, and an automated, programmable data collection system has been assembled for conducting tests to study fretting wear rates and mechanisms. Variables to be considered in this work are the environment (pH, temperature, etc.), load, frequency, alloy composition, and surface coatings. This work will involve electrochemical and mechanical measurements, surface changes, and fretting debris production. We are formulating a joint program with Dartmouth Medical School to examine the effects of fretting wear debris.

Metal-Organic Reactions - This is a new phase of our implant project. A laboratory has been set-up to investigate whether and how much of a given metal ion will be carried by blood serum albumin. This will be followed by experiments to determine specific proteins to which the metals attach. Currently two cells with porous membrane filters are in use. The metal ion content is determined by atomic absorption. Metal ions to be studied initially are those of copper, nickel, and titanium. Later, this work will be oriented toward our corrosion and metal ion release studies.

Standards Activities and Interactions - One of the important aspects of this work is assisting with the development of standards for the ASTM. Current responsibilities in the ASTM include serving as chairman of the F4.2.5.17 wear test task force, co-chairman of the joint F4-G1 Corrosion Section, and as liaison between F4 and G2 in the area of implant materials wear. Excellent cooperation with the NBS Medical and Dental Group continues as indicated earlier. There are numerous industrial and other outside contacts. Recently, we teamed up with people from Artech Corporation, The George Washington Medical School, and the George Washington School of Engineering and Applied Science to do an in-depth review and analysis of the status and requirements of porous metal implants. Additional collaborative efforts are in progress with the FDA, VA, NIH, and Tulane University to plan an Implant Retrieval Symposium for the Spring of 1980. There is considerable interest in the work of this project from the community at large and more than twenty presentations were made this past year to visiting students and groups.

Materials Preparation

D. P. Fickle and F. S. Biancaniello

This laboratory is equipped with a wide variety of melting, fabricating, and processing equipment and carries out numerous activities in support of the research program needs for special alloys, reference materials, and research specimens. A principal activity this year has been the development of an electron beam system for melting surface layers under controlled conditions of input power, scanning speed, and melt depth. Rapidly solidified surface layers (coatings) result from this technique and have been made on several ferrous alloys to study their wear properties. A summary of the past year's activities supporting the Division research program follows.

- Prepared alloys and specimens for positron annihilation studies to detect defects: nickel foils, Ti-Al alloys, annealed Ti foils, nickel foils rolled and annealed in high vacuum, nickel foils rolled and annealed in hydrogen, $Pt_{95}Cu_5$ alloy, rolled and annealed, nickel foils annealed in hydrogen atmosphere with controlled cooling rate.
- Prepared Cu_3Sn and Cu_6Sn_5 alloys for corrosion studies on dental alloys.
- The following alloys were prepared for use in superconductive devices for temperature fixed points: directionally solidified boules of $AuIn_2$ and zone refined $AuAl_2$; Rhodium 99.5 Iron 0.5 alloy, hot rolled for low-temperature resistance thermometers.
- Prepared nitrogen free alloys, $Ni_3Al_{0.9}Ti_{0.1}$, $Ni_3Al_{0.5}Ti_{0.5}$, $Ni_3Al_{0.7}Ti_{0.3}$ by vacuum electron beam melting for EXAFS studies.

  Prepared Pd and Pd_{77} Cu_6Si_{17} alloys for metallic glass solidification studies. Conducted directional solidification and rapid solidification experiments utilizing this material.
- Rolled Pb shielding and gold foil for use in synchrotron x-ray studies.
- Pb-Sn alloys were prepared for Solute Convection Induced Macrosegregation studies in Off-Eutectic Alloys.
- An electron beam welding apparatus was acquired and modified to prepare raster scanned and melted surfaces on steels for wear studies. A table designed for x-y rectalinear motion was modified and automated so that rastered surfaces could be generated easily. A rotating table was designed and constructed to generate high speed scans at speeds up to 60 cm/sec.
- Annealing studies were carried out on two composite materials.
- A series of binary Ti-Al alloys were prepared: 94Ti 6Al, 92Ti 8Al, 88Ti 12Al, Ti Al, Ti_2 Al and Ti_3 Al (intermetallic compound ratios). These include as-cast and heat treated alloys for NMR studies. Specimens for metallographic examination were prepared as well.
- A set of Ti-Al specimens were prepared for magnetic susceptibility studies. The compositions were; 94Ti 6Al, 92Ti 8Al, 90Ti 10Al, 88Ti 12Al, 85Ti 15Al, 80Ti 20Al and 70Ti 30Al. These alloys were heat treated at temperatures of 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, and 1100 °C.
- Pure Ti and Ti_3 Al compositions will be prepared and heat treated at selected temperatures to study high temperature phases.
- Prepared FcCrNi standard material for microhomogeneity applications.
- Prepared Cu and CuZn alloy specimens for studies of diffusion induced grain boundary migration.
- Numerous heat treatments carried out on steel wear specimens.

METALLURGICAL CHEMISTRY FOR DURABILITY

The stability of alloy phases is the central theme of this task's activities. This theme is developed in data, theory, and experiment. Phase diagram data is a direct objective of part of the task's research and services. A joint effort mandated by agreement between the Directors of the National Bureau of Standards and the American Society for Metals has been undertaken to provide critically evaluated phase diagram and other constitution data as well as related bibliographic material. Technical oversight of this program and work on selected systems is being carried out by the Alloy Data Center (supported in part under this task and by the Office of Standard Reference Data). ASM continues to support a Research Associate at NBS for this project. Dr. Joanne L. Murray, a NRC-NBS Postdoctoral Fellow with us, has now been appointed Chief Analyst of the Alloy Data Center, and will devote special attention to new methods of on-line graphic display of phase diagram data in collaboration with the Applied Mathematics Division of NEL. The phase diagram of the Ti-Al system is being studied experimentally with a number of different techniques as a part of a new Navy program to improve titanium processing technology. In addition, phase diagram data are being exploited in the solution of problems in areas of critical national need; for instance, materials are selected for study as electrocatalysts in hot phosphoric acid on the basis of available phase constitution data; here, surface phase stability is of utmost importance. In fair measure, the task members' established scientific competences are challenged and stimulated in the course of this work; for example, studies of alloying led to fundamental inquiry into the definition of electronegativity concepts; catalysis research on non-noble alloys required better understanding of the electronic structure of refractory hard metals and of the definition of charge transfer in these materials. A Symposium on the Theory of Alloy Phase Formation was organized and held at the New Orleans meeting of the AIME. A method for applying d-electron energy band parameters to prediction of heats of formation of transition metal alloys has been developed.

Synchrotron x-ray absorption studies (EXAFS) are being carried out at the Stanford Synchrotron Radiation Laboratory. Mössbauer techniques have been used to quantitatively identify phases in several materials. New results have been obtained in a DoE-DoD fuel cell catalyst program. We are working on the NASA soft Al project described elsewhere, focusing on the understanding of both stable and metastable phases produced by processing, and devising methods for nondestructively detecting them by hardness, eddy current, and positron annihilation measurements. New work on the latter completed this year is described under Task, "Alloy Properties Science for Structure Characterization." The new initiative on materials processing includes proposed phase diagram work. Task workers are strongly involved in committee work, including chairmanships of the Committee on Alloy Phases of the Metallurgical Society of AIME and ASTM Committee D42 on Surface Analysis.

In addition to its fundamental scientific interest, advancement in the understanding of phase diagrams is essential to permit greater flexibility in development of new alloys chosen on the basis of mechanical properties, ease of processing, cost, and energy use as well as in providing substitute alloys and composites. Our work is described in more detail in the following two sections: Alloy Phase Stability and Alloys for Fuel Cells and Catalysis.

Technical Activity

Alloy Phase Stability

L. H. Bennett, J. R. Cuthill, J. L. Murray, and L. J. Swartzendruber

We are pursuing a program of three interconnected parts: critical data evaluation and compilation of phase diagrams; experimental phase diagram work on systems selected to support the evaluation program; and the theory of alloy phase stability, stressing semi-empirical methods and the identification of those physical parameters most vital to successful phase stability predictive schemes.

The Alloy Data Center has established a collaborative alloy phase diagram critical evaluation program with the ASM. Formalized last year, this joint effort has two key aspects: (1) development of an on-line indexed bibliographic system starting with the current ASM automated system for the METADEX data base; and (2) the organization and preparation of critical compendia for binary and multicomponent alloy phase diagrams. On the first aspect, during the current year, significant improvements have been made in the METADEX system. More thorough scanning of literature sources and more extensive indexing have been introduced, and a contract let for separate, quicker access to the subset of alloy phase diagram data. To achieve the second aspect of this joint program, an International Council of distinguished experts has been established to advise on various aspects of the critical evaluation effort, and panels formed to deal separately with binary and higher order systems. A Bulletin of Alloy Phase Diagrams will be published; the first number is in preparation and is expected to be available early next year. Considerable progress has been made in developing software for on-line graphic display of phase diagram data through application of spline fitting techniques to published phase diagram data. Graphics software incorporating phase diagram prediction techniques and thermodynamic data are also under development. This graphics work is being carried out in collaboration with the Applied Mathematics Division of the National Engineering Laboratory. A research associate supported by ASM has spent a second summer with us, editing materials amassed under the auspices of OSRD and other agencies for a comprehensive, complete revision of the Hansen phase diagram compilation.

Of course, we are not attempting to evaluate all systems ourselves at NBS. Evaluations will actually be carried out throughout the world at institutions recommended by the International Council. Priorities will determine which important classes of systems are evaluated first. At NBS, we are concentrating on certain systems which can act as models in that they embody many of the practical experimental and theoretical difficulties universally encountered, with the objective of establishing criteria for critical phase diagram evaluation ("standards of evaluation").

We have chosen for immediate evaluation work the Ti-Al system. It is an ideal system for establishing criteria for critical evaluation. Many conflicting reports of the Ti-Al phase diagram have appeared in the literature. A number of experimental difficulties contribute to this situation. Contamination easily occurs in long anneals: oxygen cannot be removed, Al may make hydrogen removal difficult, and surface hydrides make optical microscopy very difficult. Short anneals lead to non-equilibrium situations. Another difficulty (pointed out by John Cahn) is that not all phase transitions need be first order. The Landau rules permit the transformation of α to a DO_{19} structure to be second order, for example. Thus, previous investigators may have been misled by assuming that two phase regions must occur between these phases. The Ti-Al system also possesses other special theoretical interest; alloying of an early transition metal (i.e., a metal with only bonding d-states) with a nearly free electron metal poses a unique theoretical challenge. In addition, Ti alloys have important present and potential practical advantages. Their high corrosion resistance makes them attractive for marine and chemical processing applications and their high strength to weight ratio makes them valuable in aviation and space technology. With better understanding of its phase diagrams, and other basic data, it may be possible to reduce titanium processing costs so that titanium alloys could substitute for some stainless steels, as a means of reducing the U.S. dependence on imported chromium.

We are carrying out new, more carefully controlled experimental work on Ti-Al, both to clarify the phase diagram of this important system and to serve as a guide to selection of critical evaluation methods. In addition, the use of ternary and higher Ti-Al-X systems, of great interest to the Navy, has been restricted by processing problems and long-term embrittlement. At the root of these durability and processing problems is incomplete understanding of the phase stability of these systems. We are investigating the binary and higher order systems (the latter with partial support from the Navy) with many of the conventional techniques for determination of phase diagrams, for example, scanning electron microscopy, electron microprobe, x-ray diffraction, hardness measurements, and specialized techniques such as NMR and magnetic susceptibility where appropriate. A high temperature metallographic microscope is being installed; this instrument is capable of operation in ultrahigh vacuum or in inert gas atmospheres. Vapor pressure studies by the isopiestic technique will soon be initiated.

Experiments are underway on several other problems of fundamental significance to phase stability. The EXAFS technique is being used to study metastable glassy phases in Ni rich Ni-P alloys on which we have previously published NMR results, and to study model alloy components of the complex Ni-based superalloys such as the γ' phase $Ni_3Al_{1-x}Ti_x$. The latter work is being undertaken to obtain data on elemental distribution among the phases present in the superalloys, information necessary to make predictive schemes such as PHACOMP more reliable. The Mössbauer effect is a technique which can often both quantitatively measure the presence of an alloy phase and determine various properties of that phase. We have used this technique to (1) characterize the magnetic, electronic, and defect structure of a new phase of potassium ferrite of possible interest in high temperature applications, and (2) to study the magnetic properties and identify and quantitatively measure the phase composition of a type of high strength steel fiber known as "Schladitz whiskers." The work (1) was performed in cooperation with the Ceramics, Glass, and Solid State Science Division and with a visiting scientist from the U.S.S.R., and (2) with the Chemical Stability and Corrosion Division. Papers have been submitted for publication describing these two experiments. Studies are being conducted to determine the applicability of positron annihilation as an adjunct technique in phase diagram determinations. Emphasis will be placed on Ti-Al alloys and on obtaining details concerning hydrogen-metal interactions in this alloy system. We have exploited the sensitivity of positron annihilation radiation to correlate positron Doppler-broadening with hardness measurements on cold rolled high purity and commercial grade Ti as a function of annealing temperature. The positron annihilation measurements revealed defect changes which occurred at temperatures well below the recrystallization temperature and which were not detected by hardness measurements. A paper describing this work is in press.

An invited talk was presented at a recent CALPHAD Meeting in Stockholm, on the application of predictive methods to, and critical evaluation of experimental data on, the Ti-Al system. Figure 1 shows the result of one such predictive method.

A critical survey of various phase diagram determination methods is being carried out simultaneously with the experimental work. An essential part of this work is a weekly informal study session on alloy phase stability. Current emphasis is on the experimental and predictive aspects of Ti-Al phase diagram determinations.

The major thrust of our theoretical studies continues to be analysis of the physical parameters important to empirical, thermodynamic, and *ab initio* schemes for the prediction of alloy phase and structural stability In collaboration with R. E. Watson, a paper has been prepared and submitted for publication describing a method for applying d-electron energy band parameters to prediction of the heat of formation of transition metal alloys. A Symposium on the Theory of Alloy Formation was organized and held at the New Orleans meeting of the AIME.

Dr. Joanne L. Murray, an NRC-NBS Postdoctoral Fellow with us, has now been appointed Chief Analyst of the Alloy Data Center, and will devote special attention to the development of on-line graphic display of phase diagram data, as well as participating actively in our program of theoretical phase diagram predictive schemes. Prof. T. B. Massalski will be joining us in the fall as a consultant and next year for an extended visit. He will serve as chairman of the International Council's Panel on binary alloys and will participate actively in both our Ti-Al experimental program and in our theoretical work on predictive techniques, particularly in thermodynamics.

Our activity in ASTM continues. Task workers participate in ASTM Committees D32 on Catalysis, E42 on Surface Analysis, E13 on Molecular Spectroscopy, B5 on Cu and Cu Alloys, and E7 on Nondestructive Evaluation. L. H. Bennett serves as chairman of the Committee on Alloy Phases of the Metallurgical Society of AIME. L. H. Bennett and J. R. Cuthill are the official NBS representatives on the Joint ASTM-SAE Committee on the Unified Numbering System in Metals and Alloys.

We continue to prepare the circular "Comments" for the Committee on Alloy Phases of the AIME.

Alloys for Catalysis and Fuel Cells

A. J. McAlister and J. R. Cuthill

Development of successful fuel cells will significantly increase the efficiency of fuel utilization and markedly reduce our national dependence on foreign energy sources. For low temperature acid fuel cells, a number of problems are performance limiting. Scarce and expensive Pt, now used as both fuel and air catalysts should be replaced or more efficiently used, and air catalyst supports more resistant to corrosion at cathodic potentials are needed. Despite these difficulties, many practical advances are being made. The DoD has successfully employed small cells of a few kilowatt capacity in transportation and portable power source applications, while in the area of power generation, DoD and EPRI are sponsoring installation of a 4.8 megawatt, naptha fed pilot assembly in lower Manhattan.

Many challenging scientific problems are encountered in the area of fuel cell research. In the past, we have focused our expertise in the electronic and physical properties of refractory hard metals, compounds of transition metals with light metalloids, on a search for acid stable, hydrogen oxidation catalysts to substitute for Pt as the fuel electrocatalyst in low temperature acid fuel cells. We observed, for the first time in our laboratory, some measure of activity and voltage stability in Re metal, $W_{0.5}Ti_{0.5}C$, and WP, and strong activity in the ternary $Mo_{1-x}W_xC$ (1-x = 0.7, 0.8) which is isostructural with the known strong, CO poison-resistant fuel electrocatalyst WC.

In the past year we have completed comparative studies of the Mo rich ternary with WC, and showed it to be equally active and corrosion resistant for anodic oxidation of H_2, to catalyze the H_2 reaction by the same mechanism as WC (see Figure 2), and to be equally tolerant of CO in the fuel feed. We have also demonstrated that proton discharge is rate limiting on these carbides, in contrast to Pt where chemisorptive desorption is the slow step. These data were presented in an invited talk at the National Fuel Cell Seminar in June, and a paper describing these results has been submitted for publication.

Intrinsic to all problems in heterogeneous catalysis are questions of surface alloy phase stability. Factors which are important to such stability include reduced coordination at the surface, surface curvature and the effects of surface tension, particle-substrate interactions, the effects of extremely small particle size, and surface reconstruction in the presence of electrolyte and applied potential.

Several intriguing and difficult experiments aimed at more thorough understanding of H_2 oxidation on non-noble fuel electrocatalysts are underway. Studies of H_2 oxidation on the cubic W-Ti-C alloys as a function of metal content are being pursued, to compare the mechanism of the hydrogen reaction with that on hexagonal WC. (Pure TiC is inactive.) Two lines of research aimed ultimately at understanding the geometry of the active sites on the carbides are being undertaken. Both Raman and EXAFS studies are capable of yielding microscopic information on catalyst surfaces in situ. A Raman cell has been completed and tested for electrochemical and optical performance. Measurements on carbides will soon begin. A thin wall EXAFS cell, for fluorescent EXAFS studies of very small carbide particles in situ is being designed.

Other areas of current research include the efficiency of the carbides as Pt supports (synergistic improvement of Pt's CO tolerance may occur, and Pt may be more efficiently distributed on the carbides). Equipment for preparing carbide supported Pt by precipitation and reduction of Pt salts has been assembled, and the first samples prepared. In addition, we have observed several refractory hard metals to remain passivated at potentials well beyond the O_2-reduction potential, and will test them for performance as non-corroding Pt cathode catalyst supports.

J. R. Cuthill is chairman of ASTM Committee E42 on Surface Analysis. During the current year, two standards have been sent to press and the Proceedings of a Symposium on Ion Sputtering has been published. Two symposia are arranged for the coming year, on Interfacial Analysis and on Quantitative Surface Analysis. A. J. McAlister is a member of E42 and of ASTM Committee D32 on Catalysis as well.

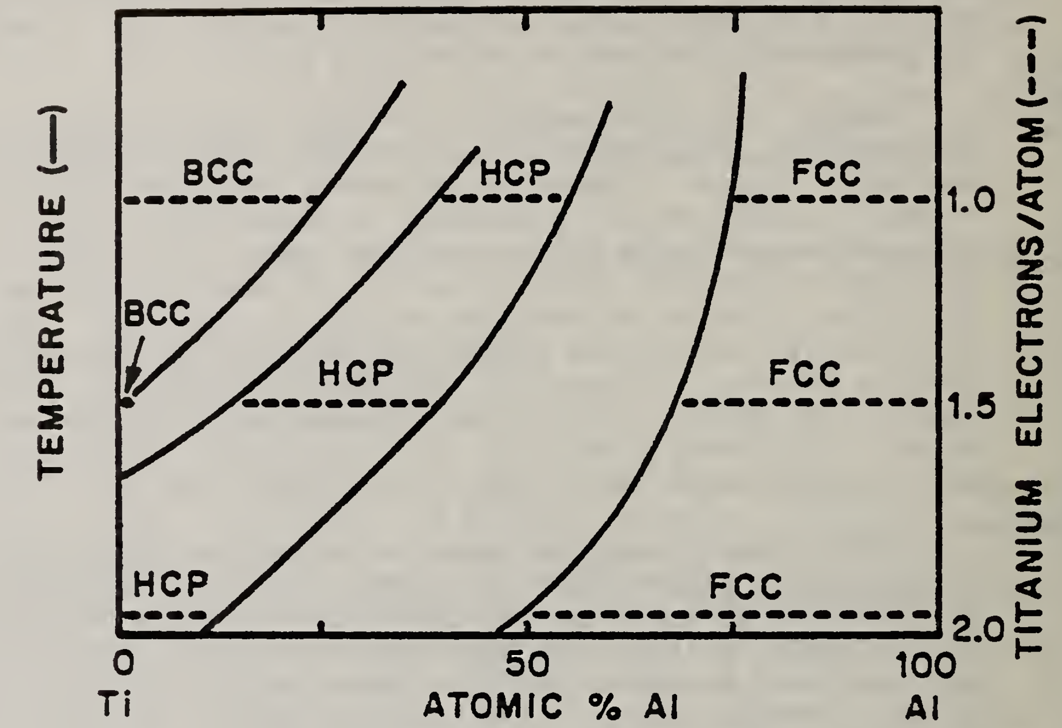

Fig. 1. The Engel-Brewer correlation is one of several empirical methods of predicting alloy phase stability. All theoretical models are most difficult to interpret or apply to transition - nontransition metal alloys such as Ti-Al.

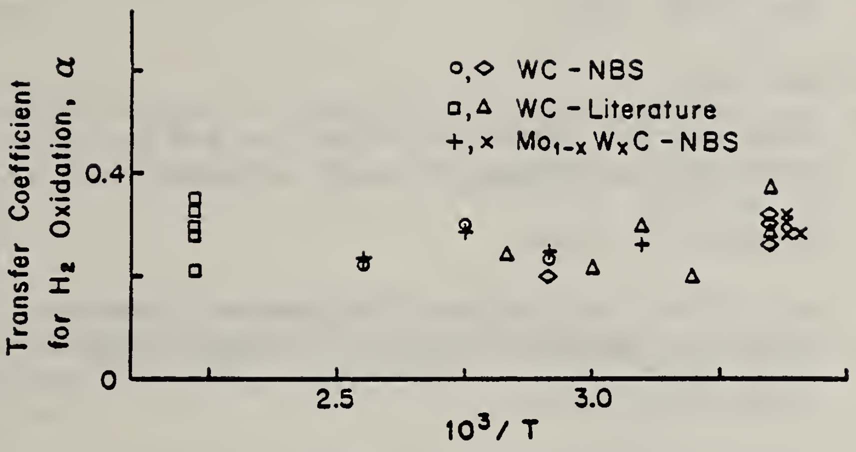

Fig. 2. Transfer coefficient, α, for various prepared carbide samples. In contrast to i_0, α is independent of preparative method.

Other Division Activities

Sponsored Conferences

Detection, Diagnosis, and Prognosis - System Applications
Mechanical Failures Prevention Group, 28th meeting, San Antonio, Texas
November 28-30, 1978.

Symposium on the Theory of Alloy Formation
Annual Meeting of the AIME, New Orleans, Louisiana
February 18-22, 1979.

Advanced Composites: Design and Application
Mechanical Failures Prevention Group, 29th meeting, Gaithersburg, Maryland
May 23-25, 1979.

Invited Talks

Wear Debris: Formation Mechanisms and Analysis
AIME/ASM Conference, St. Louis, Missouri
A. W. Ruff
October 16, 1978.

Solid Particle Erosion: Introductory Remarks
NACE Conference on Corrosion/Erosion; Berkeley, California
A. W. Ruff
January 25, 1979.

Solid Particle Erosion of Metals and Ceramics
Golden Gate Metals and Welding Conference, San Francisco, California
A. W. Ruff
February 1, 1979.

Metallurgical Studies of Wear and Erosion
Martin Marietta Research Laboratories, Baltimore, Maryland
A. W. Ruff
April 24, 1979.

Microscopic Aspects of Wear in Metals
Navy Tribology Meeting, Annapolis, Maryland
A. W. Ruff
May 22, 1979.

Measurements and Standards for Dry Wear
American Chemical Society Conference on Corrosion and Wear, Washington, D.C.
A. W. Ruff
June 5, 1979.

Hume-Rothery's "Old Metallurgist" Revisited: A Discussion of
Digital Processing of Transient Signals with Special Reference to
Acoustic Emission
Second International Conference on Acoustic Emission and Materials
Evaluation sponsored by Inst. of Acoustics and British AE Working
Group, London, England
R. B. Clough
April 1979.

Digital Processing of Transient Signals with Special Reference to
Acoustic Emission
Atomic Energy Research Establishment, Harwell, England
R. B. Clough
April 1979.

The Use of Metals as Surgical Implants
Biomaterials Seminar, Johns Hopkins University, Baltimore, Maryland
A. C. Fraker
March 1979.

Microstructural Changes in Copper Due to Abrasive, Dry and Lubricated
Wear
International Conference on Wear of Materials - 1979, Dearborn, Michigan
L. K. Ives
April 1979.

On Determining Stress in Bolts Ultrasonically
ARPA/AFML Review of Progress in Quantitative NDE, Scripps Institution
of Oceanography, La Jolla, California
D. E. MacDonald
July 1979.

On Determining Stress and Strain and Texture Using Ultrasonic
Velocity Measurements
1979 International Ultrasonics Symposium, IEEE, New Orleans, Louisiana
D. E. MacDonald
September 1979.

An Atomic Model of Strain Induced Martensitic Transformation
Intl. Conf. on Martensitic Transformations
D. E. MacDonald
June 1979.

Female Chemistry (Non-Chauvinistic)
Chemical Society of Washington, George Mason University, Washington,
D.C.
G. J. Mattamal
April 1979.

EXAFS: A Local Structure Probe
University of Maryland (Baltimore County)
A. J. McAlister
March 1979.

H_2 Oxidation on Mo-W Carbide Alloys in Acid Electrolyte
National Fuel Cell Seminar, Bethesda, Maryland
A. J. McAlister, M. I. Cohen and L. H. Bennett
June 1979.

Nuclear Hyperfine Positron Annihilation Methods for Measurements of Longitudinal Force in Rails
Department of Energy, Washington, D.C.
L. H. Bennett
February 26, 1979.

Current Research in Acoustic Emission at NBS
European Acoustic Emission Working Group, Risley, England
J. A. Simmons
October 1978

Elastodynamic Green's Tensor for an Isotropic Plate
Theoretical Physics Division, United Kingdom Atomic Energy Research Establishment, Harwell, England
J. A. Simmons
October 1978.

Theory and Experiment of Titanium Alloys
CALPHAD Conference, Stockholm Sweden
J. L. Murray
May 1979.

Alloy Phase Stability
The Physics Club of Richmond, Richmond, Virginia
L. H. Bennett
April 1979.

Parameters in Semi-Empirical Theories of Alloy Phase Formation
Annual AIME/TMS Meeting, New Orleans, Louisiana
L. H. Bennett
February 1979.

Costs of Corrosion
1978 Greater Boston Section Corrosion Control Meeting, Boston, Massachusetts
L. H. Bennett
October 1978.

The ASM/NBS Alloy Phase Diagram Program
General Electric Corp., Schenectady, New York
L. H. Bennett
November 1978.

Materials Stability at High Temperatures, Reliability of Materials for Solar Energy
Solar Energy Research Institute Materials Workshop, Denver, Colorado
J. R. Manning
December 1978.

Defect Gradient Effects on Diffusion in Irradiated Alloys
Oak Ridge National Laboratory, Oak Ridge, Tennessee
J. R. Manning
August 1979.

Morphological Stability
Defense Advanced Research Projects Agency, La Jolla, California
S. R. Coriell
July 1979.

Surface Tension Measurements of Liquid Gallium
NASA Headquarters, Washington, D.C.
S. C. Hardy
June 1979.

