REPORT

of

ARPA MATERIALS RESEARCH COUNCIL

1969

December 1969

Contract No. DAHC 15-67-C-0062, No. P-004
Materials Science Office
Advanced Research Projects Agency

Department of Chemical and Metallurgical Engineering
The University of Michigan
Ann Arbor, Michigan

INTRODUCTION

This report describes the activities and output of the ARPA Materials Research Council for the year ending December 31, 1969, the second year of operation of the Council.

The idea of a Materials Research Council originated in 1966 when several individuals in materials and material sciences including Dr. Robb Thomson, Director of the Materials Science Office of ARPA, discussed the possibility of bringing together 20-30 outstanding people in the materials field for an extended period each year to examine this area of study and relate their concerns and interests to those of DOD in these fields. The aim was not to form a policy or advisory group but a working group. The group was to be briefed on the current state of emerging problems and was to be challenged to develop solutions, or a consensus for approaches to the possible solutions of such problems.

Subsequent development of this idea led to the formation of the ARPA Materials Research Council and the bringing together of a group for an extended period of study during the summer of 1968 for the first summer conference. The concept proved to be so fruitful that the Council was continued through 1969 and plans are currently being projected through 1970.

It has not been the principal purpose of the Council in its two years of operation to concentrate on current high-priority and highly focused materials problems. This type of problem is usually in very competent hands, and is invariably part of a larger systems problem. The intrusion of the Council into such problems, while possibly of some benefit, would be divisive and cause back-tracking and be wasteful of the efforts of all groups involved. The Council has indeed occasionally worked on such problems and expects to do so in the future, but the real value of the Council lies in using it for its long-range and broad vision. A primary strength of the Council lies in its ability to recognize and work on future critical needs, rather than on current critical problems.

The initial concept that the members of the Council should be among the most able and highly qualified individuals in the Country in their respective fields in order to bring their expertise to bear on the complex materials problems of DOD has proved to be a wise decision. The quality of the people in their respective fields has been such that the entire group, physicists, chemists, and engineers, have interacted in such a fashion that they are probably one of the most coherent, versatile and knowledgable groups working in materials science and materials engineering in the Country. It is noteworthy that the group consists of essentially the same individuals in 1969 as in 1968. Only three individuals of the 1968 group were unable to take part in the 1969 operation and two of these plan to return to the Council when prior commitments are completed.

Since the personnel of the Council is drawn largely from the academic community it was felt that exposure to longer range subjects would influence the direction that their research and that of their students and colleagues might undertake. This has taken place to a marked degree. Follow-on work from problems encountered in the Council has emerged at most of the institutions represented by the Council membership. Several graduate students are actively pursuing problems first formulated by the Council. They include such topics as surface chemistry, the physics of surfaces, fracture analysis, stress corrosion, plasticity, high-temperature thermodynamics, composite materials, refractory materials, electronic properties, optical properties, etc. The interdisciplinary nature of the group is reflected in the wide range of researches that have been generated as a result of the problems discussed in the Council.

PROJECT ORGANIZATION

The technical direction of the ARPA Materials Research Council is delegated to a nine-man Steering Committee, who are representative of the various disciplines embodied in the Council. Membership on the Steering Committee is normally for a period of three years with replacements occurring each year. The functions of the Steering Committee are:

a) Work with ARPA and interested parties who contact ARPA, to select problem areas for consideration by the Council.

b) Select Council members, specialists and consultants to work with the Council.

c) Evaluate and direct project activities.

d) Participate in project management.

The current Steering Committee is as follows:

Professor Elliott W. Montroll,
Secretary of the Steering Committee
Department of Physics & Astronomy
University of Rochester
Rochester, New York 14534

Professor Michael B. Bever
Department of Metallurgy & Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor Morris Cohen
Department of Metallurgy & Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dean Daniel C. Drucker
Engineering College
University of Illinois
Urbana, Illinois 61801

Professor Herbert S. Gutowsky
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Professor James A. Krumhansl
Department of Physics
Clark Hall of Science
Cornell University
Ithaca, New York 14850

Professor John L. Margrave
Department of Chemistry
Rice University
Houston, Texas

Professor William Prager
Division of Engineering
Brown University
Providence, Rhode Island 02912

Professor George H. Vineyard
Brookhaven National Laboratory
Upton, Long Island, New York 11973

Professor W. Kohn, Department of Physics, University of California, San Diego and Professor W. A. Tiller, Department of Materials Science, Stanford University served on the Steering Committee until August when they were replaced by Professor Vineyard and Professor Cohen. Professor Montroll replaced Professor Krumhansl as Secretary of the Steering Committee at that time.

To carry out the work of the Council a contract has been arranged between ARPA and The University of Michigan. The Project Director is M. J. Sinnott, Professor of Chemical and Metallurgical Engineering.

The following functions are performed by the University:

a) Coordination of planning, through the Steering Committee.

b) Providing a central, responsive contact point and clearing house for all Council affairs.

c) Negotiate consulting agreements with the project participants, and to handle all administrative and financial affairs.

d) Publish the reports issued by the Council.

The current contract terminates April 1, 1970.