Nuclear Hyperfine and Positron Annihilation Methods for Measurements of Internal Stress
Department of Transportation, Washington, D.C., Conference on Methods for Measuring Internal Stress in Parts
L. H. Bennett and L. J. Swartzendruber
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Magnetic Leakage and Force Fields for Artificial Defects in Magnetic Particle Test Rings
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Thickness of Gold Coating Measured with a Calibrated SEM
D. B. Ballard and F. Ogburn
to be published in Plating and Surface Finishing a Journal of the American Electroplater's Society (1979).

SEM Studies of Dental Casting Alloy Corrosion Behavior
H. Weber and A. C. Fraker
Proc. of the Electron Microscopy Society of America Meeting (1979) to be published.

An Atomic Model of Strain Induced Martensitic Transformation
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OYO BUTSURI (Applied Physics) (in Japanese) 48, 143-149 (1979).

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G. G. Cohen and M. Kuriyama
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M. Kuriyama, W. J. Boettinger and H. E. Burdette
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R. W. Armstrong, W. J. Boettinger and M. Kuriyama
(to be published in Journal of Applied Crystallography).

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W. J. Boettinger, H. E. Burdette and M. Kuriyama
Advances in X-ray Analysis, Vol. 23 (in press).

X-ray Polarization Rotation
M. Kuriyama and G. G. Cohen
Physical Review B (in press).

Experiments in Acoustic Emission Waveform Analysis for Characterization of AE Sources, Sensors, and Structures
N. N. Hsu and S. C. Hardy
Elastic Waves and Nondestructive Testing of Materials, AMD-Vol. 29 (1978).

An Approach to Acoustic Emission Signal Analysis - Theory and Experiment
N. N. Hsu, J. A. Simmons and S. C. Hardy
Materials Evaluation (1978).

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J. R. Manning
Applications of Space Flight in Materials Science and Technology, NBS Special Publication 520, pp. 102-104 (1978).

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Magnetic Leakage and Force Fields for Artificial Defects in Magnetic Particle Test Rings
L. J. Swartzendruber
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Positron Annihilation Study of Defects in Titanium
R. C. Reno, L. J. Swartzendruber and L. H. Bennett
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Magnetic Properties and Hyperfine Interactions in β''' Phase of Potassium Ferrite
V. P. Romanov, G. A. Candela, R. S. Roth and L. J. Swartzendruber
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Nuclear Magnetic Resonance in $LaNi_5$
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Stacking Solutions in w-phase Systems and Quasielastic Scattering
B. Horovitz, J. L. Murray and J. A. Krumhansl
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Economic Effects of Metallic Corrosion in the U.S.
L. H. Bennett and A. W. Ruff, et al
Proceedings of NACE Corrosion Conference, Atlanta, Georgia, 1979.

Seminars for Staff and Guests

Dr. P. J. Blau
Microstructure-Based Models for the Sliding Wear and Friction of Single-Phase Metals
March 6, 1979.

Dr. Charles Schwarz
Used Oil Analytical Techniques and Test Methods
May 21, 1979.

Prof. M. J. Furey
Chemical Aspects of Boundary Lubrication
May 31, 1979.

Dr. S. Weisman
Forged High Strength Vitallium Alloy
February 9, 1979.

Dr. E. Smethurst
Fretting and Corrosion Fatigue Behavior of Implant Alloys
June 13, 1979.

Dr. H. Wadley
Acoustic Emission During the Deformation and Fracture of Metals
August 1979.

Dr. Donald Polk
Thermal and Mechanical Behavior of Zr-Cu Metallic Glasses
May 18, 1979.

Dr. D. B. Oulton
Non-Linear Theory of Interface Stability During Solidification
July 1979.

Dr. G. Purdy
Diffusion-Enhanced Grain Boundary Migration
May 1979.

Prof. Dr. B. Predel
Thermodynamic Investigations of Liquid Alloys
September 1979.

Prof. J. B. Vander Sande
Applications of Scanning Transmission Electron Microscopy to Problems in Materials Science
December 8, 1978.

Dr. M. J. Loretto
Electron Microscopy and Stacking Faults
June 1979.

Dr. R. Mehrabian
Rapid Solidification Processing
December 13, 1978.

Dr. K. T. Hartwig
Materials Processing Methods for a Large Superconducting Cable to be Used for Energy Storage
December 21, 1978.

Dr. L. Schlapbach
Structure, Magnetic and Surface Properties of $LaNi_5$ and FeTi Hydrides
December 27, 1978.

Dr. J. C. Williams
A Review of the Deformation Behavior of α-Titanium
April 26, 1979.

Dr. R. J. Schaefer
Surface Coating Application by High Power Lasers
June 7, 1979.

Dr. S. J. Rothman
Tracer Diffusion in Austenitic Fe-Cr-Ni Alloys
May 10, 1979.

Dr. E. M. Breinan
Advances in Rapid Solidification Laser Processing
May 1979.

Dr. S. A. Brown and K. Merritt
Implants, Corrosion and Metal Allergy: Studies in Animals and Man
April 26, 1979.

Dr. A. D. Pelton, Dr. C. W. Bale and Dr. W. T. Thompson
The F*A*C*T* (Facility for the Analysis of Chemical Thermodynamics) Computer System and its Application in the Compilation and Evaluation of Phase Diagrams and Thermodynamic Data of Solutions
June 29, 1979.

Dr. I. Hansson
Research at the Laboratory of Applied Physics 1 on Ultrasonic Cavitation Erosion, Plasticity, and Fatigue
July 2, 1979.

Dr. J. Hamilton
Surface Segregation in Alloys: Experiment and Theory
July 25, 1979.

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L. H. Bennett, C. K. Chiang, M. I. Cohen, A. L. Dragoo, A. D. Franklin and A. J. McAlister
NBSIR (in press).

NBS: Properties of Electronic Materials
J. R. Manning
NBSIR 79-1767.

Technical and Professional Committee Participation and Leadership

ASTM E9, Task Group 3, Residual Stress Effects in Fatigue
J. A. Simmons.

Society for Experimental Stress Analysis, Technical Committee on Residual Stress
J. A. Simmons.

ASTM E28, Mechanical Testing; Residual Stress Standards
J. A. Simmons.

American Society for Mechanical Engineers, Ad Hoc Working Group on Acoustic Emission
J. A. Simmons.

ASTM/ASME, Joint Task Group on Acoustic Emission System Calibration
J. A. Simmons.

ASTM E7, Nondestructive Testing; Subcommittee on Acoustic Emission
J. A. Simmons
Vice-Chairman.

ASTM F4, Surgical Implants; Resources; Test Methods
A. C. Fraker.

ASTM G2.91, Subcommittee on Terminology and Definitions
L. K. Ives
Chairman.

ASTM G2, Subcommittee on Erosion by Solid Particle Impact, Wear, Erosion and Wear
L. K. Ives.

International Council for the ASM/NBS Program for Alloy Phase Diagrams
L. H. Bennett.

SAE-ASTM Unified Numbering System for Metals and Alloys
L. H. Bennett.

Metallurgical Society, AIME, Committee on Alloy Phases
L. H. Bennett
Chairman.

ASTM E7, Nondestructive Testing
L. H. Bennett.

International Council for the ASM/NBS Program for Alloy Phase Diagrams
J. R. Cuthill.

ASM Handbook Committee on Definitions
J. R. Cuthill.

SAE-ASTM Unified Numbering System
J. R. Cuthill
Alternate Representative.

ASTM E42, Surface Analysis
J. R. Cuthill
Chairman.

ASTM E42, Surface Analysis
A. J. McAlister.

ASTM D32, Catalysts
A. J. McAlister.

ASTM B5, Copper and Copper Alloys; Methods of Test
L. J. Swartzendruber.

ASTM E4, Metallography
L. J. Swartzendruber.

ASTM E7, Nondestructive Testing
L. J. Swartzendruber.

Maryland Institute of Metals
W. J. Boettinger
President.

Solidification Committee of the Metallurgical Society of AIME
W. J. Boettinger
Chairman.

ASTM B7, Light Metals and Alloys; Aluminum Alloy Ingots and Castings
W. J. Boettinger.

Solidification Committee of the Metallurgical Society of AIME
S. R. Coriell.

Advisory Board for International Journal Diffusion and Defect Data
D. B. Butrymowicz
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National Materials Advisory Board, Committee on Aluminum Powder Alloys
J. R. Manning.

Mass Transport Activity of American Society for Metals
J. R. Manning.

Process Modeling Activity of American Society for Metals
J. R. Manning.

Materials Processing in Space Panel of the NASA Applications Steering Committee, Supporting Research and Technology Subcommittee
J. R. Manning.

Executive Committee of Washington Chapter of American Society for Metals
S. R. Coriell.

Editorial Board of International Journal of Crystal Growth
R. L. Parker
Deputy Principal Editor.

US-USSR Joint Committee on Electrometallurgy
R. L. Parker.

Visiting Committee for Metallurgy and Materials Science Department of Carnegie-Mellon University
R. L. Parker.

International Council of Scientific Unions, Committee on Space Research (COSPAR)
R. L. Parker.

Council of International Organization of Crystal Growth
R. L. Parker.

Executive Committee of American Association for Crystal Growth
R. L. Parker.

Electronic Materials Committee of the Metallurgical Society of AIME
R. L. Parker.

ASTM A1, Steel, Stainless Steel, Related Alloys; Castings
R. L. Parker.

Florence Review Committee, Review of Scanning Electron Microscopes
D. B. Ballard
Chairman.

ASTM E4, Metallography; Electron Metallography; Scanning Electron Microscopy
D. B. Ballard.

ASTM G2, Erosion and Wear
A. W. Ruff
Vice-Chairman.

ASTM G2, Erosion and Wear
A. W. Ruff
Editorial, Chairman.

ASTM F4, Surgical Implants, Resources, Metallurgical Materials
A. W. Ruff.

ASM, Metal Progress
A. W. Ruff
Editorial Committee.

ASM, Division of Materials Testing and QC
A. W. Ruff
Councilor.

ASTM E28.13, Measurement Methods for Residual Stress
D. E. MacDonald.

ASTM B6, Committee on Die-Cast Metals and Alloys
R. Mehrabian
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Process Modeling Activity of American Society of Metals
R. Mehrabian.

US-USSR Joint Subcommittee on Electro-Slag Remelting
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Visiting Committee for the Department of Metallurgy and Materials Science, Carnegie-Mellon University
R. Mehrabian.

Solidification Committee of the Metallurgical Society of AIME
R. Mehrabian.

Composite Committee of ASM-AIME
R. Mehrabian.

Second International Conference on Rapid Solidification Processing
R. Mehrabian
Chairman.

National Materials Advisory Board Committee on Amorphous and Metastable Materials
R. Mehrabian.

National Materials Advisory Board Committee on Superalloy Powder Alloys
R. Mehrabian.

Adjunct Professor of Metallurgy and Mining Engineering, University of Illinois at Urbana, Champaign, Illinois
R. Mehrabian.

Consulting and Advisory Data Centers

Alloy Data Center
L. H. Bennett, J. L. Murray, J. R. Cuthill and D. J. Kahan.

Diffusion in Metals Data Center
M. E. Read and D. B. Butrymowicz.

CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION

CERAMICS, GLASS AND SOLID STATE SCIENCE DIVISION

Hans P. R. Frederikse, Chief
J. Bartlett, Administrative Aid
M. A. Clevinger, Administrative Aid
B. A. Hyde, Adminsitrative Aid
K. R. Morgan, Clerk Stenographer
E. R. Smith, Administrative Aid

The Ceramics, Glass and Solid State Science Division was formed in April 1978 during the Bureau-wide reorganization implemented at that time. This Division, with a staff of just over 50 is one of six Divisions that make up the Center for Materials Science. Its history goes back several decades: the (somewhat larger) predecessor was called the Inorganic Materials Division, which received that name in 1964. During the quarter century before that date the Division was known as the Mineral Products Division.

The present activities of the Division can best be described in terms of the Task Structure:

Task 1215-1.	Structural Chemistry for Ceramic Processing and Durability
1215-3.	Structural Methods for Processing, Manufacturing, and Durability
1215-4.	Properties, Structure, and Standards for Glass and Optical Materials
and 1215-5.	Durability of Ceramics and Glass in Service Environments

Another way of classifying the Division's work would be by disciplines: Solid State Chemistry (1), Solid State Physics (4b), Structure of Crystals (Crystallography) (3), and Structure of Glass (Vitrous State) (4a). Because most of the Division's activities are concerned with ceramics, glass, and optical materials, there is much emphasis on high temperature research.

A lot of the work has to do with materials characterization as a basis for scientific understanding and technological applications. Characterization logically leads to four activities that relate to major Bureau programs:

Data Centers - Crystal Data, Phase Diagrams, Materials Performance for Energy Applications

Standard Reference Materials - Glass Properties, X-ray Standards, Thermal Expansion

Nondestructive Evaluation - Eddy Current, Light Scattering

Resource Recovery and Recycling - Waste Glass, Fly-ash (incinerators)

Characterization also implies special, sophisticated measurement techniques. Within the Division there are a number of experimental facilities, some of which are used throughout CMS and NML and are partly supported by those units. A partial list of these instruments includes the Raman facility, the diamond anvil pressure cell, the Scanning Electron Microscope, a number of x-ray diffractometers (among which is a microdiffractometer), DTA and TGA equipment, an apparatus for thin film deposition and characterization, and instrumentation for measuring the refractive index n (as well as dn/dT and dn/dP) of optical materials.

During this year two events took place that have thoroughly affected the operation of the Division. The first was a result of internal (NBS) reprogramming and the second was caused by a sudden change in policy of the Department of Energy.

During the summer of 1978, it was decided that the Bureau would embark on a sizable program in the area of Electronics (VLSI) and that this activity would be strengthened by a transfer of half a dozen scientists from the Solid State Materials Group of this Division to the Center for Electronics and Electrical Engineering. During the first half of FY 1979 this group was encouraged to educate themselves in the area of semiconductor physics and to start some experimental work in this field. The actual reassignment (accompanied by a transfer of a significant part of the Division's base funds) took effect on February 25, 1979. Although the departure of one half of the Solid State Materials Group constitutes a severe loss, the remaining half guarantees the continuation of solid state physics research which is essential to the Division's program. This group contains a number of scientists well versed in the optical and transport properties of materials.

The second event was the sudden cancellation by the Department of Energy of funds earmarked for the continuation of the six-year old NBS-DoE program on development of MHD-materials. Although about one-third of this money was restored in the second half of the fiscal year, the financial health of the Division required a reduction of force involving five staff members.

At the end of FY 1979 it appears that the Division has recuperated rather well from these two shocks.

The Glass Technology Group has initiated a program concerned with the preparation and properties of glassy films ranging in thickness from nanometers to micrometers. Scientifically, the emphasis will be on glass formation in films, especially complex layers produced by coevaporation. The possible applications are numerous, including coatings for optical components and solar panels, optical waveguides, film capacitors, displays, etc. During this fiscal year a thin film facility, consisting of separate deposition and characterization chambers was designed, procured, and assembled.

The NDE program on eddy currents for flaw detection in metals has stirred considerable interest of industrial groups and workers in other government laboratories. Another NDE project concerned with the perfection of optical surfaces has just been started.

High pressure research, carried out with the aid of the Bureau's diamond anvil pressure cell, is continuously meeting new challenges both at NBS, and elsewhere. A careful study of CuCl, conducted in cooperation with scientists at Bell Labs. and Stanford University, has shown that this material undergoes a number of phase transitions below 110 kbar, but does not become a superconductor.

Currently, several groups of solids known as "modulated structures" are receiving broad attention from solid state chemists. Several compounds of the scheelite structure [e.g., (LaTh) NbO_{4+x}] that are being studied in this Division, appear to be interesting examples of this group.

Cooperation between scientists at NBS, HDL, and at a ceramics company in Gaithersburg have led to the development of a fluidic-electrochemical (CSZ) cell which measures both the temperature and the partial oxygen pressure of gases and vapors at temperatures up to 1700 °C.

A summary of NBS work on refractive indexes and related parameters of some 14 optical materials (including several halides, oxides, and glasses) was published in February of this year. These data are of prime importance for the design of optical systems, especially for those set ups that involve high power lasers.

Considerable amounts of time and effort were devoted to the formulation of new plans and proposals usually in collaboration with other individuals or groups in NBS. An example of such an undertaking was the preparation of an "Initiative on Materials Processing" (later called "Materials Transformations") between August 1978 and January 1979. Originally, the initiative was divided in four parts: a) thermal processing, b) thermo-mechanical processing, c) coatings and films, and d) powders and particles. The Division was involved in all four items, but only the contribution to part a), which described a program on Glass-Ceramics, made it to the final draft stage. Apparently, because of funding limitations imposed on the overall initiative, even this program is not included in the Bureau's total budget proposal for FY 1981. At present, attempts are being made to strengthen the "Coatings and Films" section as a separate Initiative Proposal. Similar plans are being contemplated for "Powders and Particles." It is obvious that the Division is very much interested in Ceramic Processing and Glassmaking and consequently wants to participate in a Processing (or Transformations) initiative.

Several other studies were conducted during the past year:

A. Composites (included in FY 81 budget, mainly polymers).

B. Interfaces: the application of High Resolution Electron Microscopy will be very important. Dr. Roth intends to spend in FY 80 3 months at the University of Arizona to familiarize himself with this instrument.

C. High intensity x-rays. Members of the crystallography group are part of the competence building effort in this field, involving use of 2 NBS-NRL experimental stations of the synchrotron radiation facility at Brookhaven, which is presently being constructed.

D. Mass and Charge Transport. The Division has a considerable stake in this area in connection with its work on MHD electrodes and fast-ion conductors, etc. The problems of high temperature ionic and mixed ionic-electronic conduction, and their relation to crystal structure are central to the mission of the Division. Recently, discussions have started between members of this Division and of the Chemical Stability and Corrosion Division and the Metal Science and Standards Division aimed at a strengthening of the Center's competence in the area of Transport Processes.

The following pages describe in detail this year's technical and scientific achievements under each of the four Tasks.

Technical Activity

STRUCTURAL CHEMISTRY FOR CERAMIC PROCESSING AND DURABILITY

The major goals of this Task are:

to provide methods and obtain data for the construction and evaluation of phase diagrams of systems containing oxides, sulfides, oxynitrides, etc. Attention will be focused on aluminum-silicates with additions of one to six other oxides, which form the basis of the very important (coal) slags;

to study the composition, phases, and properties of various oxide systems with either random or ordered defects or partly-ordered (modulated) structures and to unravel the relation between the charge transport and nonstoichiometry of these compounds; and

to assess the potential of ceramics and related materials for use in energy conversion devices, for catalyzing chemical processes, and for storing both beneficial and harmful elements and compounds.

As these goals are very broad it is necessary to be more specific in the subtasks under investigation. The materials actually examined in the course of this study can be divided into two groups. The first group consists of the seven most abundant oxides which make up the composition of coal slag and of most high volume refractory ceramic materials (Na_2O, K_2O, CaO, MgO, FeO_x, Al_2O_3, SiO_2). The second group consists of materials of interest for electronic ceramics, electrodes, catalysts, ionic conductors, dielectrics, etc.

The experimental determination of complex phase equilibria in a multicomponent system is a very laborious and time-consuming effort. Therefore, we are seriously examining existing computer programs for prediction of phase equilibria from thermochemical data. We hope eventually to be able to modify such programs to be useful for the prediction of solid-solid and solid-liquid equilibria in complex systems of interest to the ceramic industry.

During the last several years and especially since July 1974, as a response to the national need, much of the work has been directed to the area of materials research for energy conversion. Most staff members in the Task are now working directly on materials problems in several energy-related disciplines. The list of publications resulting from these studies during the past year includes three non-archival summary reports and one large review of materials research. Each of these was preceded by numerous monthly and/or quarterly reports. In addition, twelve talks were given. Many visits were also made by Task members between November 1978 and October 1979 to other university, government, and industrial laboratories concerned with materials research in energy-related activities.

Phase Equilibria

Calculation of Phase Diagrams

L. P. Cook, R. S. Roth, and D. P. Birnie

In an attempt to treat the complexity of crystal/liquid interaction and liquid/liquid separation in seven component silicate melts, recently developed theories of silicate melt structure have been applied and extended. The model used has been derived from that of Masson and others, who based their approach upon the principles of polymer chemistry. The model used is quasichemical in that it deals not with the actual species involved, but with a quantity which summarizes the essential properties of these species, in this case the relative numbers of bridging and nonbridging oxygens in the melt structure. A reasonable amount of success has been encountered in interpreting the liquidus surface of the primary phase field of $KAlSiO_4$ in the system K_2O-CaO-MgO-FeO_x-Al_2O_3-SiO_2 using modified versions of this theory. Similarly, experimental data on high temperature immiscible liquids coexisting with $KAlSiO_4$ has been duplicated surprisingly well using modified versions of the theory with appropriate assumptions. Such interaction between calculation and experimentation provides the best hope of obtaining the necessary understanding of important high temperature silicate equilibria in a finite amount of time.

It is anticipated that programs for the calculation and display of complex silicate equilibria will be developed in the near future on our system. Currently available and undergoing evaluation and modification are programs for the calculation of binary and ternary subsolidus phase diagrams using limited experimental data, and also for the derivation of thermodynamic data from phase diagrams. Such programs will find application in all areas of phase equilibrium research and utilization, but especially in any future research related to fossil fuel conversion and nuclear waste disposal. Ultimately, published equilibrium diagrams may be analyzed and discussed with the aid of such programs.

Preparation of "Phase Diagrams for Ceramists"

L. P. Cook, R. S. Roth, T. Negas, and R. Bird

Editing of the 1300 commentaries and diagrams for the 1980 Supplement is approaching completion. While the number of commentaries is about 50% larger than in the 1975 Supplement, the individual commentaries are somewhat shorter, and so it is anticipated that the new Supplement will be about the same size as preceding editions. As of August 1 the totals for the various chemical groupings were: metal-oxygen (110); oxides (388); oxygen-containing radicals (77); halides only (324); halides with other substances (179); cyanides, sulfides (69); oxycarbides, oxynitrides (10); aqueous systems (112); CO_2-containing systems (18); and systems with H-C-N-O-S gases (32). It should be noted that oxycarbides/oxynitrides, CO_2-containing systems, and gas-containing systems are new categories. It is anticipated that the oxycarbide/oxynitride categories will continue to expand with increasing interest in these relatively new materials, especially the SIALONS. To aid the ceramist in dealing with the increasingly numerous problems related to ceramic-gas and ceramic-fluid interaction, a new section containing relevant gas phase equilibria has been added. It has been convenient to distinguish a separate section for phase equilibria in systems containing CO_2-bearing fluids, as these involve primarily high pressure equilibria.

Use has been made of an "intelligent" terminal with editing capability to store entries for the 1980 Supplement on magnetic tape, and sort them according to the "Phase Diagrams for Ceramists" classification scheme. Using other programs in conjunction with the central computing facility, a cumulative index is being prepared. Use of sorting routines has proved indispensable in carrying out the final editing and arrangement of the publication. It is anticipated that the computer will become used much more extensively in "Phase Diagrams for Ceramists" data processing.

The aid of two additional contributing editors has been enlisted. Professor D. Kolar of the Josef Stefan Institute, Ljubljana, Yugoslavia, is assisting with the Eastern European phase equilibrium studies for which English translations are difficult to obtain. Dr. J. Coutures, CNRS, Odeillo, France, is helping with the refractory rare-earth oxide systems, many of which are being studied in his solar furnace laboratory. A meeting of U.S. contributing editors, as well as Prof. F. Glasser, University of Aberdeen, was held at the American Ceramic Society Annual Meeting (May 1979) in Cincinnati.

Most of the material from the first list of some 700 references with 1700 phase diagrams for potential inclusion in the 1983 Supplement has been received from the contributing editors. However, review of this material and mailing of additional lists has been delayed pending completion of editing of the 1980 Supplement, anticipated by October 1, 1979.

Crystal Chemistry

Crystal Chemistry of Potential Mixed Conductors and Electrode Catalysts

T. Negas, R. S. Roth, J. L. Waring, M. C. Austin, and C. L. Skarda

An investigation of the thermochemistry in the $YFeO_3$-$Ca_2Fe_2O_5$ system was completed. The perovskite, $YFeO_3$, accommodates <0.10 Ca in $Y_{1-x}Ca_xFeO_3$. Although excellent p-type conductors, the perovskite-based materials are limited by melting at temperatures as low as ~ 1420 °C. Several nonstoichiometric materials within the Ca-rich portion of the system were detected but not characterized completely. Results were reported by R. S. Roth, T. Negas, and C. L. Skarda at the American Chemical Society Conference, 1979.

Varying levels of dopants in $Y_{1-x}M_xCrO_3$ (M = Ca, Mg) and in $YCr_{1-x}Mg_xO_3$ were investigated using specimens prepared by thermal sintering and hot pressing methods. Reduced materials (∿ 10^{-15} atm, P_{O_2}) are highly resistive and characterized by Cr^{3+} and oxygen vacancies, $Y_{1-x}Ca_xCr^{3+}O_{3-x/2}$. After oxidation at elevated temperatures ($P_{O_2} > 10^{-6}$ electrical conduction is of the p-type and stoichiometries conform to $Y_{1-x}Ca_xCr^{3+}_{1-x}Cr^{4+}O_3$. Under oxidizing conditions, $YCrO_3$ incorporates Ca^{2+} at least to x = 0.10. However, the material at x = 0.10, when reduced, disproportionates to a multiphase assemblage. Reoxidation, involving re-solution of exsolved phases, result in severe fissuring of dense ceramics. Correlations were made among electrical data, processing parameters, bulk and microchemistry, and microstructure. Thermal diffusivity/expansion data were obtained. Results were reported by T. Negas, W. R. Hosler and L. Domingues at the International CIMTEC Conference, Italy, 1979.

In cooperation with HDL and a private company, a ceramic sensor for simultaneous measurement of P_{O_2} and T° was developed. The device combines a conventional P_{O_2} sensor (ionic conductor, e.g., doped ZrO_2) with a fluidic capillary system that measures temperature directly. A common working/reference fluid (e.g., air) is utilized. Fabrication is being performed by a private company to yield prototype sensors which can be tested/calibrated in the laboratory. Patent applications were filed at HDL (T. Negas, L. Domingues, T. Drzewieki, R. Phillippi).

Crystal Chemistry, Crystallography and Electrical Conductivity In Rare-Earth Niobates and Tantalates

R. J. Cava, R. S. Roth, T. Negas, H. S. Parker, and D. B. Minor

Previous oxidation-reduction experiments in this laboratory indicated that $CeNbO_4$ and $CeTaO_4$ could be made to accommodate excess oxygen by the change of normally present Ce^{3+} to Ce^{4+}. The kinetics of the oxidation process suggested the possibility of fast oxygen transport. However, the conductivity in these materials would be difficult to study due to the limited P_{O_2}-temperature stability ranges of the oxidized polymorphs. We, therefore, decided to study the lanthanum analogues, $LaNbO_4$ and $LaTaO_4$, doped with ThO_2 and WO_3. The oxygen excess phases which result are not P_{O_2} sensitive, at least between 10^{-5} atm and ambient. In addition, in these materials in which mixed valence atoms are not present, hopping-type electronic conductivity should not occur.

Conductivities were measured on polycrystalline ceramic pellets by complex impedance techniques. Measurements at frequencies between 60 Hz and 13 MHz were made on the network analyzer in Dr. A. D. Franklin's laboratory in the Chemical Stability and Corrosion Division. An apparatus was constructed which allowed conductivities to be measured up to 1000 °C, in air or mixed gases. Studies were generally conducted at $P_{O_2} > 10^{-6}$ atm to preclude the possibility of reduction of niobium. The apparatus is also capable of measuring the Nernst potential to determine the oxygen transference number.

$LaTaO_4$ Based Materials - All rare earth niobates and tantalates (RE)(Nb,Ta)O_4 display structures which are distortions of the $CaWO_4$ structure type, except for the tantalates of La, Ce, and Pr. In earlier studies, we discovered a monoclinic-orthorhombic phase transformation in these materials at high temperatures. The structure of the orthorhombic phase was unknown. Attempts to grow large single crystals of $LaTaO_4$ from the melt (m.p. about 2100 °C) were unsuccessful as they could not be cooled through the orthorhombic-monoclinic transition without shattering. Small single crystal fragments were studied at 300 °C on a precession camera and the space group of the orthorhombic phase was determined. Its structure was determined by powder profile analysis in cooperation with Dr. A. Santoro of the NBS Reactor Radiation Division, and found to be of the $BaMnF_4$ structure type.

Accommodation of excess oxygen in this structure was studied by investigating the $LaTaO_4$-$ThTaO_{4.5}$ and $LaTaO_4$-$LaWO_{4.5}$ phase equilibria. Up to 20% $ThTaO_{4.5}$ and 25% $LaWO_{4.5}$ can be accommodated in $LaTaO_4$ at high temperatures, without any apparent crystallographic change. In the process of the study, small single crystals of $ThTaO_{4.5}$ and $LaWO_{4.5}$ were grown, and their symmetry and unit cell dimensions determined. Due to the refractory nature of the $LaTaO_4$ based compounds, acceptable high-density ceramic pellets for conductivity measurements have not yet been fabricated.

$LaNbO_4$ Based Materials - Accommodation of excess oxygen in these $CaWO_4$ related compounds was studied by investigating the $LaNbO_4$-$ThNbO_{4.5}$ phase equilibria. For compositions between $La_{0.94}Th_{0.06}NbO_{4.03}$ and $La_{0.63}Th_{0.37}NbO_{4.185}$, and $LaNb_{0.89}W_{0.11}O_{4.055}$ and $LaNb_{0.78}W_{0.22}O_{4.11}$, excess oxygen is accommodated by the formation of a 2 dimensionally modulated structure. This structure was also observed for $CeNbO_{4.08}$. The characteristics of the modulation were determined as a function of oxygen excess in the thorium doped compounds. These are the first reported oxide materials displaying two-dimensional modulation. A computer program was written to allow the indexing of x-ray powder diffraction patterns of modulated structures for up two-dimensional modulation in a host lattice of average symmetry monoclinic or higher, based on information obtained from single crystal diffraction photographs.

Polycrystalline pellets in excess of 90% theoretical density for $CeNbO_4$, $La_{0.9}Th_{.1}NbO_{4.05}$, and $La_{0.8}Th_{0.2}NbO_{4.1}$ were produced by sintering partially-reacted jet-milled powders at 1350 °C.

The reduced phase $CeNbO_4$ was studied at $P_{O_2} = 10^{-6}$ atm between 400 and 1000 °C. The conductivity of this material was quite poor, being about 10^{-5} $(ohm\text{-}cm)^{-1}$ at 1000 °C. Slow oxidation of the pellet at 520 °C to the $CeNbO_{4.08}$ phase caused it to pulverize, precluding a measurement of the conductivity of that phase.

The conductivities of $La_{0.9}Th_{0.1}NbO_{4.05}$ and $La_{0.8}Th_{0.2}NbO_{4.1}$ were measured in air between 400-1000 °C. They are about 2×10^{-2} and 7×10^{-3} $(ohm\text{-}cm)^{-1}$ at 1000 °C, respectively, with activation energies of 1.4(1) eV, a rather typical value for oxygen motion. Although transference number measurements have not been made, the characteristics of the electrode arcs in Cole-Cole plots indicate that at least partial oxygen ion conductivity is present.

Structures of Other Tantalates and Niobates

R. S. Roth and R. J. Cava

In a continuing cooperative effort with Dr. A. Santoro, Reactor Radiation Division, several large batches of single phase well crystallized oxides have been prepared and characterized by conventional powder x-ray diffraction and by neutron diffraction total profile analysis. A paper has been prepared and submitted with Dr. M. Marezio of Grenoble, France, on the refinement of the structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$ at room temperature. Neutron diffraction data has been collected and the structure at least partially refined for $LaTaO_4$ at 300 °C, above the monoclinic → orthorhombic phase transition.

The problem of the neutron diffraction refinement of the structure of $LiTa_3O_8$ is still not resolved. It now appears likely that $LiTa_3O_8$ may exhibit incommensurate diffraction effects which show up only with neutron diffraction and not with conventional x-ray diffraction (implying that most of this effect is due to the Li^+ ions). In order to check this hypothesis it is necessary to examine a crystal of $LiTa_3O_8$ by a neutron diffraction Weissenberg (or other film) technique. It is planned to attempt this experiment at Grenoble in the coming year.

An attempt will be made to solve the modulated structure of $CeNbO_{4.08}$ by determining the average structure from the neutron diffraction total profile data and then looking at difference Fourier maps. The whole problem of the structure of modulated incommensurate oxide phases is currently under re-evaluation and the mathematical, x-ray and/or neutron diffraction effects are being closely studied. Some of the materials being studied in addition to $CeNbO_{4.08}$ and $LiTa_3O_8$ include $La_{1-x}Th_xNbO_{4+x/2}$, $LaTa_{1-x}Mo_xO_{4+x/2}$, Ta_2O_5 doped with WO_3 or other oxides, $NbZr_6O_{17}$-type phases and $3Al_2O_3 \cdot 2SiO_2$ or other mullite type compounds. A large review paper on "Thermal Stability of Long Range Order in Oxides" by R. S. Roth has been prepared and submitted for publication.

Crystalline Ceramic Materials for (Simulated) Nuclear Waste Disposal

J. L. Waring and R. S. Roth

It has been reported that synthetic rock (SYNROC) comprised of selected minerals can accept into solid solution up to about 20% of high level nuclear waste (Nature 278, 219-223 (1979)). One method postulated to form the SYNROC is by mixing appropriate amounts of TiO_2, BaO, SiO_2, ZrO_2, Al_2O_3, CaO, and K_2O and heating to 1300 °C then slow cooling to form the minerals hollandite ($BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$), Ba-feldspar ($BaAl_2Si_2O_6$), kalsilite ($KAlSiO_4$), and leucite ($KAlSi_2O_6$).

Although these minerals have been characterized in the literature, the interactions between most of the various components has not been investigated. Hollandite and zirconolite are the key components in SYNROC. The hollandite ($Ba_{1+x}Al_{2+x}Ti_{6-x}O_{16}$) is suggested to accommodate K, Rb, Cs, Ba, Se, Pb, Mg, Co, N, Cu, Cr, Fe, Mn, Mo, Rh, Sn, and Zr. The zirconolite ($CaZrTi_2O_7$) is suggested to accommodate Na, K, Ca, Sr, Ba, Pb, Y, Bi, Zr, U, Th, Ta, Nb, Ti, Fe, Mn, and rare earths.

The phase relationships between hollandite and zirconolite have not been established. In a very preliminary experiment three compositions were prepared including $Ba_{1+x}Al_{2+x}Ti_{6-x}O_{16}$ with x = 0 and $CaZrTi_2O_7$. In addition, the five starting components were formulated to yield an equimolar mixture of hollandite and zirconolite. The first specimen yielded hollandite plus rutile, indicating that hollandite does not form in this system with only one or less Ba^{+2} ions per formula unit. The second specimen yielded single phase zirconolite, as expected. The third specimen was completely melted at 1450 °C, well below the melting point of the end members, indicating the existence of a deep eutectic between these two minerals.

Experimental results as mentioned above clearly indicate that there is a need for considerably more experimentation prior to substituting simulated radioactive waste materials into these minerals.

Crystal Growth, Synthesis, and Analysis

Energy Conversion Materials

W. S. Brower and H. S. Parker

The synthesis and crystal growth of phases for identification and structural studies in support of NBS materials research programs and in collaboration with other research laboratories on a national and international basis has continued. A variety of techniques have been utilized, including melt and flux growth techniques as well as vapor transport techniques. The crystals grown for in-house research have included the silicate mullite ($3Al_2O_3 \cdot 2SiO_2$), its germanium analog ($3Al_2O_3 \cdot 2GeO_2$), $La_2W_2O_9$, $ThTaO_{4.5}$ and $ThNbO_{4.5}$. The latter two compounds are of interest as ionic conductors similar to the cerium tantalates and niobates.

Crystals of La_3TaO_7 and La_3NbO_7 were grown and provied to Dr. Jean Galy of CNRS, Toulouse, France, for structural basis. Also, crystals of Hg_2Cl_2 were grown by a vapor transport method directly onto fused quartz "whiskers" to make further handling during study unnecessary (thus avoiding any stress of the crystal). These crystals were also supplied to Dr. Galy for investigation of the structural nature of the low temperature (∼ 100 K) phase transition in this compound.

Some effort has been devoted to synthesis, crystal growth, and phase identification in the complex system $BaO-Nd_2O_3-TiO_2$. The barium titanates are well-known dielectric materials and the recent work of Dr. D. Kolar of the Josef Stefan Institute in Yugoslavia has shown that very favorable dielectric properties exist in compositions in this ternary system (Ber. Dt. Keram. Ges. 55 [7] 346-8 [1978], but the system has not been systematically investigated. As part of a collaborative effort, crystals are being grown of the reported ternary compounds and preliminary structural investigations are being conducted at NBS. Further efforts are in progress to obtain crystals and identification of other complex phases in this system.

Corrosive Reactions in Oxides

H. S. Parker, R. S. Roth, and C. D. Olson

With NASA support, the investigation of the $KFeO_2-Fe_2O_3$ portion of the K_2O-FeO_x system has been completed. The objectives of this study are to examine the nature and extent of sample-container reaction up to and including liquidus temperatures and to provide phase equilibria data of interest in the study of slag-electrode reactions in MHD systems. A further objective of the study is to consider alternate techniques for containerless processing.

It was found that chemical corrosion of platinum by compositions in the 80-100 mole percent Fe_2O_3 range was minimal at temperatures as high as 1600 °C, provided that the sealed container was of sufficient strength to avoid rupture due to the oxygen released from the Fe_2O_3 at temperatures above 1400 °C. The absence of attack was attributed to the low amount of Fe^{+2} in the specimen under the given experimental conditions. Because of excessive potassium volatility during heating at low oxygen partial pressures, compositions in this system do not appear practical for containerless experiments at this time. During the coming year, the compositions of interest will be expanded to include selected regions in the $K_2O-FeO-SiO_2$ system and from these, favorable compositions will be selected for containerless experiments in continuing collaboration with NASA Marshall Space Flight Center.

Scanning Electron Microscope

L. P. Cook, T. Negas, D. B. Minor, and C. D. Olson

The scanning electron microscope has continued to provide essential data for phase equilibrium studies. With this instrument the necessary correlation between microstructure and microchemistry can be made. By careful attention to operating conditions and methods of data reduction, quantitative measurements of crystal/liquid and liquid/liquid partitioning for six elements in silicate melts as a function of temperature were completed. These measurements have provided considerable information on the high temperature solution thermodynamics of multicomponent K_2O-rich melts. It is anticipated that, with the aid of appropriate software, quantitative analysis of oxygen content using the windowless energy dispersive x-ray detector will allow determination of Fe^{+2}/Fe^{+3}-ratio in iron-rich melts.

This facility was utilized extensively to examine electrode/insulator materials tested at the U-02, Moscow, USSR, facility during Phase III (and final) of the USA/USSR joint MHD effort (summer 1978). Electrodes (36) were fabricated from doped-$LaCrO_3$, $LaAlO_3$-$LaCrO_3$ solid solutions, and doped-$LaCrO_3/ZrO_2$-based composites. Insulation was monolithic MgO or $MgAl_2O_4$. Additionally, the performance of the MgO-based insulating wall provided by the USSR was evaluated.

STRUCTURAL METHODS FOR PROCESSING, MANUFACTURING, AND DURABILITY

The program of the Crystallography Group is applied to both to this task and to Task 12155, Durability of Ceramics and Glass in Service Environments. The latter portion of the program is reported in Task 12555. The objectives of the program are to: provide x-ray and thermal expansion SRM materials; publish *Crystal Data*; publish standard x-ray patterns with JCPDS-International Centre; develop new high pressure x-ray method for radial distribution of liquids, correlate with and extend range of our viscosity measurements; determine structures of compounds of interest to industry and government (FDA); develop measurement methods for selected area diffraction and elemental analysis; and improve measurement methods by x-ray diffraction of spacings and intensities.

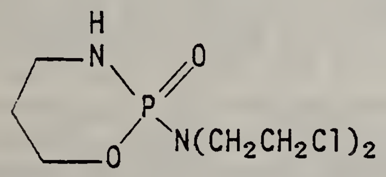
Crystal Structure Analysis

A. D. Mighell, C. R. Hubbard, and J. K. Stalick

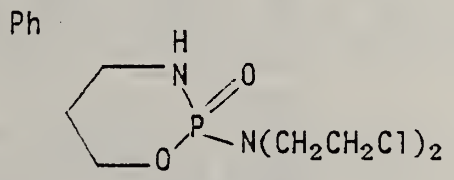
FDA Structural Work: During the year we have collaborated with various scientists at the FDA, Catholic University, Cambridge University (England), and the University of Groningen (Holland), to solve structures of interest to the Food and Drug Administration.

In modern drug studies special emphasis is being placed on the correlation of stereochemistry with the biological activity of a given drug. Single crystal x-ray diffraction provides the structural data required to establish the exact three-dimensional geometry of drugs that are clinically active. From such data one can establish the basis for rationally designed drugs with great potential for the treatment of such diseases as cancer, Parkinson's disease, and schizophrenia. This year x-ray work has been carried out on a compound closely related to cyclophosphamide (an anti-cancer drug), and on two rigid analogs of dopamine (an anti-Parkinson's disease drug).

Anti-cancer drug [Collaborative effort with Prof. G. Zon and V. Himes of Catholic University]: Cyclophosphamide (CP) is a well-known drug which is effective for treating a broad spectrum of human cancers. Among the numerous ring-substituted (CP) analogs that have been studied recently, 4-phenylcyclophosphamide (4-Ph-CP) has been found to be highly active against lymphoid leukemia. Consequently an x-ray structure analysis was carried out on 4-Ph-CP. Unambiguous correlation of stereochemistry and anti-cancer activity in the 4-Ph-CP system will add to a growing body of knowledge on CP and its derivatives and should lead to more potent drugs for the treatment of cancer.



CP



4-Ph-CP

Anti-Parkinson's disease drug [Collaborative effort with J. Rodgers of Cambridge University and Alan Horn of the University of Groningen]: The crystal structures of two tetraline derivatives were determined as part of a study of structure-activity relationships in psychotropic drugs. These rigid analogs of dopamine are especially important as they allow one to correlate molecular conformation with clinical activity. Our structure work not only gave the conformation of these dopamine analogs but also revealed a novel type of stereochemical disorder in both structures.

Miscellaneous Structural Work: Because of the nature of our single-crystal diffraction facility and our close ties with related techniques [e.g., powder diffraction, neutron diffraction, and neutron profile analysis] many collaborative projects with other groups at NBS and at universities are now taking place.

The Syntex diffractometer has been used to identify and characterize unknown crystals, to determine unit cells so that powder patterns can be indexed, and to collect sets of data. Sets of data have been collected for Professor Stewart at the University of Maryland, for Dr. Appleman of the Smithsonian Institution, for Dr. Mathau of the Dental Association, and for Drs. Block and Piermarini. In the latter case data were collected under varying conditions of pressure.

It is hoped that our collaborative work can be expanded and that the x-ray facility can serve as an area facility. Such collaboration helps us to develop the necessary tools [hardware and software] to solve diverse problems in materials science.

Lattice Theory [Collaborative effort with A. Santoro]: Reduction and derivative lattice theory have been applied to the registration of solid state materials; new techniques have been devised to study intra- and interlattice relationships.

a) Registration of solid state materials: A highly sensitive method to identify (or register) solid state materials has been devised. For each compound a solid state registry number is assigned that is based on its lattice and chemical composition. The method has been extensively employed to routinely register materials entering the Cambridge Crystallographic Data Base and the NBS Crystallochemical Identification Tables.

b) Symmetry determination: We have classified all materials in the NBS Crystal Data File according to reduced form. This classification has allowed us to make an analysis of the relationship between the lattice metric symmetry and the crystal-lattice symmetry. It was found that the symmetry predicted from the reduced form is consistent with the crystal symmetry in 97% of the cases. On the basis of this analysis, a symmetry determination procedure that can be adapted to an automated diffractometer has been devised.

c) Inter- and Intralattice relationships: In the study of crystalline materials, it is often necessary to find the relationships between two or more crystal lattices, either identical or different from one another. Typical cases in which a knowledge of lattice relationships is required occur, for example, in the critical evaluation of data to be included in such major compilations as the Crystal Data and Powder Data Files, in the analysis of twinning and coincidence-site lattices, in the study of interrelated structures, in the evaluation of the results obtained for powder indexing procedures, in single-crystal diffractometry, and in many other areas of crystallography.

A practical method to determine matrices relating arbitrary cells of two or more lattices has been devised. The relevant properties of the lattices can then be derived from the nature of the transformation matrices.

This new method for establishing lattice relationships should have an impact on the study of material properties and durability. The method will be used to study coincidence-site lattice relationships, to study the twin laws for materials in the Crystal Data file, to devise better algorithms to index powder patterns, to register materials entering the crystallographic data files, and to identify unknown crystalline materials.

Crystal Data

A. D. Mighell, J. K. Stalick, and R. J. Boreni

The purpose of the Crystal Data project is to collect, to critically evaluate, and to disseminte data on solid state compounds with special emphasis on durability. During the year we have worked on a new subfile of metals and intermetallic compounds, expanded our basis data evaluation program, and constructed a computer file for the identification and characterization of solid state materials.

Metals and Intermetallic Data File: A computer data base of critically evaluated data on metals and intermetallic materials is being built in collaboration with Drs. L. Calvert and Yu Wang of the National Research Council of Canada. This is a collaborative effort consisting of several steps: data will be collected, abstracted, and edited in Canada; a computer printout or a magnetic tape will be sent to NBS; the data will be critically evaluated a second time by NBS editors and computer routines; a computer data base will be built at NBS; publications will be derived at NBS directly from the metals data base.

Basic Data Evaluation Program [Collaborative effort with C. R. Hubbard]: Our data evaluation program has been significantly expanded during this year. New routines to enhance the critical evaluation of data are being added. These routines are designed to check the reported symmetry, to calculate figures of merit for the d-spacings of a powder pattern, and to calculate a quality index for cell parameters. The evaluation program is designed not only to evaluate data, but also to build a data base from which all products can be derived. This program is designed to be used jointly by the Editors of the Crystal Data File and the JCPDS Powder Diffraction File.

Identification: Crystallochemical Identification Tables. These tables will contain key crystallographic data on approximately 60,000 materials. The computer file will be finished in the Fall of 1979. From the computer file, a publication will be derived (in collaboration with B. B. Molino and C. Messina of OSRD) by computer typesetting procedures.

The file is designed so that one can identify an unknown material from any primitive cell of the lattice. The computer version of the file could be attached directly to an automated diffractometer. It is planned to explore the feasibility of such an approach with the Nicolet Co.

Powder Diffraction

C. R. Hubbard and S. J. Carmel

Standard patterns: Six associates of the JCPDS-International Centre for Diffraction Data (M. E. Morris, Director; H. P. McMurdie, Consultant; E. H. Evans; J. deGroot (Retired May, 1979); B. Paretzkin; and M. D. Owen) continue to collaborate with two NBS employees (C. R. Hubbard and S. J. Carmel) in producing powder diffraction data and in editing and evaluating data from the literature. Section 16 of NBS Monograph 25 will be published in September, 1979. It is the 26th of the series of "Standard X-ray Diffraction Powder Patterns." Section 16 contains 58 experimental patterns and 28 calculated patterns, as well as a review of methods used at NBS for obtaining both the experimental and calculated patterns.

The major emphasis of the JCPDS is to produce subfiles for selected markets. Such subfiles enable a user to search for an unknown material or chemical without the necessity of dealing with the entire file of approximately 30,000 compounds. Subfiles currently available are: (1) Frequently Encountered Phases, (2) Minerals, (3) Metals and Alloys, and (4) NBS patterns. Future subfiles are forensic materials and ceramics. M. E. Morris is the chairperson for reviewing and improving the Frequently Encountered Phases (FEP) subfile. Under her direction the associateship is replacing poor patterns in the FEP subfile with high quality patterns. Of the 58 experimental patterns of Section 16, Monograph 25, nearly 85% are for the FEP subfile. In FY 80 the majority of the experimental patterns will be for this subfile. The other experimental patterns will be minerals, forensic materials, or ceramics.

The majority of the calculated patterns were of drugs listed on the Drug Enforcement Agency list which were also absent from the file. Data for these calculations were obtained from the Cambridge Data Center.

JCPDS Activities: NBS staff members continue to participate in technical activities of the JCPDS. C. R. Hubbard is chairman of the Educational Subcommittee. This subcommittee has prepared a tutorial workshop on use of the Powder Diffraction File (PDF) which was presented to over 200 scientists at three national meetings. The subcommittee is also committed to organizing scientific sessions at the Denver X-ray Conference and other meetings such as the session on Crystallographic Data Bases for Chemists to be presented at the ACS meeting in Washington, D.C., September 1979. In less than one year the powder diffraction search/match component of the Chemical Information System (CIS - a coordinated package of over 10 chemical data bases organized by NIH and EPA) has become the third most used component. A. D. Mighell and C. R. Hubbard continue to advise on the development of the JCPDS-NIH/EPA agreement to place the PDF on the Chemical Information System's international computer network. They also continue their efforts to improve the editorial process of the JCPDS and serve on various subcommittees. The JCPDS task group on data base design (C. R. Hubbard, chairman, A. D. Mighell, member) has evaluated options for data entry. The recommended choice is a CRT terminal with forms input capability and local storage. A HP2645 terminal has been programmed and tested for input to AIDS, the data evaluation program. To move to a computer based data base AIDS must be expanded. Jointly with Crystal Data, new input formats and data items have been documented. Programming modifications and enhancements are to be completed by September 1979. The completed program will be made available to the JCPDS and scientists throughout the world. The use of a common program for data evaluation and data base building will likely lead to data sharing and cross checking between the JC and Crystal Data.

Symposium on "Accuracy in Powder Diffraction": The symposium was held at the National Bureau of Standards, Washington, D.C., June 11-15, under the sponsorship of NBS, the National Research Council of Canada, and the International Union of Crystallography. The chairman was S. Block, and C. R. Hubbard was a member of the organizing committee. Talks covered all aspects of accuracy in the powder method and various applications. The proceedings will be published by the NBS and will be available from the National Technical Information Service, Washington, D.C.

Guidelines for Publication of Powder Patterns: The ACA committee on guidelines for publication of powder patterns (C. R. Hubbard, member) presented a preliminary report at the ACA Winter meeting and a final report at the NBS Symposium on Accuracy in Powder Diffraction. The need for the guidelines is a result of the growing size of the Powder Diffraction File, the greatly increasing use of computer search/match methods, and the recent developments in improved data collection. The quality of the file of reference patterns is the limiting factor in phase identification. Reference patterns from NBS are often far superior in both d-spacing and relative intensity values to those reported in the literature. The proposals of the ACA committee, which closely parallel the techniques and methods used at NBS, have been forwarded to the ACA for presentation to the International Union of Crystallography.

Phase Identification: An unusually large number of samples were submitted to C. R. Hubbard and S. J. Carmel for qualitative phase analysis by powder diffraction. Included were samples of SiC (α or β polymorph), compounds from ashing recycled oils, zinc phosphate samples, and dental ceramics from Dental Research. C. R. Hubbard and C. R. Robbins participated in a national round robin on analysis of low temperature ash of coal. The main constituents found in the coal ash were quartz, calcite, pyrite, illite, kaolinite, and marcasite. (Also see Materials Characterization and Analysis - C. R. Robbins.)

Energy Dispersive X-ray Diffraction

F. A. Mauer

A detailed study of factors affecting intensity and resolution in energy dispersive powder diffraction has been carried out in order to optimize the experimental conditions for obtaining x-ray diffraction data with the diamond anvil cell. Improvements in equipment and techniques have led to obtaining better data in less time and, thus, have enhanced NBS capabilities for high pressure crystallographic studies.

The factors studied include size, intensity distrubition of the white radiation source, absorption in the diamonds, beam divergence and partical size of the sample, as well as collimator and slit system design.

Radiation from a tungsten tube has been found to give the best approximation to the desired white radiation source. The characteristic lines of the L series of tungsten occur below 12.1 keV where the absorption in the diamond is so severe that no useful data could be recorded in any case. A digital offset of 256 channels is used to eliminate this useless portion of the spectrum.

A considerable enhancement in the intensity of the region of interest in a diffraction pattern by a judicious selection of the diffraction angle, 2θ, is possible. An improvement by more than a factor of ten can sometimes be realized. We have modified the design of the diamond cell to provide an exit window for the diffracted beam extending from 0 to 27° in 2θ. This extended range not only provides the needed flexibility for optimizing 2θ, but also makes it possible to observe reflections which would occur beyond the limit of the Ewald sphere for CuKα radiation. We have also devised a graphical representation of powder patterns which is useful in selecting the best diffraction angle to avoid interference from characteristic lines and sample fluorescence. By plotting E versus $1/\sin\theta$ for each $d_{hk\ell}$ a series of straight lines through the origin is obtained which show at a glance the location of each diffraction line at any diffraction angle.

Because of the extremely small volume of the sample in the diamond anvil cell, the number of crystallites is often too small to justify the basic assumption of powder diffraction--that all possible orientations are represented with equal probability. As a result, lines may be missing, or their intensities may be greatly distorted. Increasing the divergence of the x-ray optics is a possible approach to the alleviation of this problem, but leads, in turn, to line profiles that may be shifted with respect to the true energy calculated for a given d-spacing. Powders must be ground to a particle size well below 30 μm (400 mesh), or the sample must be oscillated to obtain reproducible intensities, with none of the line missing. With these precautions, as well as accurate alignment of fine collimators to eliminate diffraction lines from the gasket and scatter from the diamond, it is possible to obtain good patterns with low background and well resolved peaks in about four days. Results on CuCl, CdS, and ice VII are presented in the section on high pressure studies. Further, substantial reduction in the time required to obtain diffraction patterns and improvements in their accuracy will have to await the availability of a synchrotron or rotating anode x-ray source.

Standard Reference Materials

C. R. Hubbard

The powder diffraction SRM project began with the certification of SRM-640 Si powder as a 2θ standard. This SRM has sold over 550 units since 1975. A large d-spacing SRM to supplement the Si powder has been the subject of an extensive search. Criteria have been established and several candidate materials identified (MoS_2, sodalite, phlogopite, fluorophlogopite, muscovite, and acid phthalates). Sources of large quantities of each of these materials are being located. By September 1979 one or two materials will be selected. Using powder and single crystal methods the selected materials will be certified during FY80. The cell parameters must be accurate to a few parts in 10^5. To achieve this level of accuracy improvements in determining peak location and calibrating the powder diffractometer are required. Least squares programs for calibration purposes have been developed. Methods to locate peak positions to a few thousandths of a degree have been surveyed. One or two methods will be implemented. For quantitative analysis and for testing instrumental intensity response five materials were selected and preliminary measurements were completed in FY78. To improve on accuracy of the relative intensities (I^{rel}) and reference intensity ratio (I/Ic) measurements a sample rotator has been modified to work with one of the automated units. I^{rel} and I/Ic certification will be completed in FY79. The discrepancy between the experimental and calculated patterns of α-Al_2O_3, the primary reference material for reference intensity ratios, has been ascribed to aspherical electron density in preliminary work done collaboratively with L. Calvert of NRCC. I/Ic values can be calculated from single crystal structural data and a numerical constant based on the structure of α-Al_2O_3. Reducing the error in the numerical constant from α-Al_2O_3 will reduce the error in derived I/Ic values and thereby lead to more accurate quantitative phase analysis. The reference intensity ratio method of x-ray powder diffraction quantitative analysis is a fundamental constant method for quantitative phase analysis. Measurement of these constants has been improved at NBS and methods are reported in Monograph 25. NBS-260 publication on use of 2θ standards and intensity standards are to be completed in FY79.