The members of the Council in addition to the members of the Steering Committee are as follows:

Professor Nico Bloembergen
Div. of Engineering & Applied Physics
Pierce Hall
Harvard University
Cambridge, Massachusetts 02138

Professor Bernard Budiansky
Div. of Engineering & Applied Science
Harvard University
Cambridge, Massachusetts 02138

Professor Pol E. Duwez
W. M. Keck Laboratory of
Engineering Materials
California Institute of Technology
Pasadena, California 91109

Professor Willis H. Flygare
Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois 61801

Dr. John J. Gilman, Director
Materials Research Center
Allied Chemical Corporation
P.O. Box 70
Morristown, New Jersey 07960

Professor Robert Gomer
James Franck Institute
University of Chicago
5640 Ellis Avenue
Chicago, Illinois 60637

Professor Alan Heeger
Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Professor John P. Hirth
Metallurgical Engineering Dept.
Ohio State University
Columbus, Ohio 43201

Professor Walter Kohn
Department of Physics
University of California, San Diego
La Jolla, California 92037

Professor Erastus H. Lee
Department of Applied Mechanics
Stanford University
Stanford, California 94305

Professor Frank A. McClintock
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor Howard Reiss
Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Professor Paul L. Richards
Department of Physics
University of California, Berkeley
Berkeley, California 94720

Professor J. Robert Schrieffer
Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Professor Alan J. Sievers
Laboratory of Atomic & Solid State Physics
Cornell University
Ithaca, New York 14850

Professor Charles P. Slichter
Department of Physics
University of Illinois
Urbana, Illinois 61801

Professor Robb M. Thomson
Department of Materials Science
State University of New York
Stony Brook, New York 11790

Professor William A. Tiller
Department of Materials Science
Stanford University
Stanford, California 94305

Professor Michael Tinkham
Department of Physics
Harvard University
Cambridge, Massachusetts 02138

PROBLEM SELECTION

In 1968 the Steering Committee, working with the ARPA Materials Science Office, arranged a series of briefings with various DOD agencies to examine those areas which were believed most appropriate for consideration by the Council. As a result of these meetings and subsequent discussions with the entire Council, four general topics were chosen for detailed examination: composite materials, shock propagation, constitutive relations at high temperatures and pressures and underground sensing. At the 1968 summer conference, consultants and specialists worked with the Council to define more closely the problem areas, and to inform the Council members of related programs and progress. Individual members then worked either independently or in small subgroups on various segments of the problem areas and, after discussion and analysis, issued reports.

While the above procedure was reasonably successful in directing the work of the Council, further improvements were put into effect in the 1969 operation. The original concept of holding a summer conference when the entire Council could devote its concentrated efforts to a few selected issues proved to be a valid and fruitful procedure, but it was evident that more detailed preparation prior to the summer conference was necessary in order to use the talents of the Council efficiently and to follow up on the consequences of the Council output. To achieve this, procedures were established for individuals or subgroups of the Council to undertake follow-on activities such as visits to DOD installations and DOD contractors or continuing investigations at home institutions to prepare for the following conferences. Professors Thomson and Vineyard assumed responsibility for follow-on work in the area of shock and constitutive relations. Professors Bever and Krumhansl performed the same function in composites. After the 1968 meeting the potential new area appraisals for evaluation and follow-on were as follows: Emp studies-Schrieffer; Lasers-Montroll; Corrosion-Tiller; Tunneling-Kohn; New Materials-Margrave.

In February, Professors Thomson and Vineyard visited Los Alamos Scientific Laboratory, Sandia Corporation and AFWL to discuss shock waves in solids. The purpose was to uncover new problem areas, to study related experimental work, and to sense the response to our efforts in this area from the 1968 conference. Technical discussion with individuals at these various laboratories disclosed considerable interest in studies of the Grüneisen constant, atomic structure of a shock wave, electrical effects of shock in solids, dislocation structures under shock, wave dispersion in periodic structures and shock measurements.

Professor Schrieffer, with Dr. Huggins of ARPA Materials Science Office, visited the Sandia Albuquerque facility in April to discuss EMP problems. Representatives of Sandia Albuquerque, Sandia Livermore and LRL discussed several aspects of magnetics and dielectric problems that were of potential interest to the Council.

Professor Bever, in follow-on work on composites, attended the Washington University-Monsanto Composite Materials Conference in St. Louis in April and presented a paper at that conference. He also followed up three-dimensional weaving techniques developed by AVCO and GE for the production of composite materials.

Professors Tiller, Bever and Reiss formed a subgroup of the Council to survey the area of corrosion to determine what activities might be profitably examined and studied by the Council. In March a detailed briefing of the above group in corrosion problems in the aerospace industry was arranged by Dr. George Martin of North American Rockwell Corporation to give an indication of the scope of the corrosion problem in just one specific industry. Professor Roger W. Staehle of Ohio State University Corrosion Center was commissioned to write a position paper for the Council dealing with the overall national picture on corrosion and possible ways of grappling with this immense problem.

The status of certain materials problems in high-energy laser systems was reviewed by Professor Montroll. Several groups outside the Council are actively working in this specific area, and he acted as liasion between these groups and the Council.

A subgroup of Margrave, Gutowsky and Sinnott examined the heat-sink problem suggested by J. Persh of ODDR & E. A conference at the Pentagon was attended by Persh, Reilly, McLain, Bloom, Margrave and Sinnott. Following this meeting, Sinnott attended a further meeting on the subject at Lockheed.

The Steering Committee met in Washington in April to review the activities of the various follow-on groups, to select the areas of study for the Council, and to arrange briefing sessions for the entire Council to be held in May.

At the April meeting it was obvious that our interests in shock and EMP matched those of Sandia and Dr. S. Buchsbaum of that organization was invited to participate in the May meeting. Further work on composites, particularly the interface and fracture problems, were approved for Council study, along with a more detailed inquiry into 3-D composites and methods of evaluating these materials. The laser topic was not selected as a principal subject for the Council in 1969. It is receiving intensive attention by other groups, and while we may be of some assistance and have some interests, particularly in laser optics, no large effort was planned.

Corrosion is such a large and complex field that the Steering Committee decided to limit our coverage in 1969 to stress corrosion. A small group was to survey this problem and, depending on their analysis, the subject might receive more emphasis at later conferences.

There has been a continuing interest on the part of the Council in new materials, materials for extreme conditions, and the ultimate properties of materials. These topics were also chosen for study during the 1969 conference.