High Pressure Studies

S. Block, G. J. Piermarini, and R. G. Munro

During this year we have conducted a survey of the literature on high pressure research with the diamond anvil cell. The survey covered the years 1960 through 1978. Figure 1 shows not only the importance of the development of the diamond cell at NBS in the early sixties but indicates the even greater significance of the NBS-pressure scale introduced during the period 1972-75.

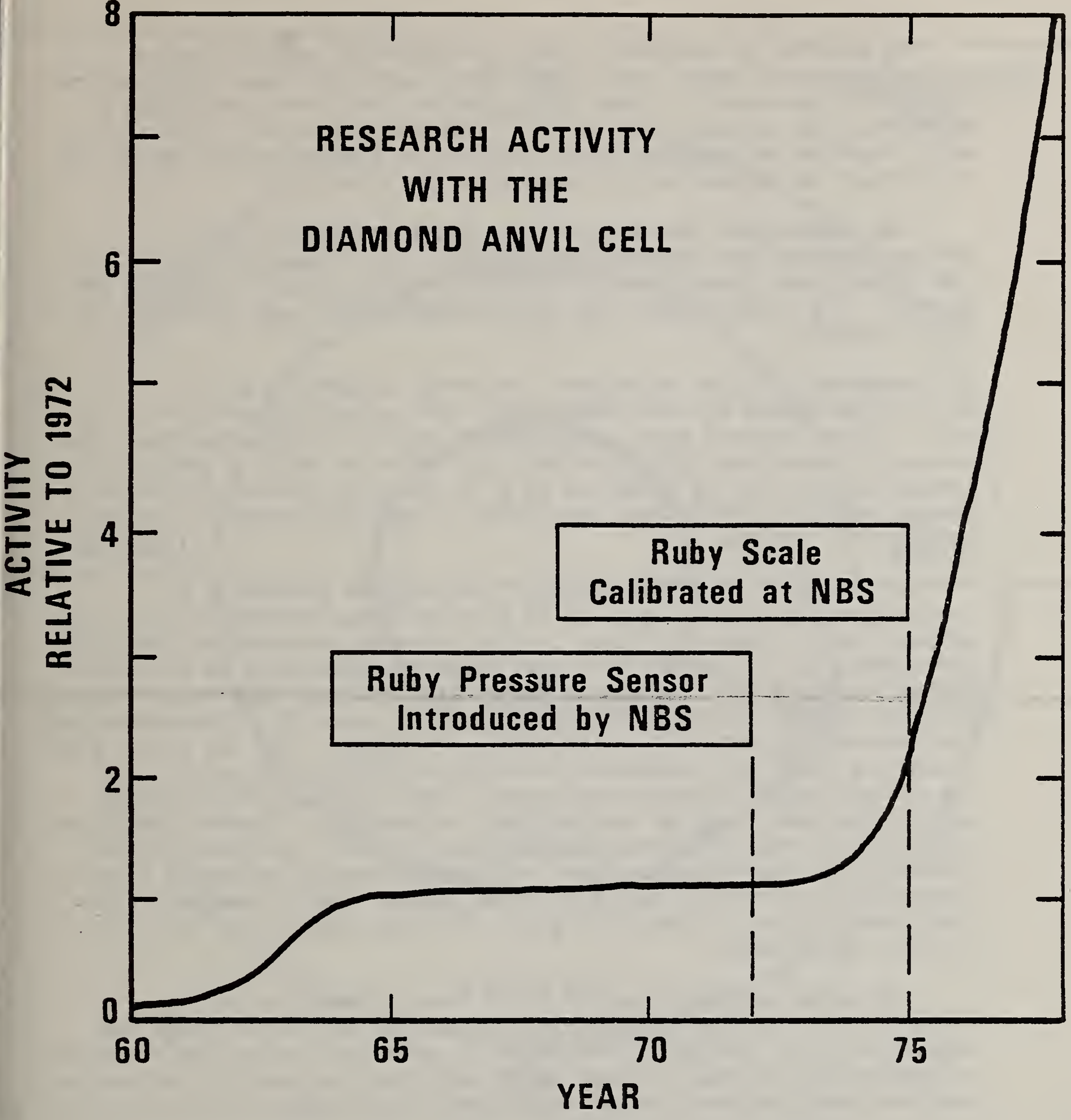
The fact that the experimental chamber is easily and conveniently accessible by radiation (light, x-rays) has stimulated research in structure, phase transition, bonding, mass transport, and electrical properties. Recently we have carried out work on viscosity, structural, and electrical properties of semiconductors, compressibilites of S_4N_4 and H_2O, and initiated work on the melting point of refractory metals.

Viscosity: The recently developed diamond anvil cell falling-sphere viscometer has been utilized to measure the pressure dependence of the viscosity of stable and metastable n-butyl chloride. This substance was chosen as being suitable for a cooperative intra-NBS investigation of metastable states of matter. The equilibrium freezing pressure (2.3 GPa) and the glass transition pressure (4.2 GPa) were determined at room temperature by separate measurements to identify the region of metastability (2.3 GPa $\leq p \leq$ 4.2 GPa). The viscosity was then obtained starting at a pressure of 1.94 GPa. This transport property was found to vary smoothly through the transition from the stable to the metastable state.

The viscosity results for n-butyl chloride were also used in conjunction with the critical point viscosity model,

$$\eta = A(1-P/P_g)^{-\nu}$$

where η is the viscosity, P_g is the glass transition pressure, and A and ν are other parameters. Use of the model makes it possible to obtain a reasonable estimate of the glass transition pressure if the viscosity as a function of pressure is known for sufficiently high pressures. Values of P_g have been determined in this fashion for n-butyl chloride, 4:1 methanol-ethanol, and isopropyl alcohol, and the results have been used to confirm the ruby line-broadening method of determining glass transition pressures. For the noted liquids, the model yields, respectively, 4.6, 10.2, and 5.1 GPa for P_g, and the ruby method yields 4.2, 10.4, and 4.5 GPa.


RESEARCH ACTIVITY
WITH THE
DIAMOND ANVIL CELL
ACTIVITY
RELATIVE TO 1972
0
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YEAR
Ruby Pressure Sensor
Introduced by NBS
Ruby Scale
Calibrated at NBS

Fig. 1

In addition to confirming the line-broadening method finding P_g, the viscosity model might prove to be useful for describing the properties of lubricants. Since lubricants are used under conditions of widely varying stresses, the value of the exponent in the viscosity model could be an important consideration for evaluating the ability of a lubricant to respond to the changes in the stress.

The temperature dependence of the glass transition in 4:1 methanol-ethanol was determind by the ruby line broadening method. At -48 °C the glass transition is 5.65 GPa yielding $\Delta Pg/\Delta T$ = 0.68 GPa per degree. This value agrees with values obtained at lower pressures for other alcohols.

Metastable States of Matter: An energy dispersive x-ray diffraction system is under development for use with diamond anvil cells. Since diamond anvil cells without special design features place unusually large restrictions on the acquisition of data, a theoretical investigation is being conducted by R. G. Munro to examine the consequences of these limitations for radial distribution function analysis and for cell designs.

An illustration of the nature of the problem created by a limited set of data can be given in terms of a two-dimensional information plane as shown in Figure 2. The plane is described by the polar coordinates (r, Θ) where r is a real space distance and Θ is an integration variable for computing a radial distribution function. The value of the RDF at distance r is obtained by means of an integration of the information contained on the circle of constant r in the plane. The variable Θ forms the integration variable extending from zero to 2π. The plotted points indicate the points in the plane at which experimental data have sampled the available information. The most reliable calculations require information samplings from all quadrants of the plane with an increasingly larger information density occurring as one proceeds from the first quadrant to the fourth. As an example, in the case shown, it can be seen at a glance that the computation for r=0.1 will not be reliable.

The method of investigation is to form a comparison of the reliability of various computational procedures and to construct the comparison as a function of the degree of data limitation. An exact set of data having an exactly known radial distribution function is used so that the absolute error can be determined in each case.

Cuprous Chloride: Electrical, optical, and x-ray diffraction experiments have been carried out on cuprous chloride by us and F. A. Mauer in cooperation with A. Jayaraman, T. H. Gabelle, and G. W. Hull, Jr., of Bell Telephone Laboratories.

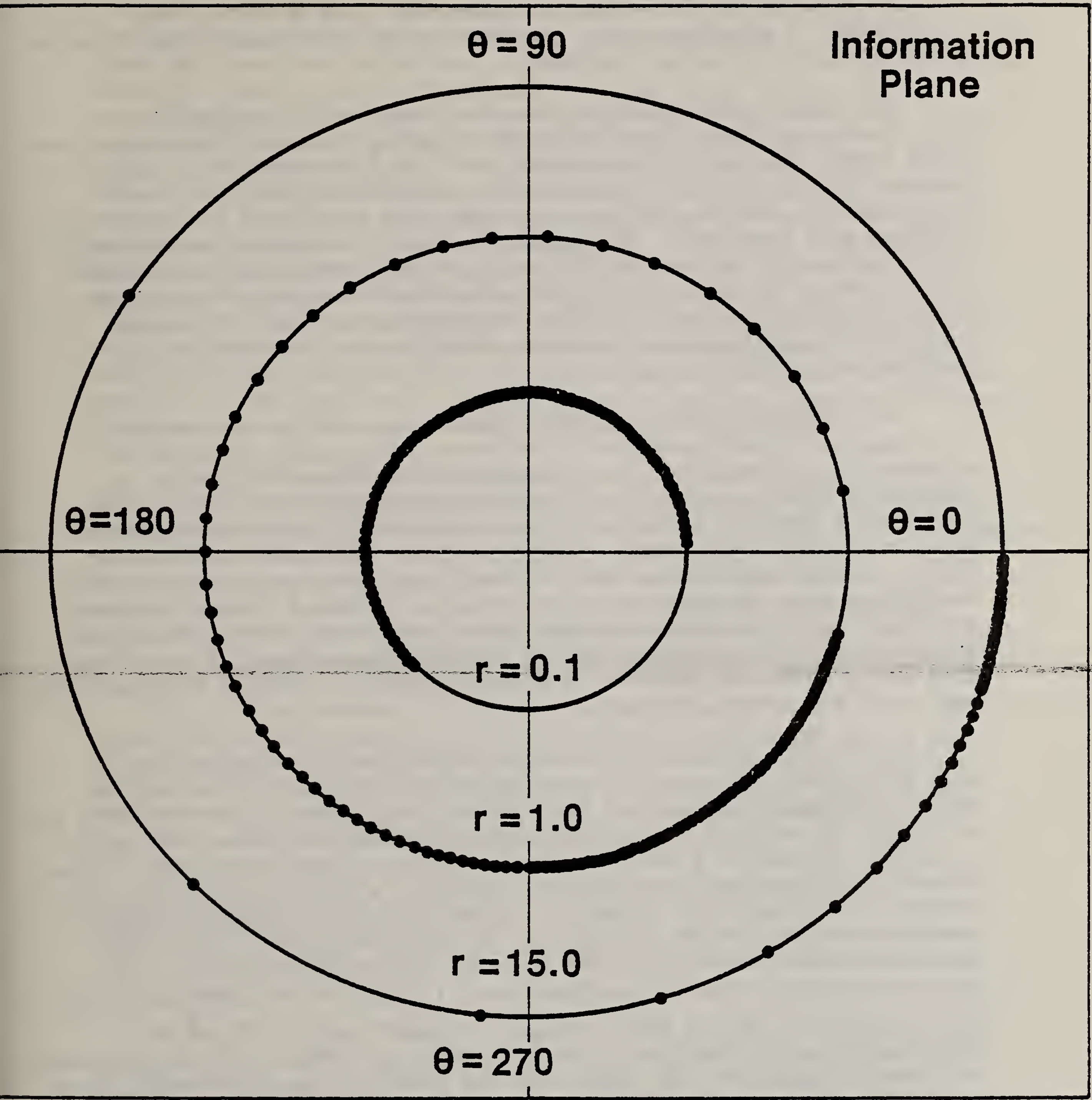

Fig. 2

The behavior of CuCl under pressure has received much attention recently, prompted by the reports that it undergoes a transition to a metallic state at about 4.0 GPa.

The pressure dependence of the electrical resistance of CuCl to pressures up to 14.0 GPa was measured using a recently developed two-probe method adapted to the diamond anvil high pressure cell. An improved version of this method which increases reliability of the measurements, employs a nickel wire mesh as a substitute for the single tungsten wire electrode. Two probe electrical resistance measurements were also made in a diamond cell using an ungasketed anvil arrangement. Bell laboratories also measured the electrical resistance of CuCl in a piston-cylinder device to 5.0 GPa, using a cylindrical CuCl sample encased in a teflon sleeve and with copper contacts on either end serving as electrical leads.

The results of our electrical measurements, which were made on four samples of CuCl prepared by different methods, do not show any evidence for a "metallic" IIa phase even after repeated cycling, as previously reported. No significant photoconduction effect has been observed in the CuCl sample which was determined by carrying out the measurements in the absence of light, in dim red light, and in white light. In the experiments done in the piston cylinder device no large resistance drop was observed in the range of 0.1 to 5.0 GPa, in agreement with our diamond cell results. Employing a polarizing microscope and the ruby fluorescence method of pressure measurement, a transition at 4.6 ± 0.2 GPa was observed in single crystal of CuCl in a hydrostatic medium of 4:1 methanol-ethanol.

The results of our x-ray studies, using both film techniques with ungasketed CuCl samples and a newly developed energy dispersive method with gasketed samples, confirm the transitions from zincblende to tetragonal structures at 4.4 GPa and from tetragonal to the NaCl type structure at about 8.0 GPa. Our x-ray pattern of the black opaque phase taken in an ungasketed diamond anvil consists of NaCl-type lines. We, therefore, believe that in the NaCl phase of CuCl a disproportionation reaction sets in, in the presence of large sheer stress. It is well known that CuCl is unstable with respect to disproportionation. Possible disproportionation reactions are: (1) $2CuCl \rightarrow CuCl_2+Cu^\circ$; (2) $3CuCl \rightarrow Cu^{+}Cu^{++}Cl_3+Cu^\circ$; and (3) $4CuCl \rightarrow Cu_2^{+}Cu^{++}Cl_4+Cu^\circ$ (5,16). In each disproportionation reaction elemental copper is formed, and the presence of a small amount of free copper (of the order of even a percent) could cut off visible light transmission.

In summary, we found no evidence for a dielectric-metal transition either in our resistance measurements or optical observations in CuCl up to 12.0 GPa under hydrostatic or quasihydrostatic pressure environment. We showed that the black opaque phase has the NaCl-type structure and suggest that the opacity might be due to disproportion of CuCl, to free

CdS: Electrical and structural properties of CdS as a function of pressure and temperature was undertaken with F. A. Mauer, (Sponsored by Department of Defense, Watervleit Arsenal). The semiconductor-conductor transition was measured electrically, by energy dispersive x-ray diffraction, and observed microscopically. The transition is dependent on particle size. Single crystals transform at 2.65 GPa while powders transform at 3.25 GPa. Interestingly the slope $\Delta P/\Delta T$ is negative. At 100 °C the transition occurs at 2.49 GPa and at -44 °C the transition is at 3.20 GPa. All measurements were in a 4:1 methanol-ethanol solution and therefore hydrostatic. The glass transition of this solution at -48 °C was determined to be 5.65 GPa. Electrical measurements were carried out in the dark because CdS is highly photoconductive. The two methods of electrical measurement discussed in the CuCl section were carried out to determine whether there was significantly different conductivity perpendicaular and paralled to the pressure axis. No significant difference was found and therefore the transformation is uniform and not in a layered configuration.

X-ray diffraction studies were carried out above and below the transition. The transition is from the zincblende structure where each atom is tetrahedrally coordinated to the sodium chloride structure where each atom is octahedrally coordinated. Preliminary results indicate that the low pressure phase has a volume compressibility of -3.1% to the transition and an additional -19.3% upon transforming to the high pressure form. This large volume change probably explains the increase of x-ray linewidth we observed when the sample was rapidly decompressed.

S_4N_4: The compressibility of S_4N_4 was studied with J. K. Stalick (sponsored by Department of Defense, AROD) to a pressure of 4.2 GPa using the new single crystal diamond anvil pressure cell. A single crystal of S_4N_4 was first mounted on a glass fiber and the unit cell determined by centering 15 reflections on the Syntex diffractometer. The cell parameters of the monoclinic unit cell (a = 8.791(1), b = 7.1735(13), c = 8.700(1) Å; β = 92.47(1)°) agree with those obtained from a single crystal placed within the pressure cell with no external pressure applied. Unit cell data were also determined at pressure of 1.3, 3.0, 3.7, and 4.2 GPa. At 4.2 GPa the cell parameters decrease to a = 8.156(21), b = 6.667(5), c = 8.162(8)Å; α = 89.93(7), c = 91.74(16), γ = 89.90(15)°. The volume of the unit cell decreases from 548.1(2)Å^3 to 443.7(13)Å^3, a reduction of 19%, while the a and c axial lengths become equal within the accuracy of the measurements. The monoclinic metric symmetry is retained to 4.2 GPa.

It is planned to attempt compressibility measurements at higher pressures. This may not be possible owing to the increased broadening of the reflections with increased pressure, which results in the larger standard deviations reported.

ICE VII: In collaboration with G. E. Walrafen of Howard University, high pressure Raman and x-ray diffraction experiments were carried out on water. The group at Howard University carried out Raman studies in a diamond anvil cell. They determined that the O-H vibrational frequencies of ice VII shifts downward with pressure and they expected that the shift would correlate with O-O distances. We carried out powder diffraction studies using wavelength dispersive film and energy dispersive counter techniques. These x-ray studies were carried out to 20.2 GPa. As ice VII is body centered cubic the O-O bond distance is simply related to the cell constant $d_{O-O} = \sqrt{3}/2\ A_0$. The cell dimensions change from 3.355 Å at 2.36 GPa to 3.035 Å at 20.2 GPa indicating a Δ/V_o of 26% and a shortening of the O-O bond distance from 2.906 Å to 2.638 Å. There is a sharp break in the compressibility at approximately 15.86 GPa with very little change afterwards in A^0(3.052 to 3.035 Å). This probably indicates that the repulsive forces become highly significant.

Melting Point: Work was initiated on the pressure dependence of the melting point of refractory metals (Sponsored by Department of Defense, Watertown Arsenal). The first material to be studied is tantalum. This is a joint effort with A. Cezairliyan of the Thermophysics Division of the Center for Thermodynamics and Molecular Science. They will use their millisecond heating apparatus to determine the melting points. Resistive heating will be used. A sample configuration has been designed, built, and tested at ambient pressure outside the cell. The sample configuration gives an excellent melting point and a diamond anvil cell has been modified to accept the sample and be compatible with the millisecond temperature apparatus. Experiments are currently underway to test these modifications.

Thermal Expansion

T. A. Hahn

Thermal expansion measurements have been somewhat curtailed because of manpower limitations. Nevertheless, quite a range of materials was investigated, mainly on request of research groups in and outside NBS. The thermal expansion of Incoloy 800 was measured for the Fracture and Deformation Division. Incoloy 800 is a high temperature corrosion resistant alloy that is being extensively used in high temperature energy related plants. The thermal expansion was measured on a candidate MHD electrode material spinel $9[Y_{0.85}Ca_{0.15}FeO_3] + CaZrO_3$ to support work in our Division. Plus, measurements are in progress on the recertification of SRM 736 Thermal Expansion Copper. The original stock of the material has sold out.

As has always been the case, we continue to support other NBS activities by providing thermal expansion data and consultation on expansion measurements. For example, R. S. Polvani (Fracture and Deformation Division) is concerned with the long-term stability of beryllium used in gyroscopes. One source of instability was shown to be the thermally generated microstresses in the Be due to natural inclusion of BeO with its much lower thermal expansion. A paper on this topic, in collaboration with R. W. Armstrong (University of Maryland) was presented to the Maryland Institute of Metals.

Consultation with R. P. Whitlock of the Dental Section on the measurement of the thermal expansion of dental porcelain has contributed to the understanding of the failure of porcelain coatings on base metal dental protheses.

We also consulted with a variety of people who were trying to resolve measurement problems or merely contemplating setting up thermal expansion laboratories. A few of these include G. Gill and M. Haller of Dentsply International, W. Wagenbreth of P. T. B., and A. Clark of NBS Boulder. Requests for information on thermal expansion and its measurement or requests for NBS papers on thermal expansion were supplied to about twenty different people this year. A couple of notable requests were: 1)information on the thermal expansion of fused silica at low temperature that is of critical importance in an apparatus designed by B. Cabrera of Stanford University for a test of general relativity; and 2) correspondence with S. J. Bennett of NPL on the thermal expansion of copper and the possibility of joint thermal expansion standards with the U. K.

We also continue to support ASTM activities in Committee E37 on Thermal Expansion. Presently both the dilatometric and interferometric test method are being revised and a new test method is being written for TMA apparatus which is extensively used in the plastics industry.

Materials Characterization and Analysis

C. R. Robbins

Power Plant Ash: This is a highly variable material. Its chemical composition and physical properties are primarily functions of fuel feedstock, variances in plant equipment, burning methods, station loading, aging, and collection, separation, and storage methods. Whether the ash is to be regarded and managed as a large volume mineral resource or as a hazardous waste remains to be seen. There is an urgent need for chemical and physical characterization of these materials.

A collaborative effort with the Office of Recycled Materials to study power plant ash has been initiated. The study will involve development of quantitative methods of phase analysis by x-ray powder diffractometry and will be complemented by several instrumental methods of chemical analysis. The work will produce a body of information on the behavior of a broad spectrum of fuel feedstocks, burned in a variety of plants under known operating conditions. This systems approach has not been explored before. The study will provide data needed for ash management techniques and for a better understanding of leaching mechanisms. It could lead to improvements in precipitator and scrubber designs, and to better utilization of coal byproducts.

A collaborative study with the Smithsonian Institution (V. Steponaitis, Predoctoral Fellow in Anthropology) of prehistoric pottery from Moundville, Alabama, is near completion. Moundville is the second largest Mississippian site in eastern North America and was occupied between A.D. 900 and A. D. 1600. A quantitative mineralogical study by optical and x-ray methods has identified the raw materials used, and the range of firing temperatures reached in making the pottery. Physical property measurements (made in collaboration with another group at NBS) have been correlated with the phase composition of the pottery.

Work with the Fracture and Deformation Division (E. R. Fuller, Jr.) has continued in the form of phase analysis of candidate refractories and cements for energy-related applications. Analysis was by conventional x-ray methods on materials previously subjected to extreme environments.

A collaborative study with the NBS Data Center for Energy Applications (H. M. Ondik, R. C. Dobbyn) has been completed. Chemical reactions that occurred in the refractory lining of the Conoco Coal Development Company's Gasification Pilot Plant (Rapid City, South Dakota) after nine months of operation were studied by optical, SEM, and x-ray diffraction methods.

PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS

The objective of this work is to develop techniques for synthesizing glasses and crystalline solids of special compositions, shapes, structures, and properties; to propose and improve methods for the measurement of chemical and physical properties of glasses and crystals in bulk and in thin film form; to study relationships between properties, structure, and constitution; to assist the glass, ceramic, and optics industries; to provide standard reference materials of use to glass-related and other industries; and to characterize glass and crystalline materials for use as optical components and solid state electrodes.

Physics and Chemistry of Glass

W. K. Haller

Glass, because of its chemical inertness, electrical resistivity, transparency and unique forming characteristics, is one of the most widely used materials. Its applications range from architecture, packaging of beverages and pharmaceutical materials, heat insulation, reinforcer in medical devices, and lasers, to countless applications in the electronics industry. Every year brings new uses of glass, such as encasement of nuclear waste, solar energy devices, laser fusion target shells, etc. Glass is furthermore found in nature as obsidian, and abundant waste products such as coal and blast furnace slags are mainly in the glassy state. The unique structure of glass permits its synthesis over a wide range of stoichiomeries. This characteristic and the fact that it can be produced with extreme homogeneity and in many shapes has made glass the favorite material for analytical standards. There are many defense and national security-related applications of glass. NBS is considered as a national center for glass science and applications in the U.S.A. and its Glass Section has a particularly close relationship with industry and other government agencies.

Vaporization from Glass Melts

D. M. Sanders, J. T. Wenzel, and W. K. Haller

Sodium borosilicate vaporization is of interest to the glass industry because compounds containing boron and sodium appear to have substantial vapor pressures under industrial conditions. These vapors are quite corrosive to tank refractories and the loss of boron is of concern because of its increasing expense and scarcity. The addition of small amounts of boron to soda-lime-silica glass lowers melting and fining temperatures without changing viscosity-temperature characteristics in the glassforming range, potentially leading to substantial energy savings. Boron is also used as a major component in glasses having superior chemical durability for medical fluid containers, chemical lines, and glass fiber thermal insulation. These glass compositions are also resistant to thermal shock, making them useful for applications such as laboratory and kitchenware.

This past year was devoted to establishing experimental procedures for the study of vaporization of boron-containing species from glass melts. Pure boric oxide was chosen as the first system of study in order to establish the collection and analysis techniques. First it was established that steam cleaning of the collection tubes (coated with condensed boron compounds) was necessary to insure the complete transfer of boron compounds from the tubes to an aqueous analyte solution. Second, atomic absorption spectroscopy was found to be the only suitable analytical technique for the determination of boron concentrations in the analyte solution. Atomic emission spectroscopy was tried, but sodium gave unacceptably high interferences with the boron signal. A graphite flameless atomizer emission technique was tried also, but severe memory effects from one run to the next were observed, making this method unacceptable too. Sodium interference in boron analysis by atomic absorption was determined to raise the apparent boron concentrations by less than 10%, for equimolar concentrations of sodium and boron in the analyte. Boron did not interfere with sodium analysis using atomic emission spectroscopy.

After the boron analysis technique was perfected, the reactive vaporization of molten boric oxide with water vapor was studied, in order to collect reference data on a pure substance for future use in a comparison with boric oxide solutions. The temperature of measurements was 1100 °C, and water vapor partial pressure was varied between 1 torr and 200 torr. It was found that for low water vapor partial pressures the log-boron vs. log-pressure dependence was nearly linear with a slope of one-half, while for higher water vapor partial pressures the slope was three halves. This is consistent with a model which proposes the existence of two vapor species above a boric oxide glass melt: HBO_2 is predominant at low water vapor partial pressures, and H_3BO_3 is predominant at high water vapor partial pressures.

Finally, the reactive vaporization from a 16.5-16.5-67.0 mol % sodium borosilicate glass melt was studied, also as a function of the water vapor partial pressure. In contrast to pure boric oxide, the vapor pressure of both sodium and boron was constant for all water vapor partial pressures studied. This interesting result is in apparent contradiction to published experiments, performed, however, under ill-defined conditions. Additionally, the vaporizing species was found to be equimolar in boron and sodium, suggesting that it is probably sodium borate.

Glassy Multicomponent Films

D. M. Sanders and E. Farabaugh

In fiscal year 1980, we will start the production of glassy thin films by simultaneous vapor co-deposition from electron beam and electrically heated sample sources. The purpose of this program will be to explore glass formation by vapor deposition, to investigate the structure of such glasses and to produce amorphous optical reflection and antireflection coatings which have physical properties which meet or exceed those found for presently used polycrystalline films. In the structural study, glassy thin films will be prepared using molecular beam co-evaporation of glass-forming constituents. The composition of the molecular beam mixture will be monitored and controlled by a microprocessor-based mass spectrometer and a quartz-crystal oscillator controller. The composition of the resulting thin films will be analyzed using ESCA, SIMS, AUGER, ISS, and Atomic Absorption Spectroscopies. The beam density and composition will be systematically varied at different substrate temperatures to obtain conditions where preferential bonding will manifest itself in the dependence of film composition on vapor composition.

If this approach proves successful it will provide an experimental basis for determining which, if any, of the many theories of glass structures is correct. In addition, the knowledge of stable compositions in multicomponent glass systems will provide detailed information concerning compositions having maximum homogeneity and minimum absorption and scattering; such data will be useful for producing low loss integrated optics.

In fiscal year 1979, we completed construction of the facility to prepare and analyze amorphous thin films. The facility consists of a deposition chamber having a Titanium sublimation pump (1000 l/s), a Cryopump (4000 l/s), and a Turbomolecular Pump (450 l/s). The chamber has all metal seals and is capable of an ultimate vacuum of 5×10^{-10} mb. The chamber contains fixturing to monitor the reflected and transmitted light during deposition to determine when 1/4 wave optical thicknesses are obtained. To carry out depositions, the chamber contains a triple electron beam evaporation module to permit simultaneous evaporation from three crucibles. In addition, heated boat sources can be added as needed. All sources are controlled using process controllers driven by the output from a microprocessor mass spectrometer. A quartz-crystal monitor is used to determine the thickness of the co-deposited film.

The deposition chamber is connected to a surface analysis system capable of AUGER, SIMS, ISS, and ESCA spectroscopies. Transfer from the deposition position to the analytical position is accomplished using a 40" magnetic linear manipulator without exposing the deposited film to atmosphere.

Viscosity of Glass Near the Strain Point

D. R. Swerdlow, J. T. Wenzel, and D. J. Cronin

This project involves the design and operation of a beam-bending viscosimeter for the rapid determination of glass viscosity in the 10^{10}-10^{15} poise range (sag point to strain point. The apparatus is particularly suitable for glasses (such as fluorophosphates) which cannot be drawn into fibers because of steepness of viscosity curve and/or surface degradition, and, since only small samples are required, for glasses which cannot be cast in large pieces.

Several modifications to the apparatus were made this year. The transducer and head assembly were improved, resulting in more precise measurements and less apparatus drift, and the sample holder was improved, which gave increased dimensional stability and defined distances more precisely. These improvements made possible the absolute measurement of the viscosity of NBS SRM 711, in addition to the slope of the log-viscosity vs. temperature curve. Agreement with published values for the viscosity and its temperature dependence was excellent. Studies on fluorophosphate glasses showed that they increase viscosity by a factor of 10 for each 12 °C decrease in temperature. Because of this strong temperature dependence of the viscosity of the fluorophosphate glass, the temperature uniformity limits the precision of measurements severely.

Standard Reference Materials for the Glass Industry

Liquidus Temperature SRM

M. J. Cellarosi

The liquidus temperature of a glass is the minimum temperature at which a melt can be held for a long period of time without formation of crystals. This property is especially important to the glass industry for development of new glasses and to insure high productivity with minimum expenditure of energy.

During the year, NBS research continued to identify and rectify flaws in the gradient method testing procedures. Several factors were identified as causing experimental difficulties and faulty liquidus determinations. Therefore, applicable ASTM procedures were tightened. These factors involve the shape and age of platinum boats, test length, methods of visual observations, steepness of temperature gradient, temperature determinations, thermocouple calibrations, surface vaporization and crystallization, and crystal phases observed. Because of these findings, two participating laboratories are repeating the round robin. NBS is cooperating with these labs to resolve their difficulties.

Other factors were identified by NBS to restrict liquidus precision. These factors were discussed at meetings of ASTM Committee C14.04 (Physical Properties of Glass). They include the dependency of liquidus on the thermal history of sample during test, and on the rates of crystal growth and solution. Because of these dependencies, liquidus can be affected by a particular temperature gradient, heat capacity, and recovery rate for different furnaces.

An impressive number of laboratories have cooperated in the round robin activities related to this SRM project. The results represent their best efforts in terms of the method and equipment available. The gradient method is common practice and is widely used in research and production throughout the glass industry. The glass selected for this SRM is a soda-lime glass, whose liquidus temperature represents the major part of glass production (e.g., window and container glass). In this context, activities to produce this SRM were started by NBS, and certification should be completed by the end of December 1979.

Viscosity SRM

D. J. Cronin and M. J. Cellarosi

NBS Glass Viscosity SRM's have an important role in glass research and manufacture. The viscosity of glass is of practical importance in all stages of the manufacturing process. This importance is expected to increase as greater emphasis is placed on productivity and better quality for glass products.

The glass industry relies on NBS to provide a long-term supply of viscosity SRM's. Because these SRM's sell well, NBS inventory is shrinking and renewal will be necessary in the next few years. Enough lead time is required to plan and carry out new viscosity SRM programs.

During the year, modern torque measurement instrumentation was purchased. This equipment was checked and was found to be in proper working order. Plans for the new facility have been made and work was started on the building of a new high temperature furnace. This new facility will enable NBS to carry out measurements at higher temperatures than the old apparatus and produce data with greater precision and accuracy with less labor.

Dielectric Constant SRM

M. J. Cellarosi

The glass industry through ASTM C14.04 (Physical Properties of Glass) lists this project as a priority item.

The proposed SRM is needed to upgrade and standardize measuring systems for dielectric constant of glass. This need was confirmed by a survey conducted by NBS on behalf of ASTM. An SRM for this property will support the expanding role of glass in countless electrical/electronic applications (e.g., insulation, controlled electrical leaks, windows for electro-magnetic waves, energy storage, envelopes for devices, substrates, encapsulation, capacitors, etc.). Moreover, this SRM will help in energy conservation efforts (e.g., low-loss insulators and dielectrics).

Glass Dielectric Constant SRM's are also expected to be of interest to the plastic industry. The inherent long-term stability of glass makes it superior to plastic standards for calibration purposes.

NBS heads and ASTM task group on round robin testing, and on the development of standard methods for the determination of the dielectric constant of glass.

During the year, a preliminary round robin program was organized. This activity is now in progress. For this purpose SRM 711 samples were distributed to the participating laboratories. Tentative test methods proposed by NBS were accepted by ASTM. These testing procedures specify three-terminal measurements with a guard electrode to minimize the effect of edge and ground capacitances. At this time two participating labs (NBS and Corning Glass) have reported sets of measurements. Data are encouraging as they agree within 5%.

Research is in progress to generate standard procedures that yield the greatest precision. In this effort NBS will study data and test details from participating laboratories.

This work is important to resolve dielectric constant measurement discrepancies existing in the glass industry.

Plans for Future SRM's

Melt Density SRM: There is a limited industrial interest in a standard glass with certified high temperature (molten state) density. The transport of glass through the various zones of a melting furnace and much of the stirring (convection) is determined by density gradients in the liquid glass. Designers of novel glass furnaces aim at closed constructions which are energy saving and less polluting. They also like to save floor space by increasing the height of melter units. Such designs require greater predictability of flow patterns and, hence, a better knowledge of melt densities as functions of temperature and composition.

Melt Electric Resistivity SRM: Increased use of electricity in glass melting (increased furnace capacity, less air pollution, shortage of gas and oil) has led to a demand for a melt resistant SRM.

Alternate Liquidus Temperature SRM: The present SRM candidate glass for liquidus temperature is a typical commerical composition and therefore of interest to the industrial community. However, because it is a commercial composition it presents certain difficulties in it measuring the liquidus temperature. Therefore it was sought to develop a series of glasses specifically for use as liquidus temperature SRM's which would have sharp, easily definable endpoints and could be used for temperature calibration of the equipment used to determine liquidus temperature.

A hot stage furnace was constructed and was used to make preliminary liquidus temperature measurements. It also proved useful in observing the crystallization and vaporization behavior of the glasses.

The glasses were to have the following properties: 1) liquidus temperature in the range of commercial glasses; 2) distinctive easily recognized primary phase, one which could easily be distinguished from surface crystallization; 3) crystallize easily, but not so readily that crystals form on cooling as the sample is removed from the furnace; 4) nucleation occurs in the bulk glass; 5) good durability, to avoid changes with time that could affect crystallization behavior; and 6) minimum vaporization losses at the liquidus temperature to avoid composition changes that could alter crystallization behavior or obscure the crystallization end point.

The initial phase involved the melting and testing of several congruently melting compounds that would form glasses and have liquidus temperatures in the desired range. Several of the compositions were then altered in an attempt to meet the overall property requirements. Overall a total of twenty-two glasses were melted and tested. While the results to date appear promising further work will be required before certifying any of these glasses as SRM candidates.

Glass Standard Reference Materials Liaison

M. J. Cellarosi, W. K. Haller, and D. J. Cronin

Close relations with the glass industry, R&D organizations, and active participation on various ASTM committees and other standard bodies were maintained. These activities keep NBS abreast on the needs of science and industry, and enable NBS to carry out effective SRM programs that are responsive to the most important needs of both producers and users of glass.

The glass industry through ASTM Committee C-14 on Glass and Glass Products strongly endorses NBS to play a leading role in development of glass SRM's and related measurement methods. Industry and users of glass rely on NBS participation and leadership in standards activities because of NBS neutrality and reputation as a research organization. In this context, our laboratory routinely reviews and generates inputs on methods and specifications on glass and related products. Frequent technical consultations are given on the use and applicability of SRM's and on present and future needs on standardization.

Publicity literature was issued to reflect SRM updating. This included a section on glass SRM's for the 1979 ASTM Annual Book of Standards. Several technical meetings on SRM activities, glass properties, specifications glass recycling, and nomenclature and definitions, were organized on behalf of ASTM and the glass industry. NBS is also coordinating activities to establish an industry-sponsored research associate program on glass SRM's at NBS under the auspices of ASTM.

Other Glass Standard Reference Materials

Glass SRM's for Small Particle Analysis

D. H. Blackburn

Continued interest in this work has expanded the need for different glass matrices. New matrices were developed in the following glass systems GeO_2-Li_2O-B_2O_3-Al_2O_3, P_2O_5-Al_2O_3-Na_2O and SiO_2-Li_2O-B_2O_3. Efforts will be made to include a wide variety of elements in these glasses with 15-25 elements added in 1 atomic percent amounts. The use of glasses for microanalysis standards has expanded rapidly and considerable future forgrowth is foreseen. At present 10 glasses are available from NBS as Research Material No. 30, Glasses for Microanalysis, and the same glasses as Research Material 31, Glass Fibers for Microanalysis. Standard Reference Material 470 has been issued as Mineral Glasses for Microanalysis. Presently work is progressing to issue 15 glasses as a Standard Reference for Microanalysis that have a certified chemical analysis. Several talks on this subject were given by collaborating members of the Center for Analytical Chemistry.

Fluorescent Glass Bead Standards

D. H. Blackburn, D. J. Cronin

Work has been continued in the development of fluorescent glasses and glass spheres. As mentioned in previous reports, these glasses have two major applications. One is for the purpose of marking valuable or dangerous materials and the other is for use as fluorescent standards for various instruments used in the physical and biological sciences. Future efforts will be directed toward increasing the size of the sphere producing apparatus in order to produce spheres in larger quantities and in controlling the size range depending on the application. Consideration is being given at this time to issue glass spheres as an SRM for calibrating microspectrofluorimeters. A report acknowledging our work was published by J. R. DeVoe, D. M. Sweger, and R. A. Velapoldi ("Intruder Detection Using Trace Constituent Analysis," NBSIR 78-1510-NBS Law Enforcement Standards Laboratory).

X-ray Energy Spectrometer Windows

D. H. Blackburn and D. A. Kauffman

We have developed an X-ray emission standard reference material for the calibration of windows in x-ray emissive instruments. A glass consisting of (wt %) SiO_2-42.50; BaO-2.00; CaO-1.50; MgO-20.00; ZnO-20.00; B_2O_3-10.00, and Li_2O-4.00 was found to have the proper emission characteristics and chemical durability. It is planned to issue this glass in the form of 25 mm diameter disks which are 3 mm thick. It has been assigned the SRM-number 477. Production has been started and the first casts have been found to have satisfactory homogeneity. Several committee meetings on this subject have been attended by staff members and a paper (see "Other Activities") was given at an NBS-held Symposium.

XRF Spectrometer Thin Film Standards

D. H. Blackburn

An important objective of this program is to develop thin film standards containing various elements which can be certified for elemental composition. An NBS certified thin film standard can serve the x-ray community by providing an accurate basis for the calibration of x-ray spectrometers, especially for assessing the quality of air-pollution abatement programs. Presently, calibration is performed using commercially available thin film standards which are not traceable to any NBS standard. During the past two years, we have explored the possibility of producing thin glass films of known elemental composition using a focused ion-beam sputtering technique. This work has been fully described in detail in the NBS/EPA Energy/Environment Reports of January and June 1977, and January and June 1978. Presently, the results look promising in that it appears that this method is suitable for producing an NBS certificate thin film standard. We are currently determining if glass films containing sulfur and phosphorus can be fabricated by this technique.

Special Glasses

Glasses for High Power Lasers

W. K. Haller, J. T. Wenzel, and D. H. Blackburn

The Glass Section has continued to collaborate with Lawrence Livermore Laboratory (LLL) on the development and property measurement of laser glasses for energy generation by laser fusion. This year most glass melts were made for the investigation of lasing ion behavior in different glassy environments; physical property measurements (primarily viscosity and refractive index) were continued also. In addition, the Glass Section consulted on technical problems related to laser glass for both LLL and the Department of Energy (DoE).

During the past year the Glass Section melted 81 experimental laser glasses for LLL and laboratories associated with LLL. Most glasses were fluorophosphates, phosphates, silicates, or borates which had been doped with rare-earth ions such as neodymium. Several unusual glasses were melted also. Studies made on these glasses resulted in five publications and six presentations by the LLL staff in which the NBS contributions were acknowledged.

The Glass Section has concluded its effort to develop fluorophosphate glasses with low non-linear refractive indices, because it was felt that the upper limit of improvement had been reached. The compositions which the Section developed have been chosen by the glass industry as base compositions for glasses which will be produced commercially for use as laser rods and windows, and Faraday rotators. A summary of this work has recently been published.

The "interim durability standard," a test for fluorophosphate glasses developed previously by the Glass Section, continues to be used by the laser glass community as a measure of the resistance of fluorophosphates to chemical attack. Recently, it has been applied to beryllium fluoride glasses as well.

The Glass Section is continuing to develop the capability to make optical measurements on beryllium-fluoride-based glasses provided by LLL. These glasses have such low refractive indices and high Abbe numbers that most commercial refractometers cannot measure these properties, and commercial immersion and contact liquids also do not exist. The Section has procured several inert liquids identified last year as being promising candidates for immersion/contact liquids. The fused silica vee-block for the Glass Section refractometer, which was designed and let to contract previously, is nearing completion, and should enable the desired refractive index measurements to be made.

The Glass Section continues to consult on glass-related matters for LLL and DoE, both through periodic visits by one staff member (W.K. Haller) to LLL and by telephone and letters. Examples this past year include a study of film formation on laser glasses, diagnostic work on microscopic inclusions in new, commercial fluorophosphate laser glasses, polishing of fluorophosphate laser glasses, and the production of hollow-glass micro balloons for laser fusion targets. Additionally, the Glass Section supplies technical advice to the Director for Laser Fusion at DoE on an on-going basis and participates in technical meetings.

The Glass Section has studied the viscosity, crystallization, and annealing behavior of one prototype fluorophosphate laser glass. The temperature-viscosity relationship in the 10^0 - 10^2 poise range was determined by using the rotating bobbin method and in the 10^{10}-10^{15} range it has been determined provisionally using the beam-bending technique (see other Section). Annealing studies showed that this glass could be made essentially strain-free after annealing conditions had been optimized. These studies confirm that, with respect to these properties, fluorophosphate glasses are suitable for use in high energy laser applications.

The Glass Section has begun a program of research on optical coatings for high-energy laser glasses; this is described in another Section.

The Glass Section, at the request of the DoE, organized and hosted a two-day meeting of all DoE contractors involved in the laser fusion-high energy laser program. The meeting had four sessions: laser glass development (infrared, primarily; also visible and ultra-violet); coatings for use in the infrared; ultraviolet lasers and coatings; and advanced projects. Attending the meeting were 65 persons representing 25 governmental, industrial, and academic laboratories.

Municipal Waste Utilization

M. J. Cellarosi

Under the Resource Conservation and Recovery Act of 1976, the NBS is required to provide guidelines for the development of specifications for materials recovered from wastes.

In the area of glass reclamation, NBS is cooperating with ASTM Committee E-38 on Resource Recovery, the glass industry, and reclamation facilities, to write test procedures that assess the usefulness of recovered glass principally for reuse in container manufacture. In these endeavours, NBS developed a test for refractory analysis in recovered glass that yields acceptable precision levels. This method was accepted by ASTM E-38.

NBS is also cooperating with ASTM and the glass industry on studies that attempt to identify any major technological problems that might be encountered when using recovered glass in manufacturing of containers. The objective of these efforts is to assess the significance of these problems as potential limits on the use of reclaimed glass. Examples of such problems or barriers to recycling are the influence of color mixture and refractory contamination on glass production.

Color mixed glass when added to a batch formulated for a particular glass color can be a problem. Main coloring agents used in glass container manufacture are oxides of iron and chromium. Thse agents are added in small quantities to the batch. Specific glass colorization is greatly complicated when color mixed glass is used in the recycling process. This is because the amount of colorants in the mixture can vary considerably in the course of the continuous manufacturing process.

Refractory contaminants (e.g., pieces of ceramic ware, gravel, concrete tile, spark plugs, etc.) are especially troublesome in glass manufacture. These particles, depending on their size, oftentime do not melt in the glass furnace. When this happens the particles become solid inclusions or "stones" in the glass product. Stones affect the mechanical strength and aesthetic quality of glassware.

During the year our laboratory evaluated cullet samples from a demonstration facility. Separation of non-glassy components by particle size indicated unacceptable levels by industry standards of magnetic, non-magnetic, and refractory contaminants. Also, numerous crucible melts were made and results showed a high incidence of stones, although the quality of glass excluding the stones was acceptable. It should be emphasized, however, that laboratory melts do not represent precisely actual production processes, and therefore, they can only be indicative of manufacturing trends. More work is needed in this area to correlate lab melts and production recycling recovered glass.

At present, two large-scale reclamation facilities are scheduled to come on stream in the next few months. One such facility is the $80 million project at Hempsted, Long Island, New York. This facility will use improved glass-sorting equipment designed to separate glass by colors (e.g., flint, amber, and green). Importantly, this plant should show considerable progress in controlling refractory contaminant levels.

Other reclamation plants are scheduled to open during the next few years. The glass industry plans to recycle more glass and advancements in recovery technology are needed to insure that industry is provided with a high grade, consistent, and long-term supply of cullet.

Optical Materials

Optical Materials Characterization

A. Feldman, R. M. Waxler, and M. J. Dodge

Basic optical data are needed for predicting the performance of optical components and in particular components made of optical materials that are continually being developed. Examples of recently developed materials include, "reactive atmosphere processed" (RAP) KCl and KBr, chemical vapor deposited (CVD) ZnSe and ZnS, fusion cast CaF_2 and SrF_2, hot forged KCl and CaF_2, and neodymium doped phosphate and fluorophosphate laser glasses. Many of the new materials were developed for use in high average-power laser systems. Absorption of intense laser radiation propagating through a component produces a thermal gradient in the material that causes optical path variations over the component aperture. These optical path variations are due to four effects: the direct change of index with temperature dn/dT, the change of thickness due to thermal expansion, the stresses induced by the thermal gradients, and the change of thickness due to the thermally induced stress. In laser systems for fusion research, the laser rods and discs are subject to stresses due to clamping and to thermal gradients induced by flashlamp pumping. In other systems, optical components are subjected to index variations due to varying environmental conditions.

An important highlight was the publication of a Technical Note (see publications) summarizing the data obtained under this project. Room temperature values of refractive index as a function of wavelength were presented for the following materials: commercially grown KCl, reactive atmosphere processed (RAP) KCl, KCl nominally doped with 1.5% KI, hot forged CaF_2, fusion cast CaF_2, CaF_2 doped with Er (0.001% to 3% Er), SrF_2, chemical vapor deposited (CVD) ZnSe (2 specimens), and ZnS (CVD, 2 specimens). Data for the thermo-optic constant (dn/dT) and the linear thermal expansion coefficient were given for the following materials over the temperature range -180 °C to 200 °C: Al_2O_3, BaF_2, CaF_2, CdF_2, KBr, KCl, LiF, MgF_2, NaCl, NaF, SrF_2, ZnS (CVD), and ZnSe (CVD). The piezo-optic constants of the following materials were presented: As_2S_3 glass, CaF_2, BaF_2, Ge, KCl, fused SiO_2, SrF_2, a chalcogenide glass (Ge 33%, As 12%, Se 55%) and ZnSe (CVD).

Piezo-optic Studies in the Infrared

R. M. Waxler and A. Feldman

Interesting new experimental results have been obtained from the measurement of the piezo-birefringence coefficients, $q_{11}-q_{12}$ and q_{44}, of the alkaline-earth fluorides, CaF_2, BaF_2, and SrF_2, in the infrared. For the first time, a significant infrared dispersion in the coefficients has been found due to the effect of stress on the transverse optical phonon.

Two groups, Humphreys and Maradudin at the University of California at Irvine, and Bendow, Gianino, Tsai, and Mitra of RADC and the University of Rhode Island, have calculated the effect of the transverse optic phonon on the infrared dispersion of the photoelastic coefficients of binary compounds based on expressions for the interionic potential and the interionic dipole moment. Earlier work done at NBS on the piezo-optic constants of KCl suggested that the proposed models were inadequate. However, these results were based on measurements made at only two wavelengths, 3.39 µm and 10.6 µm, with He-Ne and CO_2 lasers, respectively. It was felt that a more adequate test of the basic phenomenological model should involve more detailed dispersion data in the infrared at many wavelengths. We decided to study the stress-induced birefringence (piezo-birefringence) of the alkaline-earth fluorides in the infrared for three reasons: 1) These are important optical materials for both the infrared and the ultraviolet. 2) The positions of the transverse optic phonon frequencies of these materials fall in a region where the desired dispersion effects should be observable. 3) The materials have sufficient strength to withstand the stresses needed for observing a measurable effect.

Figure 3 shows recent experimental data obtained for the piezo-birefringence of CaF_2, BaF_2 and SrF_2 as a function of wavelength. The dispersion observed is significant, and, in fact, one of the coefficients q_{44} for SrF_2 is seen to change sign. Most recently, we have seen this effect in CaF_2 as well. The curves were drawn through the data visually; however, a computer program has been written that will be used to fit the dispersion data to a phenomenological model based on oscillator strength changes and phonon frequency shifts.

Optical Bistability

A. Feldman

As an offshoot of the program on optical materials characterization, a contribution has been made in the field of optical bistability. An optically bistable device is a device that can exist in either of two modes. At low input optical power levels, the device remains in a nontransmitting mode. If the input power level is gradually increased, to a certain critical power level, the device switches to a transmitting mode. As the power level is decreased, the device remains in a transmitting mode until a lower critical power level is reached, at which point the device switches to its nontransmitting mode. It had been shown earlier, elsewhere and independently by us, that a Pockels cell with appropriate feedback can exhibit optical bistability. Furthermore, we had shown that such a device will act as an ultralinear modulator, that is, the nonlinear dependence of the output signal on an input signal can be made arbitrarily small compared to the linear dependence of the output signal on the input signal. In addition, such a device exhibits differential optical gain and power limiting.

In a paper published this year, we have shown that the performance of a bistable optical device can be significantly altered if the transmission function is made to depend upon a linear combination of the input power and output power. When this modification is made to a device based on a Pockels cell the following can result: 1) Bistable device -- the system response more closely approximates a step function. 2) Power limiter -- optical-power regulation can be improved at output-power levels close to the input-power level. 3) Ultralinear amplitude modulator -- the operating point of the device can be maintained at the inflection point of the response curve, where the linearity is best. Analogous modifications can be made to advantage on other bistable optical systems.

Optical bistability will eventually become important because of the large growth in optical communications and optical signal processing. It does away with the need for conversions between electrical and optical signals.

Future activities:

These will center on two areas: optical characterization and research on bulk optical materials, and optical characterization of thin dielectric films to complement the thin film deposition facility under construction.

Research on bulk materials will center on dispersion effects in the thermo-optic and piezo-optic coefficients due to electronic and phonon processes.

Optical characterization of thin films would include: guided wave techniques for measuring refractive index, absorption and Raman scattering; vacuum calorimetry or photoacoustic spectroscopy in combination with tunable infrared lasers (color center lasers) for determining absorption mechanisms; ellipsometry for determining optical constants.

Refractive Index

M. J. Dodge

High precision measurements of refractive index were performed for a number of government and private users. Twelve vee-block prisms to be used for refractometers were measured at 16 wavelengths between 0.4047 and 1.083 μm for The Ceramics, Glass, and Solid State Science Division (project coordinated by J. T. Wenzel) and Muffaletto Optical Co. The index was determined for four immersion liquids at three wavelengths and at four temperatures for the State of Texas Department of Public Safety, to be used in crime laboratory identification of glass. Four liquids were measured from 0.21 to 0.5461 μm, at two temperatures for Los Alamos Scientific Laboratory, for dosimetry purposes. Other work on refractometer test plates for quality control in industrial production of glasses, corn syrup, cosmetics, and pharmaceuticals was carried out. The indices of the ordinary and extraordinary rays in MgF_2 were determined from 0.21 to 6.0 μm as an aid in the optical design of windows and other components.

Optical Nondestructive Evaluation

G. S. White and A. Feldman

The use of optical techniques for nondestructive evaluation (NDE) of materials is growing in importance. For example, holographic interferometry has become a standard procedure for detecting flaws in tires. Optical scattering techniques are in use for high-space detection of flaws in hypodermic needles and artillery shell casings. Speckle interferometry is being developed as an optical NDE tool to complement holography. It is the purpose of this project to provide a sound scientific basis for optical NDE methods.

At present, the focus of our program is on the study of light scattering from surface flaws. A scattering apparatus has been constructed for this purpose. In preliminary scattering experiments conducted with this apparatus, the beam from a CO_2 laser source was propagated normal to the surface of a brass specimen containing a groove. The groove with dimensions approximately 50 μm wide, 50 μm deep and 1 cm long was produced by spark erosion. Scattered light within a solid angle of 2×10^{-5} was measured as a function of the angle between the scattered beam and the incident beam in a plane perpendicular to the specimen groove. These measurements define a scattering function.

Representative data for an angular scan are shown in Figure 4. The structure in the scattering function resembles the diffraction pattern of a single slit, which is to be expected by application of Babinet's principle. From the spacing of the minima in the curve and using the formula for single slit diffraction, one calculates that the width of the groove should be 52 μm, in close agreement with the approximate dimension given above.

An interesting feature in Figure 4 is the double peak to the right that appears near the scattering angle $\theta = 17°$. This structure appears to be a property of the groove because when the specimen is rotated 180° about the normal to specimen surface, the double peak shifts to the left near $\theta = -17°$. This suggests that the scattered light contains more detailed information about the groove structure.

In the course of setting up the scattering experiment, it was found that the system alignment was for more critical than initially suspected. For example, if the groove was not normal to the scattering plane but deviated by only 0.3°, the scattering function would become grossly distorted and assymetric. Furthermore, assymmetry was observed in the scattering function when the axis of rotation of the detector did not coincide with the groove.