The entire Council met in Washington for a two day series of briefing sessions in May. At these meetings the various follow-on groups presented the results of their work and delineated the problem areas that would be examined at the summer conference. Dr. Orval E. Jones of the Sandia Laboratories gave an excellent resumé of the work then underway and showed how our studies might relate to this work. Further discussion by the Council showed considerable interest in what was termed "Societal" materials problems, i.e., in such areas as housing, transportation, bio-medical materials, secondary materials and waste disposal. A small subgroup agreed to give some effort to these subjects at the conference. The phenomenon of fracture is involved in the shock, corrosion, and composite areas, and so a subgroup was formed to examine the nature of fracture for possible detailed inquiry at the conference.

Task leaders were assigned to each of the problem areas to make preparations for the summer conference, and an interest poll of Council members was taken to assist the leaders in organizing the work for study.

Shock - Vineyard	Interfaces & Surfaces Tiller, Gomer	EMP - Schrieffer
Flygare	Drucker	Reiss
Heeger	Kohn	Gomer
Kohn	Schrieffer	Tinkham
Lee	Sievers	Flygare
Thomson	Thomson	Heeger
Tinkham	Heeger	Kohn
Budiansky	Bever	Schrieffer
McClintock	Cohen	
Reiss	Tiller	
Schrieffer	McClintock	
	Duwez	
	Hirth	

Stress-Corrosion - Tiller

Drucker
Gutowsky
Flygare
Reiss
Cohen
Bever
McClintock
Hirth

Laser-Optics - Montroll

Vineyard
Gutowsky
Flygare
Gilman
Sievers
Tinkham

Fracture - McClintock

Budiansky
Drucker
Hirth

Composites - Bever, Krumhansl

Drucker
Gutowsky
Duwez
Lee
McClintock
Sievers
Cohen
Budiansky
Hirth

Societal Materials - Cohen

Kohn
McClintock
Sievers
Bever

New Materials, Ultimate Properties
Margrave

Duwez
Kohn
Reiss
Sievers
Gutowsky

THE SUMMER CONFERENCE

To invite technical specialists and consultants to the Council during the July conference, the ARPA Materials Science Office made arrangements with various DOD agencies and DOD contractors as well as other governmental offices to obtain the services of their personnel.

The Sandia Laboratories cooperated by sending specialists on shock, EMP, composites and corrosion. Drs. Orval E. Jones, J. C. King, R. G. Kepler, G. A. Samara, D. S. McClosky, J. E. McDonald and R. L. Schwoebel were in attendance at the summer conference for various periods to time, and their knowledge and expertise were of invaluable assistance to the work of the Council.

Dr. Mark Wilkins of UCRL also attended the conference and provided important input in connection with shock, fracture and failure analysis.

In the areas of composites and surfaces, the Council had the services of Dr. M. L. Minges and Dr. S. W. Tsai of the Air Force Materials Laboratory, Dr. R. A. Florentine of the General Electric Company and Drs. Lurie and Lenoe of AVCO. Dr. D. O. Thomson of North American Rockwell Science Center discussed NDT testing techniques.

Assistance in the corrosion area was obtained from Dr. Floyd Brown of NRL, Professor R. W. Staehle of Ohio State University, and Professor G. M. Pound of Stanford University.

The Directors of the Air Force, Army and Navy Materials Laboratories: Dr. A. Lovelace, AFML; Dr. P. Scala, AMMRC and Dr. J. Schulman, NRL were in attendance for short periods at the conference, and contributed valuable insights to various topics under consideration by the Council.

The summer conference was held in Centerville, Massachuset at the same location as that used in the preceding year. It was chosen again because of its conduciveness to concentrated study and its proximity to M.I.T. whose library facilities were again made available for use by the Council. Real-time computer facilities were available from either the Dartmouth or Michigan Computing Centers.

CONFERENCE OPERATION

Because of prior preparation by the various subgroups, work was started immediately on the selected problems. Presentations and more detailed briefings were offered by the consultants and specialists, and attention was immediately focused on the critical parts of the various problems. Individual and subgroup efforts then continued over a two week period. Preliminary findings were discussed in seminars, position papers were circulated and the various outputs were finally collected into report form.

The reports of the Council fall into three categories:

1. Finished reports available for general distribution. Some of these were completed at the summer conference, but many are topics that were initiated last year or developed as follow-on projects and were continued during the year at the participants' institutions.

2. Research reports for restricted distribution. These represent work-in-progress and are available to anyone on request. They are usually not at the same stage of completion as the reports in Category 1.

3. Technical memoranda. These are essentially internal working papers of the Council. They represent initial ideas or concepts, suggestions for further development, status reports, position papers, etc.

Reports in Category 1 are available to anyone requesting them. Those in Category 2 and 3 will be released to those requesting them through the Project Director who will check with the authors for release.

The work of the Council is now summarized herewith by listing of the report titles and authors. Abstracts of reports in Categories 1 and 2 may be found in the Appendix to this report. Some abstracts in Category 3 are included.

I. RESEARCH REPORTS FOR GENERAL DISTRIBUTION

On Nonstructural Applications of Composites
M. B. Bever, P. E. Duwez, W. A. Tiller

Variational Methods for Dispersion Relations and Elastic Properties of Composite Materials
W. Kohn, J. A. Krumhansl, E. H. Lee

On the Prevention of the Oxidation of Graphite
R. A. Huggins

Induced Covalent Bonding Mechanism of Chemisorption
R. Gomer and J. R. Schrieffer

Theory of Induced Covalent Bonding Mechanism of Chemisorption
J. R. Schrieffer

Surface Properties of a Network Model of Electrons in Solids
E. W. Montroll

Carrier Injection and Recombination in Dielectric Insulators after X-Ray Irradiation
A. J. Heeger and H. Reiss

The Chemical Attenuation of Shock
H. S. Gutowsky

Absorption of High-Power Laser Radiation and the Mechanisms of Breakdown in Materials
W. H. Flygare