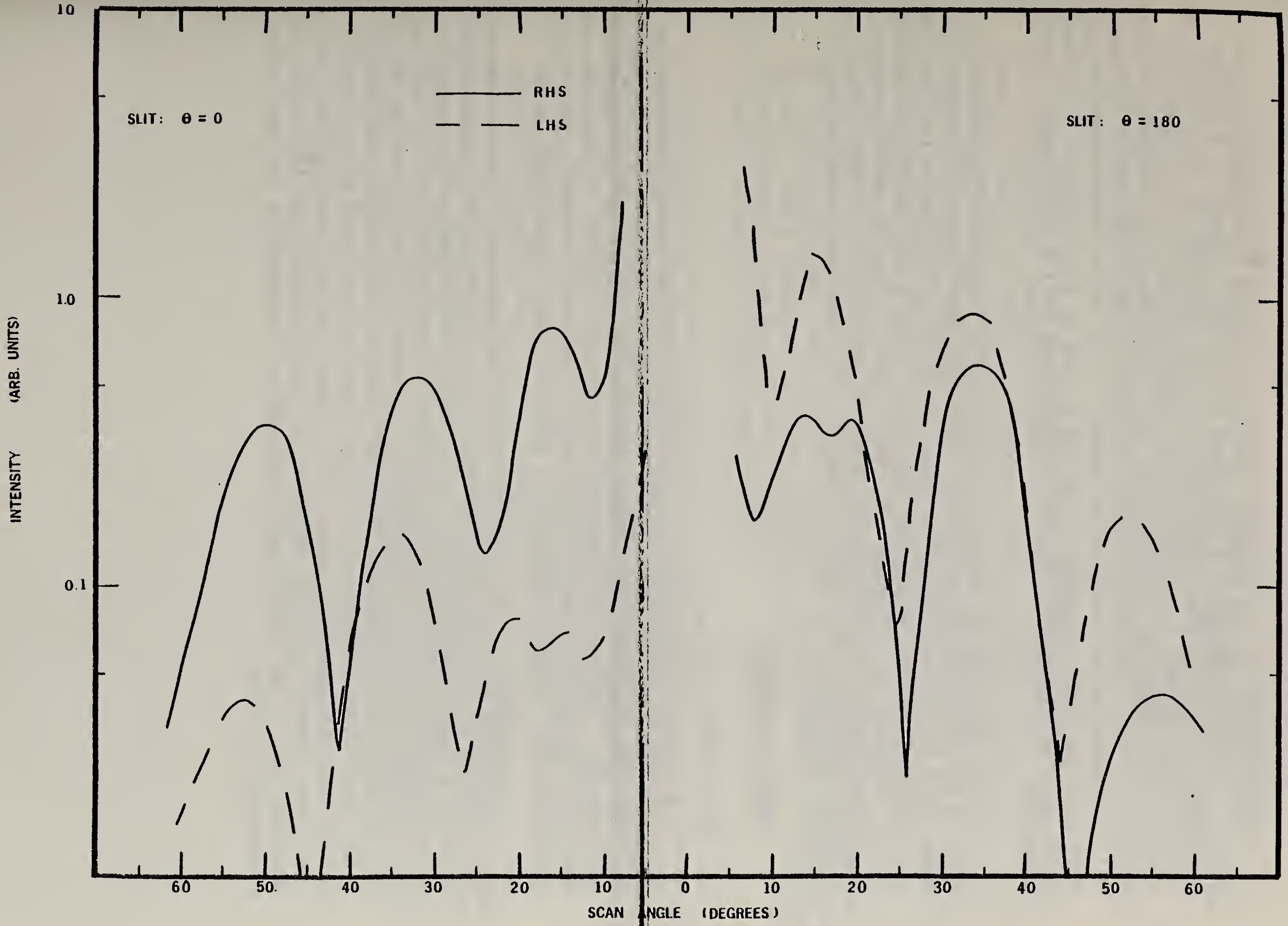

Figure 4. Typical scattering data showing the double peak shifting from the left hand side (LHS) of the sweep to the right hand side (RHS) as the slit is rotated 180°. The lower overall intensity for the θ = 0 scans also demonstrates the need to monitor beam power continuously.

Improvements of the present scattering system are presently being made. A greater emphasis is now being placed on alignment. A special alignment system has been constructed so that the axis of rotation of the detector can be made to coincide with the groove to within 50 μm. A further improvement we are making is the replacement of a manual rotation mechansim, which made measurements extremely time consuming and tedious, with a stepper motor rotation mechanism. This latter improvement should make possible future automation of the system by microcomputer. Furthermore, we plan to monitor the output wavelength of the CO_2 and the output intensity.

Plans: We plan to measure the scattering function of well characterized grooves possessing various cross-sectional shapes and sizes. The dependence of the scattering function on the polarization of the incident and scattered radiation will be examined. These measurements are expected to be important in two areas: the detection of flaws in metal surfaces; the determination of the scattering characteristics of defects in optically finished surfaces, with possible implications for the present dig and scratch standards.

Raman Scattering

M. I. Bell

Significant improvements have been made in the capabilities of the NML Raman Spectroscopy Laboratory. The range of operating wavelengths has been extended, and new software has been developed for the laboratory minicomputer. Spectra can now be acquired and stored in digital form and subjected to various types of quantitative analysis. These capabilities have been used to good advantage in several recent investigations.

An examination of the effects of ion implantation in GaAs has shown that above a critical dose a continuous amorphous layer is formed which exhibits a Raman spectrum identical to that of amorphous films produced by sputtering. Annealing by pulsed laser irradiation partially restores the crystalline order, as indicated by increased intensity in the optical phonon peak, but considerable disorder remains, with roughly 75% of the total scattering intensity still to be found in the broad bands characteristic of the amorphous phase. This result helps to explain the fact that laser annealing yields material of lower conductivity than would be obtained if all the impurities introduced by implantation had been made electrically active.

In collaboration with G. Walrafen and B. N. Krishnan (Howard University) and D. M. Sanders and S. W. Freiman, a preliminary study was carried out to determine whether Raman spectroscopy can be used to study the mechanism of stress corrosion in glasses. A stress apparatus was designed and built which permits Raman spectra to be obtained from a small volume at or near the tip of a slowly propagating crack in a glass sample.

Results on silica glass indicate a very small increase near the crack tip in the strength of minor features in the spectrum which have been attributed to defects, probably involving bonds of the form Si-OH. The observed changes were close to the limit of experimental error, but reproducible and in the expected direction. Further measurements and careful quantitative analysis will be required to confirm these results. An apparently more promising approach would be to use thin glass films in which larger regions of high strain can be created. If the exciting laser beam can be made to propagate as a guided wave in such a film, the interaction volume could be made quite large. A prism coupling device for launching guided waves in thin films was constructed and demonstrated recently, and a proposal is being prepared in cooperation with A. Feldman to seek support from the Director's Reserve for optical studies of thin films by infrared and Raman spectroscopy.

Studies of the phase transitions in several families of improper ferroelectrics have been initiated. Spectra obtained above and below the paraelectric-to-ferroelectric transition temperature in several metal-halogen boracites and propionates reveal the changes in the number and symmetry of Raman-active modes expected on the basis of the changes in crystal structure found by x-ray diffraction. Variations in the frequencies of certain modes within the boracite family seem to show regularities which may yield information on the nature of the atomic motions in these modes and differences in chemical bonding among the members of this family. Careful measurements of the temperature dependence of the Raman frequencies are needed to help establish the correct form of the free energy to be used in thermodynamic analyses of these materials. For this purpose, a high-stability, high-precision oven has been designed and built, and measurements will begin shortly.

Although Raman scattering is not generally regarded as a tool for quantitative analysis, D. Diller of NBS, Boulder, suggested that it could be used to determine the composition of hydrocarbon mixtures (such as liquified natural gas), where it might have advantages over gas chromatography (no sample extraction required) or infrared absorption spectroscopy (sensitivity to N_2). A feasibility study was performed in collaboration with Dr. Diller and R. F. Chang (Thermophysics Division), and it was found that gas phase mixtures of up to five components at pressures of 1-10 atm could be analyzed to give the relative concentrations of any two components with an accuracy of about 1%. Evidence was obtained indicating that the measurement accuracy was not limited by signal fluctuations due to the statistical nature of photon counting detection but rather by mechanical instabilities in the optical system. This observation could have important bearing on the potential of Raman spectroscopy for quantitative analysis, and it may be possible to pursue this question further in connection with high-temperature studies of methane proposed in collaboration with T. Kashawagi (Fire Science Division [NEL]) as part of a competence building initiative in the field of turbulent combustion.

In recent weeks, a study of impurity modes in silicon was begun in cooperation with R. Forman (Electron Devices Division [NEL]). Initial measurements on boron-doped samples have revealed only one of the two peaks generally reported for this impurity and attributed to its two isotopes. Further measurements on samples of various impurity concentrations and with dopings of isotopically pure boron will be needed to determine whether the conventional assignment is indeed correct.

Properties of Pyroelectrics

M. I. Bell, M. I. Cohen, and D. Horowitz (in cooperation with A. Shaulov, G. M. Loiacono, and W. A. Smith of Philips Laboratories)

Results of previous work on the pyroelectric and dielectric properties of ferroelectrics were analyzed, and a manuscript was prepared describing the improved dynamic pyroelectric response technique employed and typical results for proper and improper ferroelectrics. This paper will appear in the Journal of Applied Physics (July 1979). The implications of this work in the selection of materials for detector applications were described in a paper "Improper Ferroelectrics for Pyroelectric Detection of Infrared Radiation," by A. Shaulov, W. A. Smith, G. M. Loiacono, M. I. Bell, and Y. H. Tsuo, which was presented by Dr. Shaulov at the International Symposium on Applications of Ferroelectrics, Minneapolis, Minnesota (June 14, 1979). Further refinements in the experimental technique have been devised and demonstrated, and completion of the apparatus awaits incorporation of a microprocessor-based system for control and data acquisition, the components of which have just been delivered.

Analysis of the thermal and dielectric properties of $LiKSO_4$ and $LiCsSO_4$ was completed and a paper describing these results was submitted to the Journal of Solid State Chemistry. A similar study of $LiNH_4SO_4$ and its deuterated analogue (submitted to Ferroelectrics) established that the low-temperature phases of these crystal (below about 10 °C) are polar (pyroelectric), contrary to previous reports based on optical and x-ray techniques. This result forces us to revise our understanding of the phase transitions in these materials, and efforts are being made to formulate a phenomenological theory to describe them.

Although previous work has emphasized the very different dielectric and pyroelectric behavior of proper and improper ferroelectrics, our recent analysis of the thermal properties (entropy and specific heat) has drawn attention to the fact that in many cases these properties will reflect the behavior of the primary order parameter and exhibit the same temperature dependence in all types of ferroelectrics. The consequences of this observation are being examined carefully in the hope that they will lead to a unified treatment of both proper and improper ferroelectrics and ferroelastics.

Theoretical Modeling in Eddy Current NDE

A. H. Kahn and R. A. Spal

We have completed the calculations of the impedance of a coil which contains a conducting cylinder with a long radial surface crack. The calculations were performed by two independent methods. The first method employed an eigenfunction expansion of the magnetic field in the conductor, with the expansion coefficients determined by the fitting of boundary conditions on the surface and in the crack. The second method of calculation was by conversion of the problem to an integral equation for the eddy current density on the surface of the conductor. The advantage of the second approach is that it is applicable to any two-dimensional shape of cross-section of the conductor as well as offering an independent check on the first method of calculation.

The results of the calculations for the cylinder with a crack are shown in Figures 5 and 6. The fractional charge of the real (resistive) and imaginary (inductive) parts of the impedance are shown plotted against the ratio of crack depth to radius (d/a) for a wide range of values of the ratio of radius to skin depth (a/δ). For the case of a tight crack these calculations represent a complete solution of the problem. Open cracks can be treated as individual cases by the integral equation method.

The results described above are all related to the detection of long flaws in bodies of uniform two-dimensional cross-section, such as rods, cylinders, and strips. With this accomplishment as a start, we plan to go on to three-dimensional problems which are of greater interest. A possible problem for attack is the configuration in which an eddy current probe is passed above a conducting plane with a crack or other defect on or beneath the surface. Such problems have, in the past, been treated under the approximation that the defect size was small with respect to the skin depth. By extension of the integral equation method we plan to treat such problems more generally.

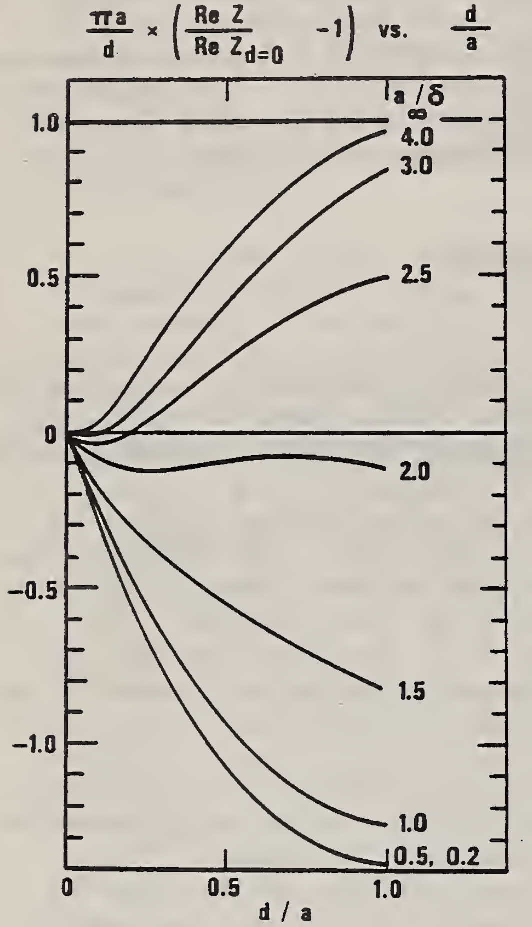

Figure 5. Fractional change of the real part of the impedance plotted against the ratio of crack depth to radius (d/a) for various values of the ratio of radius to skin depth (a/δ). The factor (πa/d) provides normalization to unity for infinite (a/δ), i.e., for infinite frequency.

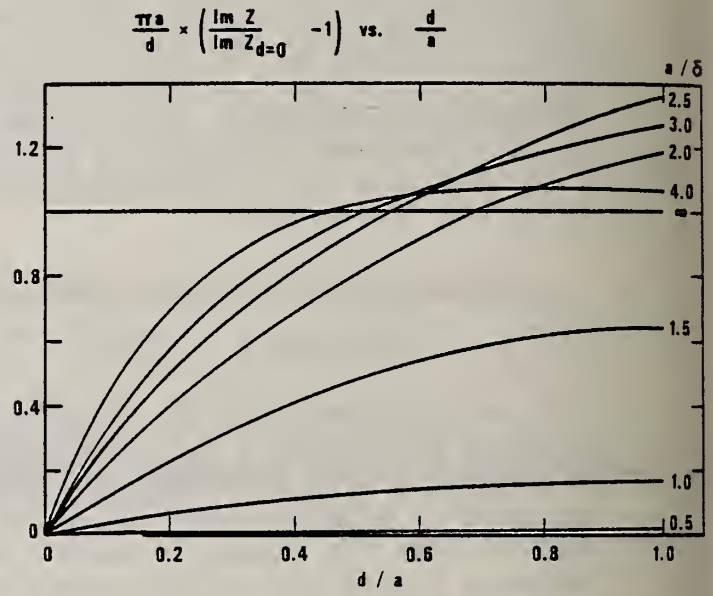

Figure 6. Fractional change of the imaginary part of the impedance plotted against the ratio of crack depth to radius (d/a) for various values of the ratio of radius to skin depth (a/δ). The factor (πa/d) provides normalization to unity for infinite (a/δ), i.e., for infinite frequency.

Electrocatalysis

M. I. Cohen

This research is directed at the need for data required for the development of materials to be used in fuel cells. The primary effort has been pointed toward methods for measuring the characteristics of potential substitutes for expensive Pt as the electrocatalyst in hot phosphoric acid fuel cells. The work has been partially supported by the DoE and has been performed in collaboration with members of the Chemical Metallurgy group in the Metal Science and Standards Division.

During the past year work has proceeded along two complimentary paths. On the one hand, we are studying the electrochemical properties of some of the refractory hard metals. Some results on one of these ($Mo_{1-x}W_xC$) will be outlined here.

We have compared the rates of anodic oxidation of H_2 on WC in phosphoric acid electrolytes at varying temperatures with the rates observed under the same conditions over the WC isostructural alloy $Mo_{1-x}W_xC$). The ternary catalyzes the reaction as effectively as WC, apparently by the same mechansim, and is equally tolerant of CO entrained in the H_2 feed. Our experiments indicate that proton discharge is the rate limiting step in the reactions on these carbides and that limitations on performance are caused by the paucity of active sites. This implies the possibility of improving the performance of these electrodes by appropriate modifications in the preparative technique.

The second aspect of this program is an on-going commitment to improving our measurement system and to maintaining its capabilities in a manner as close to the state-of-the-art as possible. This has resulted in an upgrading of the system to include a larger read-write memory capacity, a floppy disc unit, and an improved converter board. Programming improvements include a 128 point Fast Fourier Transform (FFT) program (in BASIC).

Along with this work, an educational program in Digital Electronics and Microprocessors in Instrumentation, was started. Although originally intended for members of the Fuel Cell Research Group, it soon grew. Successful completion of a series of 13 seminars occurred in June.

In addition, a video recording and display unit for use in high pressure viscosity measurements has been constructed. Initial programming of the unit is almost done. Advisory and support services to a number of groups within and outside the Division has continued. Preliminary design consultation on a field system for a DoT Program on Measurement of Corrosion of Reinforcing Bars in Concrete has been completed.

Plans:

1. Operation and performance checks, programming and permanent installation of the improved converter board is expected in 1st quarter.
2. Additional software needed for this system (and others) will be written.
3. Impedance measurements on ZrO_2 electrolytes.
4. Design and construction of the Rebar corrosion measurement system will begin in 1st or 2nd quarter.
5. Concurrent to (4) a similar system to be used for measurements of corrosion in Concentric neutral Electrical cables (for EPRI) is to be designed and started.

DURABILITY OF CERAMICS AND GLASS IN SERVICE ENVIRONMENTS

The objective of this task is to develop test methodology and collect critical data for the assessment of high temperature materials in MHD and coal gasification environments. The Division's activities in these areas are part of two programs that cover several Divisions of the Center for Materials Science: MHD-materials and Clean Utilization of Coal. Both programs are supported by the Department of Energy augmented by some NBS contributions. The work of each project is closely related to and based on the expertise of Tasks 1-4. As discussed in the preface for this Division, the DoE program was sharply reduced this past year.

Electrical Conductivity and Electrochemical Effects of MHD Related Materials

W. R. Hosler, T. Negas, and G. S. White

Electrical conductivity is one of several fundamental physical properties of materials, and other physical properties can be either studied or derived through electrical conductivity. In the development of MHD power generation systems the electrical conductivity of the component materials of the channel area must be known in order to design the system. Not only is the magnitude of the conductivity of prime importance but the conductivity process must be understood. When different materials are placed in contact with each other, chemical changes may take place at the junction boundaries especially at elevated temperatures likely to be found in an MHD channel. These chemical changes are accelerated when large currents are passed through the boundary and can result in gross electrochemical degradation of the materials. Much of this past year's work has been involved in the study of the conductivity of electrode materials and in the conductivity and the conduction process in various coal slags as well as the reaction between these slags and the electrode materials.

Very high density (<95% of theoretical) $YCrO_3$[1] has been prepared by thermal sintering techniques and the electrical conductivity has been measured over a temperature range of 25 °C to 1650 °C under several partial pressures of oxygen. As can be seen from Figure 7, the conductivity in the oxidized state is satisfactory over the entire temperature range to serve as an electrode or lead out material. Preliminary tests on this material immersed in molten slag containing an added 20 w/o K_2SO_4 and subjected to an impressed voltage and current for 20 hours indicate considerable cathode damage but low anode damage. Oxygen pressures are higher on the anode where the electrode materials should remain highly conducting.

Initial measurements on coal slags were made on Eastern slags without added potassium in an effort to understand the conduction mechanism, particularly with regard to the Fe^{+2}/Fe^{+3} ion ratio. Specially designed crucibles and measuring techniques have shown the slag conductivity to be entirely predictable depending on the previous treatment. The con-

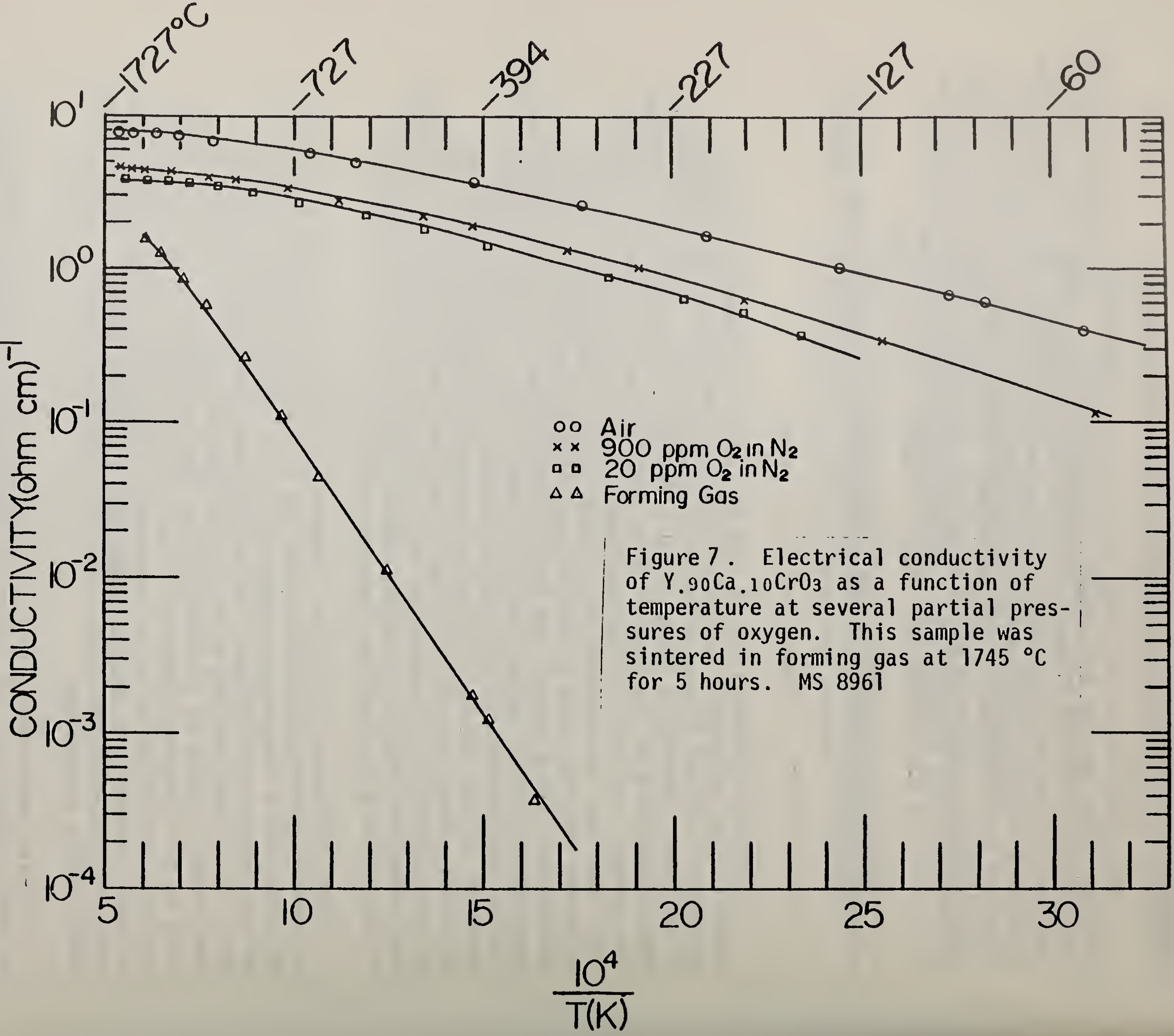

Figure 7. Electrical conductivity of $Y_{.90}Ca_{.10}CrO_3$ as a function of temperature at several partial pressures of oxygen. This sample was sintered in forming gas at 1745 °C for 5 hours. MS 8961

ductivities below about 1000 °C fall on two distinct curves of either high or low conductivity (Fig. 8) depending on the temperature from which they were quenched to 900 °C. Those samples quenched from above 1375 °C form the high conductivity slag containing Fe_3O_4 and a slight amount of another unknown spinel while those quenched from below 1375 °C form the low conductivity slag containing no crystalline Fe_3O_4 but only $CaAl_2Si_2O_8$. These measurements were done in air. The measurements repeated in an atmosphere of 5×10^{-6} atm O_2 in nitrogen showed no detectable change in conductivity magnitudes or change in the critical temperature of 1375 °C.

Ferric-ferrous ratios are being measured by wet chemistry methods.

Reference

1. Preparation and Properties of Yttrium Chromite Ceramics, T. Negas, W. R. Hosler, NBS, and L. Domingues, Trans-Tech, Inc., 4th Interantional CIMTEC Energy and Ceramic Conference, Faenza, Italy, May 28-31, 1979.

In Situ X-ray Diffraction Analysis

F. A. Mauer and C. R. Robbins

In coal gasifier systems, reactive gas components in the process atmosphere react with the protective refractory liner at high pressures and high temperatures. Degradation of the ceramic liner frequently results.

In a joint NBS-DoE program described under Task 12155 test methods and equipment have been developed to obtain critical data on the strength and phase composition of refractories under simulated gasification conditions. *In situ* x-ray diffraction analysis was used to determine phase composition and to detect polymorphic transformation at temperatures to 1000 °C and pressure to 1000 psi in atmospheres containing steam CO_2, CO, and H_2. All specimens were of compositions within the system CaO-Al_2O_3-SiO_2. They included a high alumina castable (94.4 w/o alumina, 4.5 w/o lime) and a calcined flint caly castable (55.6 w/o alumina, 4.5 w/o lime, 37 w/o silica) as well as special compositions corresponding to known bonding phases.

A series of experiments in which a test bar approximating the composition CAS_2 was heated in steam sheds new light on factors affecting the development of strength in calcined flint clay castables. An unfired test bar, compounded from CA 25 cement and silica in the form of quartz, was exposed to steam for a total of 500 hours in two series of experiments. The rather surprising observation is that a metastable phase, $Ca_8Si_5O_{18}$, not previously encountered in these studies, was formed at approximately 160 °C in preference to hexagonal or triclinic CAS_2. This new phase persisted to 525 °C and then reacted with SiO_2 over a 100 °C range to form triclinic CAS_2 (anorthite). The formation of $Ca_8Si_5O_{18}$ suppressed the formation of the important CAS_2 bonding phase by tying up the available calcium. Its occurrence is expected to delay the development of strength in green bodies and is, therefore, believed to be undesirable.