On the Strength-Differential Phenomenon in Hardened Steel
J. P. Hirth and M. Cohen

Pressure Dependence of the FeRh First-Order Phase Transition
A. J. Heeger

On the Kinetics of Irreversible Processes in Terms of the Thermodynamics of Inhomogeneous Systems
G. M. Pound, J. P. Hirth and W. A. Tiller

The Use of Solid-State Electrochemical Techniques to Limit Transport of Hydrogen Through Silicate Glasses
R. A. Huggins

Analysis of Sonar Sensing Techniques in the Earth
M. Tinkham and P. L. Richards

A Hydrogen Pump for Stress Corrosion
W. A. Tiller and J. R. Schrieffer

II. RESEARCH REPORTS FOR RESTRICTED DISTRIBUTION

Thermal and Thermoelastic Properties of Isotropic Composites
B. Budiansky

Optical Properties of Composites
A. J. Sievers

On the Stability of Ti-C and Ti-B Composite Interfaces
J. P. Hirth and W. A. Tiller

Thermodynamic Considerations Relating to the Use of Electrochemical Techniques for the Growth of Single Crystals of Borides
R. A. Huggins

On the Hardnesses of Carbides and Other Refractory Hard Metals
J. J. Gilman

Structural Model of Vitreous Oxides Based Upon Concepts of Defect Chemistry
R. A. Huggins

Energy Absorption by Martensitic Transformations in a Shock Wave
M. Cohen

Quantum Tunneling as an Elementary Fracture Process
J. J. Gilman and H. C. Tong

III. <u>TECHNICAL MEMORANDA</u>

Temperature Dependence of Stress-Corrosion Cracking
M. Cohen

Proposed Summer Studies of Biomaterials
M. Cohen

Origin of the 1/t Leakage Law for the Irradiated Capacitor
A. J. Heeger, H. Reiss and J. R. Schrieffer

New Materials - A Summary
J. L. Margrave
(Duwez, Huggins, McClintock, Sinnott)

A Brief on the Corrosion of Engineering Materials in the United States - Nature of the Problem and a Plan for Action
R. W. Staehle

Corrosion Perspective
W. A. Tiller, M. B. Bever, H. Reiss

Shock and Emp

Because of the excellent exchange of information between the Council members interested in these problems and the specialists and consultants of the Sandia Laboratories, this work was more sharply focused than were the efforts of the preceding year. Dr. Orval Jones of Sandia attended the spring meeting of the Council, became aware of the overlapping interests of the two groups, and arranged to have their specialists work with the Council members at the conference.

In the shock area, Vineyard examined the problem of the thickness of a shock front and pointed up the conflict between theory and experiment. He also proposed a criterion for determining whether a phase transformation will be produced by a shock wave in a solid. Cohen calculated the energy absorption from a shock wave by the martensitic transformation in alloys. Gutowsky, working with Professor Gordon Hammes of Cornell, who was brought in as a specialist, studied the possibility of utilizing an endothermic chemical reaction or phase change for attenuating a thermal or mechanical shock in a closed system. The effect of a shock on a porous medium led to an examination of the characterization of porosity by Bever and Cohen. Heeger reported on the pressure dependence of the first-order phase transition in the Fe-Rh system.

Thomson examined the electrical potentials when a shock front moves through a metal. Heeger and Reiss inquired into the behavior of capacitors after irradiation with a high-intensity pulse of X-rays and proposed a model to explain why the properties vary with time after such pulsing.

Composites

The work on composites resulted in a deeper penetration into specific problems than was possible last year. Bever, Duwez and Tiller continued their study of the nonstructural applications of these materials. Kohn, Krumhansl and Lee examined the propagation of elastic waves through a composite medium using variational principles. The solution of the variational equations enabled them to calculate the dispersion relations and the elastic properties of certain composite materials. Budiansky developed theoretical estimates of several thermal and thermoelastic constants of macroscopically isotropic composite materials. Sievers examined the infrared and submillimeter wave properties of crystal and fiber composites. Duwez pointed out the analogy between 3D composites and crystal structures. Kohn showed that the flow of electric or heat currents through selectively oriented fiber composites can yield very large transverse electric fields or temperature gradients.

Surfaces and Interfaces

The work carried out in 1968 on composites pointed up the fact that many of the properties of materials were critically dependent on surface or interfacial effects. Gomer and Schrieffer examined chemisorption and developed a theory based on an induced covalent bond. Huggins proposed a model which suggests a means for preventing the oxidation of graphite fibers in a metal matrix. Hirth and Tiller considered methods for stabilizing boron and graphite fibers at elevated temperature in a titanium alloy matrix. Margrave and Huggins suggested fluoridation as a technique for protecting graphite fibers from oxidation and from solution in metal-graphite composites. Margrave presented the results of studies on a low-friction high-temperature material, carbon monofluoride. Pound, Hirth and Tiller analyzed the kinetics of irreversible processes in terms of the thermodynamics of inhomogeneous systems. Montroll examined the surface properties of a network model of electrons in solids and showed that when free boundaries are introduced, a band of surface states develops. The location of the bands and their density states were calculated.

Fracture

The problem of fracture has turned up in several ways: shock, composites, corrosion and interfaces. The Council decided at the summer conference to devote more effort to this topic in the future. Professor McClintock, in a series of technical memoranda has pointed up the problem areas in brittle materials and inhomogeneous solids. He and Professor Drucker have examined the various aspects of spall fracture, hole growth and void coalescence. The connection of such studies to the design of light weight armor has been emphasized. Dr. Scala of AMRCC gave several briefings on this problem and urged the interested Council members to pursue studies in this area. Dr. Wilkins made several valuable suggestions in regard to the method of attack on this problem. Gilman proposed a new model for fracture based on a quantum-mechanical concept of the tunneling of a chemical bond between different states.

Corrosion

In the light of prior assessment of the corrosion problem, the efforts of the Council were focused on stress-corrosion. Dr. Floyd Brown of NRL gave a summary of the work currently underway in this area, and pointed up where further knowledge was required. Hirth, McClintock, Schrieffer and Tiller examined the nature of stress corrosion at several levels of observation, extending from the continuum to the atomic scale. Tiller and Schrieffer analyzed the electron redistribution in a metal due to the presence of a notch and tensile stresses which in turn causes H^+ migration and discharge. Dr. Staehle was commissioned to make a survey of the entire materials corrosion problem and he presented a plan for action in the area. His report is included in the output of the Council. A related report was prepared by Tiller, Bever and Reiss to obtain a perspective of the corrosion field.

New Materials

This is an area of considerable interest to most of the members of the Council. Margrave in his New Materials Summary outlines the general kinds of chemical and physical considerations which enter into new-materials development. Duwez discusses amorphous semiconductors and metals. Margrave reports on diamond synthesis and technology, and surface treatments for fibers of all types. McClintock discusses factors to be considered in designing light-weight armor. Sinnott analyzes the possibilities of new materials for heat-sink applications.

Societal Materials

Preliminary consideration was given to the role of materials in socially-impacted technologies, such as housing, transportation and biomedical engineering. Among these possible subjects, Cohen concluded that the field of biomaterial systems best matches the style of the Council in degree of sophistication and interdisciplinary scope. This topic has been recommended for detailed study by the Council at the 1970 conference.

Other Topics

The first summer conference took up the topic of high speed tunneling through hard rock and concluded that one of the principal problems was the detection of faults and changes in the medium in which the machine was advancing. A SONAR system was suggested but no detailed analysis was presented at that time. Tinkham and Richards at the 1969 conference made a detailed analysis of such a system. The problems of angular and distance resolution were considered and optimized for an array of 12 sensors distributed over the tunnel face. They also considered the problems of data collection and displaying the results of the analysis.

Hirth and Cohen completed their model calculations, begun last year, on the strength differential observed between tension and compression testing of martensitic steels.

Huggins inquired into the diffusion of hydrogen in silicate glasses, and showed how it could be limited based on electrochemical transport theory. This was in response to a specific problem discussed by one of the visitors in which the need for such blocking of diffusion was required.

In preparation for a closer examination of laser and laser optics problems, Flygare examined the causes of breakdown of optical materials due to high-power electromagnetic radiation. Montroll has been following this work and at future conferences will, with a subgroup of the Council, become more involved in this area.

Gilman correlated the hardness of carbides and diborides in terms of metal-metalloid interactions. Huggins developed a structural model of vitreous oxides based on concepts of defect chemistry.

Dr. Theodore Cooper of the National Heart Institute gave a talk to the Council on the problems encountered by the health sciences with respect to biomaterials and their compatibility in the human body. Particular attention was focused on blood flow and blood clotting tendencies in the vicinity of implants. Sufficient interest was expressed in these phenomena to justify in-depth studies at the next summer conference.

Follow-On Activities

It was obvious that commissioning individuals or sub-groups of the Council to carry on studies between the various meetings of the Steering Committee and the Council contributed greatly to the improved operation of the project. Such efforts will be continued in preparation for the 1970 conference. Some work will continue in the shock area with probably increased activity in EMP studies. The work on surfaces will certainly be extended since it encompasses other interests in interfaces, fracture, and corrosion. The work on fracture will be expanded as will studies on stress-corrosion. Materials problems in high-powered lasers will receive increased effort by the Council. Problems in composites will be focused more on surface, interface and environmental effects than on the actual engineering materials themselves. Biomedical materials will receive increased emphasis, and to this end work studies on polymeric materials will be initiated.

APPENDIX

Abstracts

ON NONSTRUCTURAL APPLICATIONS OF COMPOSITES

M. B. Bever
P. E. Duwez
W. A. Tiller

Potential nonstructural applications of composites are surveyed. These applications are considered systematically in terms of the basic characteristics of composites. Useful materials and devices for electrical, magnetic, optical, thermal, acoustical, nuclear and chemical applications become apparent.

VARIATIONAL METHODS FOR DISPERSION RELATIONS AND ELASTIC PROPERTIES OF COMPOSITE MATERIALS

W. Kohn
J. A. Krumhansl
E. H. Lee

The propagation of elastic waves through composite media with a periodic structure is analysed. Methods utilizing the Floquet or Bloch theory common in the study of the quantum mechanics of crystal lattices are applied. Variational principles in the form of integrals over a single cell of the composite are developed, and applied in some simple illustrative cases. This approach covers waves moving in any direction relative to the lattice structure, and applies to structures of the Bravais lattice groups which include, for example, parallel rods in a square or hexagonal pattern, and an arbitrary parallelopiped cell. More than one type of inclusion can be considered, and the elastic properties and density of the inclusion and matrix can vary with position, as long as they are periodic from cell to cell.

The Rayleigh-Ritz procedure can be applied to the solution of the variational equations, which provides a means of calculating dispersion relations and elastic properties of specific composite materials. Detailed calculations carried out on layered composites confirm the effectiveness of the method.

ON THE PREVENTION OF THE OXIDATION OF GRAPHITE FIBERS IN METAL MATRIX COMPOSITES

R. A. Huggins

A general model for oxidation at the interface between graphite fibers and metallic matrices is presented and the important thermodynamic parameters controlling this phenomenon are identified. The very significant influence of external oxides, carbide or other intermediate phases between the fiber and the matrix, and protective coatings on the fiber are discussed.