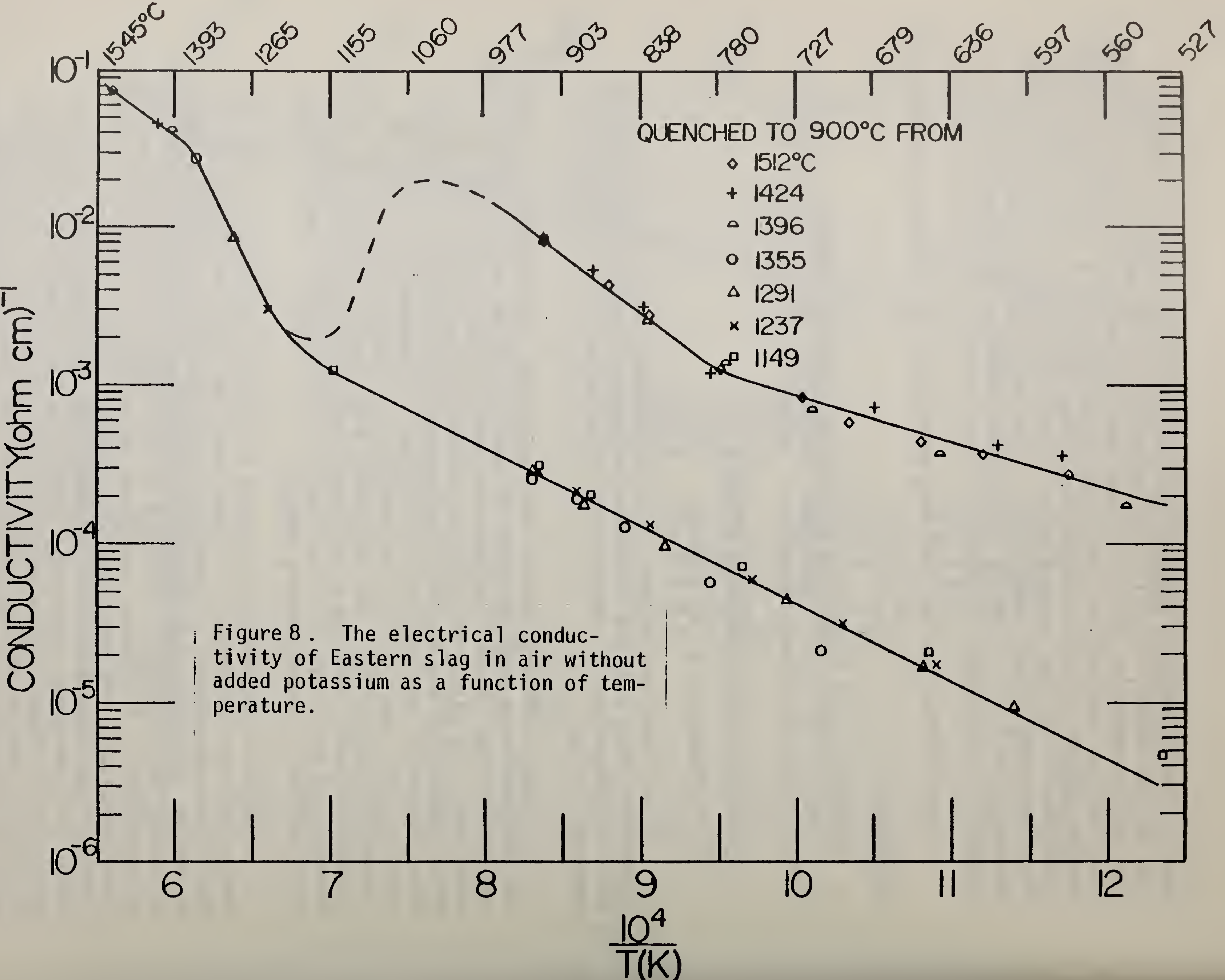

Figure 8. The electrical conductivity of Eastern slag in air without added potassium as a function of temperature.

Data Centers for Materials and Components for Fossil Energy Applications

H. M. Ondik, T. A. Hahn, A. Perloff, W. S. Brower with R. C. Dobbyn, W. A. Willard, I. J. Feinberg (562)

The Fossil Energy Information System consists of two Data Centers operating cooperatively to provide a central data base of materials and components performance and properties data. One element of the system is the Materials Properties Data Center responsible for compiling information on construction materials for coal conversion use and MHD power generation. This Center is largely staffed by personnel from Ceramics, Glass, and Solid State Science Division, Ondik, Hahn, and Perloff, with Feinberg (562). The major source of the data has been the Center's library of DoE materials research contractors' reports. There are currently some thirty projects generating materials properties and performance data for coal conversion use and about a dozen projects covering MHD power generation. Other sources are being explored and other reports of pertinent work being sought to expand the Center's information base.

Computer storage of the materials properties data base and access to it will be controlled using a commercially available data base management system. A request for proposal for computer vendors' services has been circulated, proposals have been received, and the first step of the technical evaluation process has been accomplished. As soon as the final evaluation can be made and a contract let for computer service, the building of the data base can be fully implemented.

The other segment of the information system is the Failure Information Center largely staffed by members of the Fracture and Deformation Division, Dobbyn and Willard with Brower (565). The source of information consists of reports of materials and component failures submitted to DoE on a voluntary basis by the various coal conversion plants. The information is abstracted and entered into computer storage under a system allowing high speed retrieval with a variety of search schemes. One goal of the Center is to develop the file of operating experiences and correlate them so that trends will be observed indicating primary causes of plant failures for the guidance of designers and operators of coal conversion plants.

The computer file currently contains some 500 reported failures. Several draft reports have been prepared on failure topics, and information is regularly supplied for the Failure Experiences feature of the DoE Materials and Components Newsletter, published by Battelle-Columbus. Queries are addressed to the Center concerning failure information and, during the last year, the Center responded to 68 requests for information and supplied over 2800 reports and abstracts summarizing the details of in-service materials performance.

During the past year, staff of both Centers, under the direction of R. C. Dobbyn (562) completed a detailed study of the performance of materials used in the Conoco Lignite Gasification Pilot Plant (CO_2 Acceptor Process). The study is based on the information contained in plant operating records and is not limited to reported failures. The report also contains the results of the visual examination, sampling, and laboratory study of the refractory lining of the plant gasifier vessel. Staff of the Failure Information Center have completed a feature article summarizing the performance of the refractory lining which will be submitted for publication in the Materials and Components Newsletter.

The Materials Properties Data Center currently has under way a state-of-the-art review of materials for MHD power generation. The review will deal with materials for open-cycle plants and omit materials for closed-cycle and liquid-metal-cycle plants for which there is inadequate information at present.

The two Centers are currently engaged in preparing sections of a Construction Materials Handbook for Coal Gasification--Performance and Properties Data. This Handbook will contain information gained in practical plant experience and also the results of materials research and testing programs. It will deal with the information in the context of the separate component areas of coal gasification plants, and will draw from this information an indication of possible candidate materials of construction. A separate section of the Handbook will include extended data for the chemical, physical, and mechanical properties of the candidate materials.

Slag Viscosity

W. S. Brower and J. L. Waring

Viscosity measurements have been made on two synthetic slag compositions over a range of elevated temperatures at steam pressures up to ∿ 100 psi. The compositions of the two synthetic slags were quite different in respect to their alkali content, one was high, ∿ 20 wt%, the other much lower ∿ 5 wt%. These slags were modeled to represent a high alkali western coal residue and lower alkali eastern coal residue. The high alkali composition exhibited an increase in viscosity with increasing steam pressure, whereas the lower alkali composition exhibited a decrease in viscosity with increasing steam pressure. The viscosity behavior of the high alkali slag was unexpected, the low alkali slag behaved in manner more consistent with conventional glass technology.

Other Division Activities

Invited Talks

Application of High Temperature Chemistry to Energy Related Systems
Miami University, Oxford, Ohio
T. Negas
October 1978

*Electrochemical Phase Equilibria
Fall Meeting of the American Ceramic Society, National Bureau of Standards, Gaithersburg, Maryland
L. P. Cook
November 1978

*Y-Deflection Modulated SEM Images in the Evaluation of Ceramic Surface Finish
Symposium on Science of Ceramic Machining and Surface Finishing II, National Bureau of Standards, Gaithersburg, Maryland
L. P. Cook
November 1978

Application of High Temperature Chemistry to Energy Related Systems
The American University, Washington, D.C.
T. Negas
December 1978

Thermal Stability of Long Range Order in Oxides
U.S.-Japan-Australia Joint Meeting, Symposium on Long Range Order in Solids, Honolulu, Hawaii
R. S. Roth
March 1979

Modulated Structure vs Superstructure: Systems Involving ABX_{4+x} Phases
Modulated Structure Symposium, American-Crystallographic Assoc., Kailua Kona, Hawaii
R. S. Roth
March 1979

Phase Equilibria and Crystal Chemistry in the System $YFeO_3$-$CaFe_2O_5$
The American Chemical Society, Honolulu, Hawaii
R. S. Roth
April 1979

*Liquid Immiscibility in the System $K_2O-CaO-FeO_x-MgO-Al_2O_3-SiO_2$
Annual Meeting of the American Ceramic Society, Cincinnati, Ohio
L. P. Cook
May 1979

*Conductivity Mechanisms in the Superionic Phases of AgI and Ag_2S
as Determined by Neutron Diffraction
International Conference on Fast Ion Transport in Solids -
Electrolytes and Electrodes, Lake Geneva, Wisconsin
R. J. Cava
May 1979

Preparation and Properties of $YCrO_3$-Based Ceramics
Fourth International Meeting on Modern Ceramics Technologies -
Energy and Ceramics, Faenza, Italy
T. Negas, L. P. Domingues, W. R. Hosler
May 1979

Performance of U.S. Electrodes-Insulators Tested in the USSR
U-02, Phase III
18th Symposium on Engineering Aspects of MHD, Butte, Montana
J. L. Bates, J. L. Daniel, B. Rossing, J. W. Sadler, W. Hosler,
T. Negas
June 1979

Chemical Aspects of MHD Materials
International Colloquium on Refractory Oxides for High
Temperature Energy Sources, Toronto, Canada
T. Negas
July 1979

Identification of Materials by Single-Crystal X-ray Diffraction
FACSS-V, Fifth Annual Meeting of the Federation of Analytical
Chemistry and Spectroscopy Societies.
Boston, MA
Presented by J. K. Stalick
J. K. Stalick, R. J. Boreni, and A. D. Mighell
October - November 1978

Powder Diffraction Standards and Reference Materials FACSS-V,
Fifth Annual Meeting of the Federation of Analytical Chemistry
and Spectroscopy Societies
Boston, Massachusetts
C. R. Hubbard
November 1978

The Elucidation of Molecular Structure and the Identification
of Crystalline Materials
Catholic University, Washington, D. C.
A. D. Mighell
December 1978

NSRDS Workshop on On-Line Scientific Data Bases and Systems
Crystal Data Center: Status and Potential
National Bureau of Standards
Washington, D. C.
A. D. Mighell and J. K. Stalick
January 1979

NBS Program for Fly Ash Characterization
ASME Meeting
United Engineering Center
New York, New York
C. R. Robbins
January 1979

Crystallography and High Pressure
ACA Meeting
Honolulu, Hawaii
S. Block
March 1979

Applications of the Diamond Cell in High Pressure Research
Department of Chemistry
Howard University
Washington, D. C.
G. J. Piermarini
April 1979

High Pressure Studies of Liquids and Crystals
Cornell University, Ithaca, New York
S. Block
May 1979

Correlation of the Glass Transition and the Pressure Dependence of
Viscosity in Liquids
1979 - U. S. Army Symposium on Ultra-High Pressure Phenomena
Rensselaerville, New York
R. Munro, G. J. Piermarini, and S. Block
June 1979

Optical Microscopic and Electrical Resistance Studies of CuCl at High Pressure
1979 - U. S. Army Symposium on Ultra-High Pressure Phenomena
Rensselaerville, New York
G. J. Piermarini and S. Block
June 1979

Standard Reference Materials for Quantitative Analysis and d-Spacing Measurement
Symposium on Accuracy in Powder Diffraction
National Bureau of Standards
Washington, D.C.
C. R. Hubbard
June 1979

The Reliability of Powder Indexing Procedures
Symposium on Accuracy in Powder Diffraction
National Bureau of Standards
Washington, D.C.
A. D. Mighell and J. K. Stalick
June 1979

Stereochemical Disorder in Two Dopamine Analogs: 2-Aminotetralin Hydrochloride and 2-Amino-6,7-dihydroxytetralin Hydrobromide.
ACA Meeting
Boston, Massachusetts
Presented by J. K. Stalick
J. K. Stalick, C. R. Hubbard, and A. D. Mighell
August 1979

Standard Reference Materials for Powder Diffraction
28th Annual Denver X-ray Conference
Denver, Colorado
C. R. Hubbard
August 1979

Application of an Energy Dispersive Detector to Crystallographic Studies with the Diamond Anvil Pressure Cell
American Crystallographic Association
Summer Meeting
ACA Meeting
Boston, Massachusetts
Presented by F. A. Mauer
F. A. Mauer, S. Block, and G. J. Piermarini
August 1979

Chemical Identification and Characterization: The Role of the NBS Crystal Data File
The American Chemical Society Symposium: Crystallographic Data Bases for the Chemist
Presented by J. K. Stalick and A. D. Mighell
September 1979

New Bond-Delocalized Dianions. A Crystal Structure of 1,3-(Dicyanomethylene) croconate Salt ($C_{11}N_4O_3K_2 \cdot 2H_2O$)
American Chemical Society Meeting
Washington, D.C.
Presented by V. Himes, A. D. Mighell, C. R. Hubbard, A. J. Fatiadi
September 1979

Laser-Induced Fluorescence Line Narrowing of Eu^{3+} in Lithium Borate Glasses
International Luminescence Conference, Paris, France
J. Hegarty, W. M. Yen, M. J. Weber, D. H. Blackburn
July 1978

Standard Techniques for Measuring Window Absorption and Other Efficiency Losses in Semiconductor X-ray Energy Spectrometers
Symposium on Energy Dispersive X-ray Spectrometry, NBS, Gaithersburg, Maryland
F. J. Walter, R. Stone, D. H. Blackburn, P. Pella

Glass Standards and Glass Research at the National Bureau of Standards
Battelle Research Institute, Columbus, Ohio
W. K. Haller
May 1979

Surface Derivatized Silica-Sol Particles as Immunospecific Markers for High Resolution Electron Microscopy
International Conference on "Chemistry of Solid/Liquid Interfaces"
Cavtat, Yugoslavia
W. K. Haller
June 1979

The Melt Vapor Pressure and Glassy Film Program at the National Bureau of Standards
Brockway Glass Company, Brockway, Pennsylvania
D. M. Sanders
July 1979

Development of Fluorophosphate Optical Glasses
23rd International Symposium of the Society of Photo-Optical Instrumentation Engineers, San Diego, California
W. K. Haller
August 1979

Properties of Crystalline Materials for Optics
SPIE, San Diego, California
A. Feldman
August 1979

Survey of Refractive Data on Materials for High-Power Ultraviolet Laser Applications
SPIE, San Diego, California
A. Feldman
August 1979

Improper Ferroelectrics
University of Illinois (Chicago Circle)
M. I. Bell
May 1979

Eddy Currents in a Bar With a Crack
Workshop on Eddy Current NDE
General Electric, Co., Schenectady, New York
A. H. Kahn
February 1979

AC Magnetic Fields in the Vicinity of a Crack
ARPA/AF Review of Progress in NDE
San Diego, California
A. H. Kahn
July 1979

Method for Calculating Eddy Current Distribution in Cylindrical Bars with a Crack
Symposium on Eddy Current Characterization of Materials
National Bureau of Standards, Gaithersburg, Maryland
A. H. Kahn
September 1979

Publications

Lattice Image Study of Crystal Structures of Mixed Oxides in the Systems Rb_2O-Ta_2O_5, Rb_2O-Nb_2O_5 and K_2O-Ta_2O_5 With Composition Ratios Near 1:3. Part I. Structures of "11 L," "9 L," and "16 L"
K. Yagi and R. S. Roth
Acta Cryst. A34 765-773 (1978)

Lattice Image Study of Crystal Structures of Mixed Oxides in the Systems Rb_2O-Ta_2O_5, Rb_2O-Nb_2O_5 and K_2O-Ta_2O_5 With Composition Ratios Near 1:3. Part II. Various Intergrowth Phases and Two-Dimensional Ordering of Pentavalent Ions
K. Yagi and R. S. Roth
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Y-Deflection Modulated Secondary Electron Images in the Evaluation of Ceramic Surface Finish
L. P. Cook, E. N. Farabaugh, and C. D. Olson
Symposium on Science of Ceramic Surface Finishing and Machining II, NBS, November 1978

Crystal Structures of Some Niobium-Tantalum Oxides. Part VI. The Structure of H-$LiTa_3O_8$
G. D. Fallon, B. M. Gatehouse, and R. S. Roth
J. Solid State Chem. 27, 255-259 (1979)

The Crystal Structure of the Cation-Disordered Phase $(Tl_{0.75}Pb_{0.25})_4Cl_5$
P. M. Skarstad, R. S. Roth, C. R. Hubbard, and H. S. Parker
J. Solid State Chem. 29 [2] (1979)

Characterization of Modulated Structures in ABO_{4+x} Phases
R. J. Cava and R. S. Roth
Proceedings of Symposium on Modulated Structures, Honolulu, Hawaii
March 1979

Conductivity Mechanisms in the Superionic Phases of AgI and Ag_2S
as Determined by Neutron Diffraction
R. J. Cava, F. Reidinger, and B. J. Wuensch
International Conference on Fast Ion Transport in Solids-Electrolytes
and Electrodes, Lake Geneva, Wisconsin, May 1979

Preparation and Properties of Yttrium Chromite Ceramics
T. Negas, W. R. Hosler, and L. P. Domingues
Proceedings Saint-Vincent Conference on Energy and Ceramics, Faenza,
Italy, May 1979

Performance of U.S. Electrodes-Insulators Tested in the USSR U-02
Phase III
J. L. Bates, J. L. Daniel, B. Rossing, J. W. Sadler, W. R. Hosler,
and T. Negas
18th Symposium on Engineering Aspects of MHD, Butte, Montana,
June 1979

Lead Alkali Apatites Without Hexad Anion: The Crystal Structure
of $Pb_8K_2(PO_4)_6$
M. Mathew, W. E. Brown, M. Austin, and T. Negas
J. Solid State Chemistry (In Press)

Phase Equilibria Research in Portions of the System K_2O-MgO-
Fe_2O_3-Al_2O_3-SiO_2
R. S. Roth
Symposium on Solid State Chemistry: A Contemporary Overview
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Magnetic Properties and Hyperfine Interactions in the β''' Phase
of Potassium Ferrite
V. P. Romanov, G. A. Candela, R. S. Roth, and L. J. Swartzendruber
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Neutron Powder Diffraction Study of the Structures of $CeTaO_4$,
$CeNbO_4$, and $NdTaO_4$
A. Santoro, M. Marezio, R. S. Roth, and D. B. Minor
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Thermal Stability of Long Range Order in Oxides
R. S. Roth
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Neutron Powder Diffraction Study of Ta_2WO_8
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Materials for Open Cycle MHD Generators
S. J. Schneider, H. P. R. Frederikse, T. Negas, and G. Rudins
Book Series on Material Science, North Holland Publishing Co.
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Hybrid Temperature-Oxygen Fugacity Sensor
T. Negas, L. P. Domingues, T. Drzewiecki, and R. M. Phillippi
March 1979 (Patent Pending)

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J. T. Wenzel, D. H. Blackburn, W. K. Haller, S. Stokowski, and M. J. Weber
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Surface Derivatized Silica-Sol Particles as Immunospecific Markers for High Resolution Electron Microscopy
W. K. Haller
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Surface Conductivity of Glass at the Solid/Liquid Interface
J. Jednacak-Biscan, V. Mikac-Dadic, V. Pravdic, W. K. Haller
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Eddy Currents in a Conducting Cylinder with a Crack
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A Boundary Integral Equation Method for Calculating the Eddy Current Distribution, etc.
Proceedings of the Symposium on Eddy Current Characterization (NBS/ASTM - September 1979
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Modulated Optical Spectroscopy of PLZT Ceramics
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Direct Measurement of Pyroelectric Figures of Merit of Proper and Improper Ferroelectrics
A. Shaulov, M. I. Bell, and W. A. Smith
J. Applied Physics (to be published)

Thermal and Dielectric Properties of $LiKSO_4$ and $LiCsSO_4$
M. Delfino, G. M. Loiacono, W. A. Smith, A. Shaulov, Y. H. Tsuo, and M. I. Bell
J. Solid State Chemistry (to be published)

Electroreflectance of PZT Ceramics
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Improper Ferroelectrics for Pyroelectric Detection of Infrared Radiation
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J. of Ferroelectrics (to be published)

One-Dimensional Ising with Generalized Molecular Field
G. J. Isfrate, A. Ballato, and M. I. Bell
J. Mag. and Mag. Mat. (to be published)

Dielectric, Pyroelectric, and Thermal Properties of $LiNH_4SO_4$ and $LiND_4SO_4$
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A. Feldman
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The National Bureau of Standards Optical Measurements Program: Refractive Index, Thermo-optic Constants, and Photoelastic Constants
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Survey of Refractive Data on Materials for High-Power Ultraviolet Laser Applications
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2-Ethoxy-1, 7,9-triethyl-7, 9-dihydro-1H-purine-6,8-dione; a Tetraethyl Derivative of Uric Acid
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Wall Effects in a Diamond-Anvil Falling-Sphere Viscometer
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J. Appl. Phys., Sept. (1979)

Raman Spectroscopic Evidence for Conformation Deformation in the High Pressure Phase of Polytetrafluoroethylene
J. F. Rabolt, G. J. Piermarini, and S. Block
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A Novel Bimetallic Sulfur Cluster. Crystal and Molecular Structure of a Dimer of Bis[methyldiphenylphosphinesilver]tetrathiotungsten, $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$
J. K. Stalick, A. R. Siedle, A. D. Mighell, and C. R. Hubbard
J. Am. Chem. Soc. 101, 2903 (1979)

The Diamond Cell Stimulates High Pressure Research
S. Block and G. J. Piermarini
USP Fiz. Nauk. SSR 127, [4] April (1979)
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Standard X-ray Diffraction Powder Patterns, Section 15, Data for 112 Substances
M. C. Morris, H. F. McMurdie, E. H. Evans, B. Paretzkin, J. H. deGroot, B. S. Weeks, R. J. Newberry, C. R. Hubbard, and S. J. Carmel
NBS Monograph 25, Section 15, October (1978)

On a Parametrization for Solids Under Hydrostatic Pressures
R. G. Munro, G. J. Piermarini, and S. Block
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A Preliminary Report on the Design and Results of the Second Round Robin to Evaluate Search/Match Methods for Qualitative Powder Diffractometry
C. R. Hubbard and R. Jenkins
Advances in X-Ray Analysis 22 (1979)

X-Ray Powder Diffraction Measurements in Reactive Atmospheres at 1000 °C and 7 MPa (1000 psig)
F. A. Mauer and C. R. Robbins
Advances in X-Ray Analysis 22, Plenum Press, New York (1979)

The Reliability of Powder Indexing Procedures
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Proceedings on "Accuracy in Powder Diffraction" (In Press) (1979)

An Evaluation of the Performance of Materials and Components Used in the Conoco Lignite Gasification Pilot Plant, CO_2 Acceptor
R. C. Dobbyn, H. M. Ondik, W. A. Willard, W. S. Brower, I. J. Feinberg, T. A. Hahn, G. E. Hicho, M. E. Read, C. R. Robbins, J. H. Smith, and S. M. Wiederhorn
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Studies in Conservation (In Press) (1979)

Synthesis, Crystal and Molecular Structure of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$, a dimer of Bis(tri(p-toly) phosphine copper) oxotrithiotungsten
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(3-Chloro-2-oxo-5-Nitrophinyl) (2-Chlorophenyl) iodonium, inner salt
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A. D. Mighell and J. Rodgers
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C. R. Hubbard, A. D. Mighell, and A. Fatiadi
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JACS (In Press) (1979)

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C. R. Hubbard
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Special Reports

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Oak Ridge, Tennessee

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Applications, 1979

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Used in the Conoco Lignite Gasification Pilot Plant, CO_2
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I. J. Feinberg, T. A. Hahn, G. E. Hicho, M. E. Read,
C. R. Robbins, J. H. Smith, and S. M. Wiederhorn
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and A. J. McAlister
NBSIR 79-Annual Report January 1978 - December 1978
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Sponsored Conferences

Laser Glass Conference
National Bureau of Standards, Washington, D.C.
August 2-3, 1979

Accuracy in Powder Diffraction
Symposium sponsored by NBS, NRC, IUC
Washington, D.C.
June 11-15, 1979

Technical and Professional Committee Participation and Leadership

International Commission Glass (U.S. Representative)
W. K. Haller

International Commission on Glass, Subcommittee VIII, Standard Reference Glasses
W. K. Haller
Vice Chairman

International Commission on Glass, Subcommittee A, II - Durability and Analysis
W. K. Haller

ASTM Committee C-14 on Glass and Glass Products
W. K. Haller

ASTM Subcommittee C-14.03 on Chemical Properties of Glass
W. K. Haller

ASTM Committee C-14 on Glass and Glass Products
M. J. Cellarosi
Vice Chairman

ASTM Subcommittee C-14.04 on Physical and Mechanical Properties of Glass
M. Cellarosi

ASTM Subcommittee C-14.01 on Nomenclature of Glass and Glass Products
M. Cellarosi
Chairman

ASTM Subcommittee E-38 on Resource Recovery
M. J. Cellarosi

ASTM Subcommittee E-44 on Solar Heating and Cooling Applications
M. J. Cellarosi

ASTM Subcommittee C-14.08 on Flat Glass
M. J. Cellarosi

ANSI Committee F-1 on Hybrid Electronics
M. J. Cellarosi

JEDEC (Joint Electron Devices Engineering Councils)
M. J. Cellarosi

EIA (Electronic Industries Assoc.) Committee on X-ray and Implosion TV Standards
M. J. Cellarosi

ASTM Committee C-14 on Glass and Glass Products
D. J. Cronin

ASTM Subcommittee C-14.04 on Physical and Mechanical Properties of Glass
D. J. Cronin

ANSI Committee Z-26.1 on Safety Glazing of Motor Vehicles
D. J. Cronin

ANSI Committee Z-97 on Architectural Safety Glazing
D. J. Cronin

ASTM Sbucommittee F1.02, Electronics Committee, Subcommittee and Lasers
A. Feldman, Editor

Standard Reference Materials

SRM 470 on Mineral Glasses for Microanalysis
D. H. Blackburn in collaboration with C. E. Fiori and
R. B. Marinenko

ASTM C-21 on Ceramic Whitewares and Related Products
H. S. Parker

ASTM C-8 on Refractories
W. S. Brower

Committee on Publications of the American Ceramic Society
Subcommittee on "Phase Diagrams for Ceramists"
R. S. Roth

Panel member on Review of Montana Tech - Montana State Research for MHD, October 1978
T. Negas

Consulting and Advisory Data Centers

Phase Diagrams for Ceramists Data Center
R. S. Roth, L. P. Cook, T. Negas, and G. W. Cleek

Crystal Data Center (OSRD)
A. D. Mighell, J. K. Stalick, R. Boreni

JCPDS - Ind. Centre for Diffraction Data
C. R. Hubbard, S. Block, and A. D. Mighell

Materials Information and Data Center (Fossil Energy)
H. M. Ondik, R. C. Dobbyn, A. Perloff, T. A. Hahn, and W. A. Willard

Consulting Services

Considerable time of Section members was spent in replying to inquiries from other government agencies, industry, research laboratories, universities, small businesses, and individuals. Some examples from this year are:

Department of the Treasury, Forensic Science Branch and Indiana State Police Lab needed help in criminal cases involving the matching of glass fragments against possible source objects.

Architect of the Capitol. Multiple safety glazing had been installed in some buildings under his jurisdiction. Was concerned about strange optical phenomena and requested in-situ tests for conformance with safety requirements.

New York-New Jersey Port Authority. Spontaneous breakage of ten large tempered windows. Requests information about possible cause and evidence of contractor negligence.

National Security Agency. Electrical conductive windows.

Department of Justice, Tax Division. Need technical help in tax cases against glass manufacturers. Try to establish if tin (float glass process bath) and platinum (fiber glass manufacturer) are "everlasting" or "depreciable assets."