INDUCED COVALENT BONDING MECHANISM OF CHEMISORPTION

R. Gomer
J. R. Schrieffer

A new mechanism of chemisorption is proposed. The scheme is analogous to the Heitler-London scheme of molecular theory, in that it incorporates the necessary strong suppression of charge fluctuations present in the Hartree-Foch (or molecular orbital) scheme. Since an unpaired spin density does not usually occur at a free surface, such a spin density must be induced by the absorbed atom and a covalent-like bond then formed with it. The theory gives a smooth transition from weak to strong bonding as a function of the metal and ad-atom properties.

THEORY OF INDUCED COVALENT BONDING MECHANISM OF CHEMISORPTION

J. R. Schrieffer

The recent ideas of Gomer and Schrieffer on the physical mechanism of chemisorption in a wide range of systems are developed in a new theoretical framework. The scheme is related to the Heitler-London method of molecular physics but works with non-orthogonal many-body basis states of the combined ad-atom and metal system. An effective "antiferromagnetic exchange interaction" between an unpaired spin on the ad-atom and the metal electrons is derived which leads to a treatment of the chemisorption bond from the weak bonding limit occurring on simple metal surfaces to the nearly molecular bond formed between an ad-atom and the transition metal surface atoms. Generalization of the theory to treat ad-molecules and degenerate orbital ad-atoms are discussed, as is the influence of ionic mixtures into the bond. Finally, the effect on chemisorption of many-body interactions in the metal, such as ferromagnetism, etc., is discussed.

SURFACE PROPERTIES OF A NETWORK MODEL OF ELECTRONS IN SOLIDS

E. W. Montroll

Surface properties of a network model of electrons in solids are discussed. In the model, electrons are restricted to move along lines connecting node points of a periodic network. Each node point on the network corresponds to an atom. A potential well is introduced for each atom or node point so that as the depth of the potential becomes large one has the tight binding model and as the potential vanishes and the number of node points increases one has the Sommerfeld free electron model. Exact wave functions and energy levels have been obtained elsewhere for the model when periodic boundary conditions are applied.

When free boundaries are introduced a band of surface states develop. Their depth of penetration into the crystal as a function of wave number is investigated. The location of surface energy bands is also made and their density of states is calculated.

CARRIER INJECTION AND RECOMBINATION IN DIELECTRIC INSULATORS AFTER X-RAY IRRADIATION

A. J. Heeger
H. Reiss

Capacitors containing mylar as a dielectric are able, under normal conditions, to withstand fields of 10^5-10^6 volts/ cm^{-1} without appreciable leakage. Upon irradiation with a high intensity pulse of x-rays, a current is observed to flow and to decay, over many decades of time, in approximately inverse proportion to time. The current also seems to be proportional to the initial x-ray dose. The observed behavior is explained on the basis of a model in which:

(1) The x-ray pulse generates hole-electron pairs, the holes being trapped and immobile.

(2) Holes and electrons recombine by a slow diffusion or drift-controlled process. This phenomenon, combined with Item (1), makes current injection possible.

(3) Positive holes have giant recombination cross sections which interfere with each other in such

a way that current decay occurs in the manner observed. In particular, current depends inversely on time and is proportional to the initial dose rate.

This article develops a quantitative theory for the model described.

THE CHEMICAL ATTENUATION OF SHOCK

H. S. Gutowsky

An analysis is made of some of the thermodynamic and kinetic aspects of using an endothermic chemical reaction or phase change in the solid state, as a means of absorbing or otherwise attenuating a thermal and/or mechanical shock in a closed system. A chemical reaction seems inherently unsuitable for dealing with thermal deposition alone. The prospects with respect to conversion of a mechanical shock to heating of the system are more favorable but the conditions required are too limiting for the approach to be very promising. The case of a solid-state phase change is thermodynamically and kinetically more suitable and may warrant a search for systems with the particular properties needed.

ABSORPTION OF HIGH POWER LASER RADIATION AND THE MECHANISMS OF BREAKDOWN IN MATERIALS

W. H. Flygare

This report summarizes the causes of breakdown of materials under the influence of high power electromagnetic radiation in the optical range. The mechanisms of failure in pure materials and the influence of impurities in host lattices are examined. Questions are posed for further examination and experiments are suggested which if carried out would assist in determining mechanisms.

ON THE STRENGTH-DIFFERENTIAL PHENOMENON IN HARDENED STEEL

J. P. Hirth
Morris Cohen

A brief review is presented of the strength-differential phenomenon in martensitic steels, wherein such steels are notably stronger in compression than in tension. It is proposed that nonlinear-elastic interactions between dislocations and interstitial solute atoms can contribute significantly to the observed phenomenon. A simple-model calculation indicates that the proposed interaction can account for an appreciable part of the effect.

PRESSURE DEPENDENCE OF THE FeRh FIRST ORDER PHASE TRANSITION

A. J. Heeger

The pressure dependence of the first order phase transition in FeRh is shown to be consistent with the recent model which views this transition as driven by the change in Fermi gas entropy associated with the band structure in the two phases.

ON THE KINETICS OF IRREVERSIBLE PROCESSES IN TERMS OF THE THERMODYNAMICS OF INHOMOGENEOUS SYSTEMS

G. M. Pound
J. P. Hirth
W. A. Tiller

An expression is proposed for the total reversible work effect, ψ, as the thermodynamic driving potential in situations where several state variables change in the course of a process for which there are contributions from both non-gradient and gradient terms. The effects of gradient terms on the mobilities of transporting species are also considered and expressions are given for the fluxes. Thermal diffusion is taken as a specific example. The process path and stationary state in inhomogeneous systems are briefly considered. The rate of destruction of the total thermodynamic driving potential, ψ, is hypothesized to be an extremum in the stationary state.

Purpose

In dealing with complex material structures, a number of cases arise wherein one wishes to maintain large gradients in a number of state variables of the system. A specific example is the case of a metal matrix (Ti alloy) - fiber (graphite) composite with an intermediate diffusion blocking layer (silver). After exposure to elevated temperatures in service conditions, gradients will be present in concentrations of the three major species, in the alloying elements in the titanium, in the atomic volume, in the local stress tensor, in point defects and dislocations, and in the electrical charge density. Such a problem might seem to present insuperable difficulties with regard to a detailed fundamental description of the local state of the system. Indeed, this may be the case for several more years with respect to a description in terms of quantum statistics. However, some insight into the problem can be gained by describing the situation in terms of the generalized thermodynamics of inhomogeneous media, including cross-terms between the gradient contributions of the groups of the state variables. In principle, the measurement and understanding of such cross-terms would enable one to proceed with an engineering design to optimize the performance of the complex systems. In the above composite application, for example, this could involve stabilizing the graphite fibers with respect to chemical reaction or diffusion while retaining the physical integrity of the interface and the strength of the composite. Hence, we present a description of the kinetics of irreversible processes in terms of the thermodynamics of inhomogeneous media with the above ends in mind.

THE USE OF SOLID STATE ELECTROCHEMICAL TECHNIQUES TO LIMIT TRANSPORT OF HYDROGEN THROUGH SILICATE GLASSES

R. A. Huggins

Electrochemical principles involved in transport of hydrogen ions through silicate glasses as well as some possible methods for its retardation are briefly discussed.

ANALYSIS OF SONAR SENSING TECHNIQUES IN THE EARTH

M. Tinkham
P. L. Richards

A detailed analysis is given of the performance that might be achieved with a SONAR system optimized for sensing what lies ahead of an underground tunnel face. The general problem of angular and distance resolution is considered mathematically, and a specific array is suggested which optimizes performance for a small number (12) of sonic detectors distributed over the tunnel face. It is estimated that the system could resolve reflections from about 12 distinguishable angular directions and 50 distinguishable distances for a total of some 600 distinguishable locations in the rock within a range of perhaps 100 feet ahead of the tunnel face. The problem of an easily interpretable visual display of the data is then considered. Several cathode ray tube display schemes are discussed which place different demands on the associated computational facility. Finally, some aspects of the data acquisition problem are considered. These include the mounting of the detectors, the interface between the detectors and the digital computer, and the dynamic range required of the system.

THERMAL AND THERMOELASTIC PROPERTIES OF ISOTROPIC COMPOSITES

B. Budiansky

The results of theoretical estimates are given for several thermal and thermoelastic constants of macroscopically isotropic composite materials. The composites considered consist of random mixtures of N isotropic constituents, at least (N-1) of which are presumed to be distributed in a particulate fashion, with the particles roughly spherical in shape. The results are based on "self-consistent" calculations, details of which are given in appendices.

Equations (some of which are old, but are repeated for convenience) are given for the following quantities: elastic constants, thermal expansion coefficients, heat capacities (at constant volume and constant pressure), thermal conductivity and, finally, Grüneisen and related constants.

OPTICAL PROPERTIES OF COMPOSITES

A. J. Sievers

The infrared and submillimeter wave properties of both crystal and fiber composites are considered. A variety of "taylored" indices of refraction can be fabricated for far infrared and millimeter wave application using either class of these materials. Novel interference filters can be constructed from layers of various metallic composites. We describe a particular composite structure which is completely opaque in the high frequency region where geometric optics applies but acts as a band pass filter in the far infrared. The dielectric properties of crystal composites in the diffraction regime lead to a number of interesting interference effects which may have important applications if the irregularities in the periodic structure of the eutectic crystals can be reduced.

ON THE STABILITY OF TI-C AND TI-B COMPOSITE INTERFACES

J. P. Hirth
W. A. Tiller

The problem of stabilization of boron and graphite fibers against dissolution and reaction at 600°C in a titanium alloy matrix is considered. Three approaches are (i) adsorption to the fiber interface, (ii) introduction of a diffusion blocking layer, (iii) the use of an alloying element in the matrix to reduce the thermodynamic driving force. We find that the basic data required to completely solve the problem are not available. Suggested specific alloy developments are generated by analogy with other metal-matrix systems. Both basic research programs to provide a basis for a more detailed analysis of the problem and alloy development programs based on analogy are suggested, for definite alloy systems.

THERMODYNAMIC CONSIDERATIONS RELATING TO THE USE OF ELECTROCHEMICAL TECHNIQUES FOR THE GROWTH OF SINGLE CRYSTALS OF BORIDES

R. A. Huggins

Thermodynamic aspects of the formation of borides from fused salt solvents by isothermal electrolysis in a simple model system are discussed. Particular attention is given to factors which influence the composition and defect structure of the product formed.

ON THE HARDNESSES OF CARBIDES AND OTHER REFRACTORY HARD METALS

J. J. Gilman

In a carbide or biboride the excess binding energy associated with metal-metalloid interactions must be overcome for a dislocation to move through the crystal structure. This makes possible a simple calculation of the identation hardness number in terms of the heat of formation and the molecular volume. Good agreement with measurements is found for twelve representative compounds.

STRUCTURAL MODEL OF VITREOUS OXIDES BASED UPON CONCEPTS OF DEFECT CHEMISTRY

R. A. Huggins

A defect model of the structure of vitreous materials is presented based upon the principles developed for the description of defect equilibria in crystalline solids. This model is applied to pure vitreous silica and to a solid solution of silica and the oxide of a monovalent cation. The utility of this approach to the understanding of many of the structure-dependent properties of vitreous systems is discussed.

ENERGY ABSORPTION BY MARTENSITIC TRANSFORMATIONS IN A SHOCK WAVE

M. Cohen

Martensitic transformations of the type α(bcc) $\rightarrow$ ε(hcp) and α(bcc) $\rightarrow$ γ(fcc) in iron-base alloys are shown to absorb a substantial fraction of the energy in shock waves which induce these transitions. Consideration is also given to the conditions under which the reverse transformations can be inhibited when the shock front passes on. Such hysteresis has already been demonstrated in an iron-nickel alloy, leading to the retention of the shock-induced γ(fcc) phase.