Idaho Falls Nuclear Waste Disposal Facility. Use slags as binder to solidify low-level transuranic waste. Interested in slag properties (viscosity, etc.)

Congressional Sub-Committee on Energy and Power. Wanted history of previous efforts to recover helium from natural gas using glass-membranes for separation.

Federal Trade Commission; Bureau of Customs; Dept. of Justice (Antitrust Div.). Definitions for certain glass products, manufacturing processes, uses.

International Cooperation

4th Joint Meeting of the US/USSR Working Group on Metrology, Moscow, USSR, June 25 - July 5, 1979. The delegation of 5 NBS staff members, lead by Dr. A. O. McCoubrey, included H. P. R. Frederikse (Materials Standards and Testing). The group visited the headquarters of Gosstandard in Moscow and regional laboratories in Leningrad, Yerevan and Irkutsk.

REACTOR RADIATION DIVISION

REACTOR RADIATION DIVISION

Robert S. Carter, Chief
Tawfik M. Raby, Deputy Chief
E. C. Maxwell, Administrative Officer
L. L. Sprecher, Secretary

The Reactor Radiation Division has the dual functions of operating the NBS Reactor (NBSR) and using neutron scattering methods for the study of materials. The first function includes not only the operation of the reactor, but also providing sample irradiation services for a large number of users. The second function includes, in addition to Division materials research programs, serving as a focal point of neutron scattering expertise for many other programs within and without the Bureau.

A major part of the overall Reactor Division contribution to the NBS mission and to the scientific and technical community is in fostering the utilization of the reactor by other NBS groups and outside organizations. Interactions with other scientists and organizations take the form of both collaborative efforts and independent programs which rely on utilization of the reactor and facilities provided by the NBSR staff. The extent of such interactions for FY 79 are indicated in the tables below.

Collaborative interactions are those in which workers from outside the RRD collaborate scientifically with RRD scientists on problems of mutual interest. These interactions are summarized in Table 1.

Table 1. Collaborative Interactions

	No. of Personnel FY 79
RRD Permanent Scientists	11
Non-RRD Participants	
Other NBS	18
Other Agency	41
University	29
Industrial	11
Total Non-RRD	99

Independent programs are those programs carried out independently of the Reactor Radiation Division scientific staff by other NBS Divisions and outside organizations. Table 2 summarizes these interactions.

Table 2. Independent Programs

	No. of Personnel FY 79
Other NBS	37
Other Agencies	23
Universities	20
Total	80

These tables demonstrate the extensive utilization of the NBS reactor by scientists and engineers from outside the Division. They come from 18 NBS Divisions and offices, 27 federal agencies, industrial and national laboratories, and more than 24 universities.

Many of the other agency and university collaborators have worked with us regularly for many years. Five of them (2 from the Navy and 3 from the Army) are assigned to work full time at the reactor on a permanent basis. Others regularly spend two or three days a week at the reactor. Bureau collaborative programs include measurements on ionic crystals, polymers, simple liquids, surface molecules, hydrogen embrittlement, etc. Major independent (non-collaborative) Bureau programs include trace analysis by a neutron activation analysis, standard neutron fields for neutron flux calibration and materials dosimetry, and precision gamma-ray energy measurement.

Many outside organizations use the sample irradiation services offered by the Division. Major users incude the FBI, FDA, U.S. Geological Survey, the Smithsonian Institute, Treasury Department (ATF), and the University of Maryland. Programs range from analysis of criminal artifacts to the measurement of pollutants in the environment.

Upgrading of the reactor to 20 MW is progressing. A contract for the additional cooling tower should be let by the end of September or early October. The design of the modifications to the process piping has been essentially completed except for that part which depends on details of the cooling tower which has not yet been selected. The heat transfer calculations have been completed confirming that the existing pumps can provide adequate flow when equipped with larger motors and impellers. The writing of the Safety Analysis Report is continuing.

The fabrication of new fuel elements for the NBSR is progressing smoothly. Texas Instruments is expected to deliver the first of our new elements in December 1979. This will assure us of continuity in our fuel element supply. Our present supply would have run out in January or February of 1980.

During the week of August 6-10, a serious mechanical problem developed in one of our four shim arms that control the reactor. The arm appeared to stick at certain angles. The reactor will be shut down until the shim arm is fixed. This will probably require removing it from the reactor vessel and working on it under water. A minimum of a two-month shutdown is anticipated.

It is not possible in this overview to summarize all the activities of the many outside groups that use the reactor. These can be found in the "Summary of Activities, July 1978-June 1979."[1] Some examples, however, will be given here to illustrate the broad scope of these programs that do not involve scientific collaboration with the Reactor Radiation Division. The ENDF/B V file is a basic file of neutron cross section data used in reactor physics calculations. Fundamental uncertainties in the capture cross section of U-238 were uncovered in the preparation of these files. NBS was called on by DoE to look into the problem. Careful measurements of the U-238 capture to U-235 fission cross section ratio made by the Center for Radiation Research in the Intermediate-energy Standard Neutron Field (ISNF) maintained at the reactor were able to resolve this uncertainty. Neutron activation analysis was used to determine the thickness of the palladium protective layer important to the successful operation of solar cells in communication satellites. The FDA analyzed oats from a box car load that was suspected of having killed many cattle because of impurities absorbed by the oats from the box car which had not been properly cleaned. They were able to show that the suspected contaminate, $NaSiF_6$ was in fact in the oats. The Naval Research Laboratory was able to demonstrate the efficiency of a new "gold-toning" neutron activation process for enhancing very weak images on photographic film of interest to intelligence and space agencies. The University of Maryland-NBS prompt q-ray trace analysis facility has been actively used and has demonstrated its potential for the characterization of Standard Reference Materials. The work of the FBI, the Alcohol, Firearms, and Tobacco Division of the Treasury Department, the Geological Survey, and many other smaller users continues unabated.

The scientific work of the Reactor Radiation Division and its collaborators are summarized later in this report and details given in the "Summary of Activities" mentioned earlier. A few highlights will be given here to indicate the current direction and accomplishments of the Division.

The Division competence initiative in Small Angle Neutron Scattering (SANS) has started. The conceptual design and a large part of the detailed design of a state-of-the-art facility has been completed and many components are currently being fabricated and some installation has begun. A small (20 cm x 20 cm) and a large (64 cm by 64 cm) area detector with 0.5 cm resolution have been contracted for with delivery expected early next spring. By the end of this fiscal year, two new scientists will have been hired to work on the program. (One has been working on the program since its inception.) In addition, a visiting scientist is studying the application of SANS to polymers. Considerable outside interest in the use of the new facilities has already been expressed by several outside groups.

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[1] Preliminary copies will be made available to Panel members prior to the meeting.

Other developments include the integration of a new super minicomputer into the neutron spectrometer network providing high-speed calculational capability as well as enhanced on-line manipulation of experimental data. The potential of neutron scattering as a probe of surface molecules of interest in catalytic reactions has been demonstrated. Neutron vibrational spectroscopy has been used to examine the bonding of hydrogen in transition metals at very low concentration and in a study of the structure of prototype metallic glasses. A Greens function random phase approximation theory has been developed which shows excellent agreement with experimental results on Fe and Co rare-earth compounds and explains both the excited state spin waves and spin reorientation effects. The use of neutron induced autoradiography is being developed in collaboration with the National Gallery of Art and the Smithsonian Institution for the authentication of valuable paintings. These and other highlights will be discussed more fully in the Task Reports in the next section.

The DoD program for residual stress studies has failed to develop but there is still a possibility for some work in this area. The scientist to work on the application of neutron tomography to nuclear safeguards has been hired and work is progressing in this area. We are looking forward to increased collaboration with the surface science group in the Surface Science Division. They were one of the four groups within NML to receive a share of the competence building fund made available to NBS by Congress. We also anticipate an increased collaboration with the Thermophysics Division in their study of mixed liquids and liquid metals, and expanded collaboration with the Fracture and Deformation Division in the development of neutron methods for the microscopic investigation of hydrogen in embrittled metals. During the coming year, we anticipate hiring a material scientist to develop applications of small-angle scattering to problems in materials science and work closely with other materials scientists in the Center.

REACTOR OPERATIONS AND SERVICES

The NBSR continued its leadership as one of the best utilized research reactors in the country with 25 simultaneously operable facilities surpassing that of any other major facility. Operated round-the-clock by the smallest staff of any comparable reactor, it again produced an outstanding operating record. It supports many entensive and diverse programs carried out by more than 150 scientists and engineers from within and outside NBS. These programs range from the development of standard reference materials, neutron standards and dosimetry, trace analysis of foods and artifacts, the development of energy resources, and the use of neutron radiography as an NDE tool for the determination of the structure and properties of technologically important materials. In all, 18 NBS Divisions and offices, 27 federal agencies, industrial and national laboratories, and more than 24 universities depend on the NBS reactor for vital programs.

The upgrade of the reactor power to 20 MW is progressing. The higher power will greatly enhance reactor utilization and versatility. Arrangements for the long-term supply of nuclear fuel have been completed through use of Department of Energy facilities and contractors, and delivery should commence by December 1979.

Technical Activity

Reactor Operations

T. M. Raby and J. F. Torrence

All aspects of reactor operations continued to be excellent until the middle of August when the reactor had to be shut down because of shim arm trouble. The shutdown is anticipated to last as least two months. Once again, outstanding on-line performance, reactor utilization and fuel efficiency were achieved until the forced shutdown. A summary of overall statistics is presented in the following table for the period July 1, 1978-June 30, 1979.

NBSR OPERATING SUMMARY FY 78

No. of days at 10 MW	280
On-line time at 10 MW	77%
Average U-235 burnup	52%
No. of Irradiations	2040
Hours of Irradiations	3020
Hours per Irradiation	1.5

Irradiation Services

N. A. Bickford and J. H. Ring

Again tens of thousands of samples were irradiated involving many important and diverse programs. These include trace analysis of foods, drugs, and environmental samples, forensic investigation, development of energy resources and minerals, and the analysis of archaeological treasures and moon rock samples. In addition, over half of the standard reference materials issued by the Bureau have been characterized using the reactor. The work in these areas at the NBSR surpasses that of any other research reactor in the U.S.

Many important new programs have been initiated. They include: the establishment of a national Environmental Sample Bank which will provide real-time monitoring data for pollutant trend evaluation as well as allow for more precise measurements in the future; the development of state-of-the-art measurement techniques and standards for nuclear material safeguards; image enhancement of underdeveloped photographic film; and finally the analysis of waste materials being fed to animals for their toxic effect on the food chain.

Engineering Services

J. H. Nicklas and R. J. Conway

Most of the Engineering Services effort outside of routine maintenance and surveillance has been directed toward the procurement of new fuel and the 20 MW upgrade.

All the engineering and specification questions have been resolved on the fuel element manufacturing. Production is starting and the first elements should be delivered in December 1979.

The heat transfer calculations have been completed. These have been combined with careful flow measurements on the primary system and confirmed that the present pumps do not have to be replaced. Replacement would have entailed much more extensive primary piping modifications than will be required now. New motors and larger impellers which will provide the necessary flow are now on order.

The design of the modifications to the secondary cooling system has been completed except for some details which cannot be finalized until the cooling tower choice is finalized. Some of the piping and other components have been delivered and others are on order. Certain piping modifications will be done during September which will expedite the major changes to be made later.

The cooling tower "Request for Bids" has been sent out and a contract should be let the end of September or early October. The bids include several options in an attempt to get the most effective tower we can afford.

The last two months of the fiscal year were, of course, devoted to repairing the facility shim arm so that the reactor could be put back in operation as soon as possible.

NEUTRON SCATTERING CHARACTERIZATION OF MATERIALS FOR ADVANCED TECHNOLOGIES

This task develops and applies advanced neutron scattering methods and related theoretical analysis for research on the microscopic properties of materials which affect their use of technological applications. Current areas of emphasis include hydrogen in metals, new magnetic and glassy materials, and molecular solids. The neutron inelastic, quasielastic, and magnetic scattering techniques applied provide unique information, e.g., on phase transformations, interatom bonds, electronic structure, sublattice magnetization, hydrogen diffusion, and molecular and crystal dynamics. The members of this task (and the following task) are also responsible for establishing and maintaining a center of excellence for neutron scattering and radiographic measurements including a computer-controlled network of 11 spectrometers at the reactor. Task scientists couple directly with other NBS and outside groups who require state-of-the art neutron measurement methods and expertise in their programs. Examples include long-term collaborative efforts with in-house guest workers from Army Materials, NRL, NSWC, and the University of Maryland on materials for improved microwave transmission and sonar and advanced explosive formulations; cooperative research with industrial scientists (Allied Chem., G.E., IBM) on new classes of materials with potential applications for advanced power transformers, computers, and energy storage; and research on hydrogen in metals and prototype phase transformations in solids with other national laboratories (ANL, ORNL) and universities (University of Maryland, University of Houston, University of Saarlande). In addition, staff scientists are exploring with other Divisions and Centers at NBS development of neutron scattering methods for: (1) surface analysis of chemical products and reactions on industrial catalysts; and (2) ultrasensitive microscopic analysis of hydrogen in metals.

New plans for the coming year include: (1) an expanded effort with the Fracture and Deformation Division on the development of neutron scattering for the unique microscopic study of hydrogen in embrittled metals; (2) initiating research in collaboration with the Thermophysics Division and the University of Wisconsin on the structure and dynamics of liquid metals and fluid mixtures; and (3) a new research effort in the neutron characterization of rapidly quenched amorphous rare-earth glasses with scientists from Xerox.

Technical Activity

Microscopic Properties of Hydrogen in Metals and Molecular Materials

J. M. Rowe, J. J. Rush, S. F. Trevino,* and A. Magerl*

Examples of activities and accomplishments during the past year:

- Completed first neutron scattering measurements of low-level hydrogen dynamics in transition metals in the presence of trapping interstitial impurities.

- Completed detailed neutron inelastic scattering investigation of a novel phase transition in mixed alkali halide-alkali cyanide crystals and derived theory of dipole glasses to explain results.

- Probed hydrogen vibrations and interstitial sites in prototype metallic glasses and polycrystals by high energy neutron scattering spectroscopy.

- Completed study of chemisorbed molecular reaction products on Raney nickel using neutron vibrational spectroscopy as a test of neutron scattering to probe chemical reaction mechanisms on fine-particle industrial catalysts.

- Completed first stage of computer modelling investigation of shock wave propagation in condensed phases of molecules as part of a project to study the molecular basis of chemical instabilities initiated by shockwaves.

- Finished design and began construction of high-intensity neutron analyzer for surface spectroscopy and hydrogen in metals.

Microscopic Properties of Magnetic and Amorphous Materials

J. J. Rhyne, R. C. Casella, J. Lynn,* H. Alperin,* N. Koon,* and K. Hardman

Example of activities and accomplishments during the past year.

- Our inelastic scattering studies of the Laves phase rare earth compounds which are prototype two-component magnetic systems have been expanded to include an examination of crystal field and exchange interactions in rare earth cobalt compounds as well as a further investigation of excited state spin wave excitation in iron systems.

- A Greens function random phase approximation (RPA) computer model including both exchange and crystal field contributions has been developed to analyze magnetic inelastic scattering data on rare earth systems.

- The effect of hydride formation on the magnetic spin ordering of several rare earth compounds has been examined and evidence has been obtained of the formation of a pseudo "spin-glass" state without true long range order on introduction of hydrogen into these initially strongly-coupled conventional ferrimagnetic compounds. A definitive crystallographic analysis of the site occupancy of the hydrogen (or deuterium) is also nearing completion.

- A thorough study has been completed of the crystal fields in a number of chevrel-phase compounds which show co-existent phenomena of superconductivity and magnetic ordering.

- A study of the critical point properties of a commercial ribbon amorphous alloy has been performed using small angle scattering techniques. In addition, the spin dynamics of the same alloys have been examined at several temperatures.

- A study has been initiated of spin waves in Rb $MnCl_3$, a ferromagnet with alternating strong and weak exchange couplings.

- A detailed comparison of the magnetic small angle scattering observed in amorphous rare earth alloys, amorphous transition metal alloys, and conventional ferromagnets has been initiated in an effort to establish the role of random magnetic anisotropy in forming and affecting the micro-domain structure of these materials.

- The sub-task leader was chairman of the Advisory Committee to the International Conference on Magnetism and Magnetic Materials.

NEUTRON DIFFRACTION AND RADIOGRAPHIC METHODS FOR MATERIALS UTILIZATION AND DURABILITY

This task utilizes the unique role of neutrons (due, e.g., to their deep penetration, sensitivity to light atoms, and well-defined lineshapes for precise structure analysis) in the structural analysis and nondestructive testing of materials. Task members have competences at the forefront of measurement and analysis of materials structure, including the best U.S. efforts in neutron powder diffraction and profile analysis methods, broad expertise in radiographic measurement technology, and state-of-the art computer controlled diffraction facilities. This expertise is used to develop advanced neutron diffraction and radiographic methods to provide: (1) <u>precise structure analysis</u> essential for effective use of materials (e.g,. in batteries and construction materials); (2) <u>nondestructive reference methods</u> for residual stress and texture affecting metal product performance, for improved quality assurance, e.g., in pacemaker batteries and composites, and for microstructure analysis of materials in extreme environments; and (3) <u>neutron radiography and beams standards</u> for more accurate and reliable plant and field inspections (e.g., corrosion in aircraft). Current research and measurement activities include cooperative projects with the Center for Radiation Research (NDE), Center for Building Technology (cement structure), Center for Thermodynamics and Surface Science (fluid properties), and with three CMS Divisions (materials structure and durability). This task also directly serves the Office of Nondestructive Evaluation and Nuclear Safeguards. Outside interactions and cooperative research with groups needing advanced neutron methods include NIH, NRL, Army Materials, Navy, FDA, Goddard, Smithsonian, Allied Chem., Xerox, Army, and universities on projects ranging from corrosion detection to the structure of proteins.

New plans for the coming year include: (1) cooperative research with industrial scientists on the use of high-resolution neutron diffraction as a probe of structure and chemically active sites in zeolyte catalysts and in the study of microscopic transport mechanisms in prototype ionic conductors; (2) improved methods for measuring and interpreting modulated structures in materials such as defect-oxide ceramics; and (3) the development of state-of-the art instrumentation and scientific applications for small angle neutron scattering.

Technical Activity

Neutron Diffraction Methods and Applications

E. Prince, A. Santoro, B. Mozer, H. Prask,* S. Choi,* and A. Wlodawer

Examples of activities and accomplishments during the past year:

- In our efforts to advance the method and application of high resolution neutron-diffraction-profile analysis, we have developed new approaches for constrained refinement (thermal motion effects) and background subtraction in the profile analysis procedures.
- Initiated several new applications of neutron profile analysis, e.g., in the probing of active sites in zeolyte catalysts.
- Completed a theoretical investigation of absorption corrections for Weissenberg geometry diffractometers, such as our recently developed "flat-cone" neutron diffractometer. The formulas derived will be useful for a new class of instruments employing area detectors.
- Further refined the method and applications of nondestructive, depth-sensitive neutron diffraction measurements of grain orientation profiles in alloy products subjected to different treatments during fabrication.
- As part of the NBS-NIH project on biomaterial structures, the structure of the digestive enzyme ribonuclease was refined based on x-ray data to 2.5 A resolution, and a preliminary refinement based on our neutron diffraction data was initiated.
- First results have been completed in a neutron study by NBS, NIH, and the University of Arizona scientists on the structure of high-density lipoproteins.

Radiographic Methods and Standards

D. A. Garrett, Y. T. Cheng, and M. Ganowski

Examples of activities and accomplishments during the past year:

- In collaboration with the Fracture Mechanics Division, initial attempts have been made to macroscopically visualize hydrogen migration in steel using conventional neutron radiographic methods. These studies are continuing utilizing cold neutrons in an attempt to increase measurement sensitivity.

- Work has been initiated to accurately characterize neutron radiographic beam systems. Initial results on the measurements of the L/D ratio utilizing one proposed method has yielded results in the neighborhood of 10 to 30 percent higher than would be indicated by geometrical measurements. The physics of this phenomenon is under investigation.

- The conceptual design of the vertical resonance neutron system has been completed. This system will be employed for both resonance neutron radiography and tomography. Fabrication is pending approval of the NBSR Hazards Evaluation Committee.

- Software for the resonance neutron tomography and image reconstruction of containers utilized in reactor fuel processing plants has been obtained and modified. Initial simulation experiments have proved to be successful. These experiments have indicated that different algorithms must be employed for low and high contrast material in the containments.

- Work has been sponsored by the National Gallery of Art and the Smithsonian Institution to determine the feasibility of employing neutron induced autoradiography and high resolution gamma-ray spectroscopy for the authentication and attribution of valuable paintings. The preliminary results are quite encouraging and indicate a very important role for this method in the future.

- Experiments continue to characterize the electrolyte of cardiac pacemaker batteries during rundown. Neutron radiography and x-radiography exhibit complementary results. Three-dimensional neutron radiography conducted during the past year has indicated that void formation is indeed taking place during the rundown process.

Advanced Neutron Methods: Small-Angle Neutron Scattering

C. Glinka, and A. Cinquepalma

The Reactor Division has been granted support under the NBS Competence Building Program to develop new and advanced instrumentation and scientific applications in neutron scattering from materials. The original focus of the competence building activity is small-angle neutron scattering (SANS) and its potential for unique applications in the polymer and biological sciences, solid state physics and magnetism, metallurgy and materials science, and in the microscopic nondestructive testing of bulk materials.

Much of the engineering design work has been completed for a new, state-of-the art, SANS facility. The fabrication and procurement of various components of the instrument are well underway and installation is expected to begin in September 1979. Cooperative research activities have already been initiated with NRL, NIH, NSWC, and several universities.

The new SANS instrument will utilize long wavelength neutrons (5 to 10 A) and "pinhole" collimation along an evacuated eight meter flight path to reach wave vectors ranging from 0.002 to 0.2 A^{-1}. Measurements in this region serve to probe structure in the size domain from roughly 10 to 3000 A. A unique feature of the new instrument will be a geometrically focused collimation system which will effectively utilize the entire source flux while maintaining the stringent collimation conditions necessary for measurements at small scattering angles. The data collection rate with the new instrument will be greatly enhanced over what is presently available by use of a newly developed type of position-sensitive area detector. The sensitive area of the detector is 65 cm x 65 cm (with a 5 mm resolution element) and will simultaneously record data over the entire small-angle region. The data collection will be controlled by a dedicated minicomputer which will in turn be linked to larger computers for display and analysis of the data.

The construction of the instrument, the testing and calibration of the detector, and the development of instrument software will proceed in parallel over the next year with the facility becoming operational during 1980.

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*Long-term, full-time guest worker

Other Division Activities

Invited Talks

"Application of Neutron Scattering to Biology"
University of Alabama, Birmingham, Alabama
A. Wlodawer
October 1978

"Science Fact Versus Science Fiction-A Strange Story of Polywater"
University of Alabama, Birmingham, Alabama
A. Wlodawer
October 1978

"Dynamics of Molecular Reorientations"
McMaster University, Ontario, Canada
J. M. Rowe
November 1978

"Hydrogen in Metals"
University of Virginia, Charlottesville, Virginia
J. M. Rowe
November 1978

"Neutron Scattering Studies of Macromolecules"
University of California at Lost Angeles, Los Angeles, California
Molecular Biology Institute
A. Wlodawer
November 1978

"Neutron Inelastic Scattering Spectroscopy"
Argonne National Laboratory, Argonne, Illinois
NSF Workshop on "Present Needs and Future Trends in Neutron Crystallograph
and Spectroscopy"
J. J. Rush, S. H. Chen
November 1978

"Science Versus Science Fiction: The Strange Story of Polywater"
National Institutes of Health, Bethesda, Maryland
A. Wlodawer
February 1979

"An Observation of Quantum Mechanical Tunneling and Classical
Reorientation in Solid Nitromethane."
NBS, Thermal Heat Division
S. Trevino
March 1979

"Sizing Pipeline Girth Weld from Field Radiographs"
ANS Spring Conference/Display, San Diego, California
D. A. Garrett
April 1979

"The Observation of Electrolyte Phenomena in Lithium Iodide Pacemaker Batteries with Neutron Radiographic Interrogation"
ANS Spring Conference/Display, San Diego, California
D. A. Garrett
April 1979

"Structure of High Density Lipoprotein Recombinants Studied by
Neutron Low-Angle Scattering"
Duke University, Durham, North Carolina
8th Annual Souteastern Macromolecular Structure Meeting
A. Wlodawer
May 1979

"Studies of the Structure of Ribonuclease-A by X-ray and Neutron
Single-Crystal Diffraction"
National Institutes of Health, Bethesda, Maryland
NIAMDD Scientific Counselors Meeting
A. Wlodawer
June 1979

"Studies of the Reorientations of the Methyl Groups of Solid
Nitromethane"
NSWC, White Oak, Maryland
Energetic Materials Division
S. Trevino
June 1979

"Dynamics of AlkaliCyanide"
Argonne National Laboratory, Argonne, Illinois
J. M. Rowe
June 1979

"Amorphous YFe_2--A Concentrated Spin Glass"
Joint Intermag MMM Conference
New York, New York
D. W. Forrester, N. C. Koon, J. H. Schelleng, and J. J. Rhyne
July 1979

"Critical Magnetic Neutron Scattering from Cobalt"
University of Maryland, College Park, Maryland
C. Glinka
August 1979

"Use of Contraints in Crystal Structure Refinement"
Boston University-American Crystallographic Association, Boston, Massachusetts
E. Prince
August 1979

"Studies of Ribonuclease-A by X-ray and Neutron Diffraction"
Boston University-American Crystallographic Association, Boston, Massachusetts
A. Wlodawer
August 1979

Publications and Patents

Magnetic Relaxation Phenomena in Dy-Sc Alloys
R. Abbundi, J. J. Rhyne, D. M. Sweger, and R. Segnan
Physical Review B, 18 3313 (1978).

Magnetization and Neutron Scattering Measurements on Amorphous $NdFe_2$
H. A. Alperin, W. R. Gillomor, S. J. Pickart, and J. J. Rhyne
J. Appl. Phys 50 1958 (1979).

Small Angle Neutron Scattering from Rare Earth Iron Alloys
H. A. Alperin, J. Pickart, J. J. Rhyne
J. Applied Crystallography 11 648-49 1978.

Production of Ultracold Neutrons Using Doplar-Shifted Bragg Scattering and an Intense Pulse Neutron Spallation Source
T. W. Dombeck, J. W. Lynn, S. A. Werner, T. Burn, J. Carpenter
V. Krohn, R. Ringo
Nuclear Instruments and Methods (in press).

Neutron Scattering from Coherent Admixtures of Phonons with Libronic Excitations of Dictomic Imprintion
R. C. Casella
Phys. Rev. B (submitted).

Nondestructive Investigation of Texture by Neutron Diffraction
C. S. Choi, H. J. Prask, and S. F. Trevino
J. Appl. Cryst., (in press).

1-, 2-, 3-Triaminoguanidinium Nitrate by Neutron Diffraction
C. S. Choi, E. Prince
Acta Cryst. B35, 761-3 (1979).

Effect of Hydrogen on Sublattice Magnetization of Laves Phase Rare Earth Iron Compounds
G. E. Fish, J. J. Rhyne, S. G. Sankar, W. E. Wallace
J. Appl. Phys. 50, 2003 (1979).

Neutron Scattering Studies of Hydrides of the Laves Phase Rare Earth Compounds RFe_2
G. E. Fish, J. J. Rhyne, T. Burn, P. J. Viccaro, D. Niarchos, B. D. Dunlap, G. K. Shenoy, S. G. Sankar, W. E. Wallace
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In this volume we summarize the FY79 technical activities of the Center for Materials Science. The purpose of this report is to provide current information to the materials science community about the present directions of the NBS efforts in materials science.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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