QUANTUM-TUNNELING AS AN ELEMENTARY FRACTURE PROCESS

J. J. Gilman
H. C. Tong

A new model for the elementary fracture process in solids is presented. A quantum-mechanical process driven by the local applied stress is proposed and involves the tunneling of a chemical bond from an initial bound to a final bound state. The rate of the process is independent of temperature at low temperatures but can be assisted by phonons, photons, chemical potentials and other excitations or driving forces.

SOME SPECULATIVE THOUGHTS ON STRESS CORROSION CRACKING

J. P. Hirth
F. A. McClintock
J. R. Schrieffer
W. A. Tiller

As an aid to understanding stress corrosion cracking, the distribution of stress and strain and the microstructure are discussed at several scales of observation from the continuum level down to the atomic scale. The free electron redistribution is also discussed. The automatic potential distribution generated makes the crack tip cathodic with respect to the undistorted metal. The maximum macropotentials generated are in the range -0.3 to -0.8 volts for metals having a maximum volume strain of 10% at the crack tip. Such a potential produces great enhancement of the H^+ ion concentration on the fluid side of the crack tip, i.e., the crack tip is acidic.

A HYDROGEN PUMP FOR STRESS CORROSION

W. A. Tiller
J. R. Schrieffer

A notched metal surface in an aqueous environment and under a macroscopic tensile stress will cause electron redistribution in the presence of the notch. Thermally generated H^+ ions will concentrate in the notch region, discharge to form adsorbed hydrogen which enters the metal and decreases its intrinsic strength.

THE CHARACTERIZATION OF POROSITY

M. B. Bever
M. Cohen

It is suggested that porosity in materials, whether present as an intentional or unintentional feature of the structure, merits detailed characterization by the available methods of quantitative stereology. A need, therefore, exists for an appropriate compilation of spatial relationships and measuring techniques as an interdisciplinary tool in the field of materials structure and properties. A tentative characterization scheme is presented.

ON THE IDEAL CRACK TOUGHNESS OF A BRITTLE MATERIAL

F. A. McClintock

Even in fracture without dislocation motion, there will often be non-linear, irreversible flow over a region including 10 to 100 atoms at a crack tip. Can solid state physics suggest an approximate constitutive relation for such a region so that continuum mechanics can be applied to estimate more accurately the probably large effect of such flow on crack toughness?

STRESS LEVELS REQUIRED FOR HOLE GROWTH AND VOID COALESCENCE IN SPALL

D. C. Drucker

This note offers a tentative and crude model for discussion by those knowledgeable in the field of fracture at very high stress levels.

A highly oversimplified picture is presented of the initiation, growth, and coalescence of holes in the process of spall under uniaxial strain. Dynamics enters only for wave propagation; the stress-separation relation for spalling is assumed to be given by static plasticity. The static limit stress, σ_f, is determined by the ratio of interparticle distance D to the particle size d for the many particles large enough to fracture or separate from the matrix. A lower bound $2\sigma_0 \ell n D/d$ and an upper bound

$$\frac{4\sigma_0}{3}\left(\ell n\,\frac{D}{d} + \frac{D}{3d} + \frac{1}{4}\right)$$

provide the estimate $\sigma_f = 4\sigma_0$ when D/d is in the common range around 5. The yield stress σ_0 is to be understood as the uniaxial tensile stress required at high strain rates encountered in the spall problem (and following the passage of the initial compressive wave). Details of hole coalescence play a rather small role because the wave velocity c prior to spall is high compared with the particle velocity v. The spall criterion which results is:

$$\Delta^* = \int_0^{L/c} \frac{\sigma-\sigma_s}{\rho c}\,dt \geqq m\,\frac{d}{2} \quad \text{or} \quad \int_0^{L/c} (\sigma-\sigma_s)dt \geqq \rho c\,\frac{md}{2}$$

in which Δ^* is half the separation distance at the stage, say m = 3, when σ_s, the average stress on the plane of separation, becomes zero or negligibly small. The impinging tensile stress wave σ of length L and velocity c is a function of time; σ_s is a function of Δ, the separation at any time t, say

$$\sigma_s = \sigma_f\,\frac{1-\frac{1}{m}\frac{2\Delta}{d}}{1+\frac{2\Delta}{d}}$$

It is likely that when spall occurs at relatively low stress levels and long times, holes grow and coalesce on a very large number of planes so that m is larger than 3. It is possible that m be appreciably smaller for a sharp pulse. This is a refinement far above the crude level of the analysis presented here.

MICROSTRUCTURAL SCALE

D. C. Drucker

This note treats the question of flow or yield strength and the significance (or rather the lack of significance) for many alloys of the structural details observable in the ordinary optical microscope. A comparison of pearlitic and spheroidized steel is added to the earlier analysis of an aluminum-silicon system.

INTERACTIONS BETWEEN SHOCK WAVES AND ELECTRONS IN A METAL

R. M. Thomson

When a shock front moves through a metal, electrical potentials are generated. The fields are caused by (1) band structure changes due to pressure increases, (2) fields generated by variations in electron and ion accelerations within the shock front, (3) thermoelectric potentials due to temperature changes, and (4) scattering of electrons by the shock front itself. Items 1-3 are relatively simple, and (1) and (2) are worked out here. Calculations for (4) are underway, and preliminary indications are described.

THE THICKNESS OF STRONG SHOCK FRONTS IN SOLIDS

G. H. Vineyard

Theories of shock fronts are briefly reviewed. Conventional continuum theories are shown to lead to the prediction that the thickness of the front is of the order of magnitude

$$h = \frac{\eta}{\rho_o u_o}$$

where η is the viscosity, ρ_o the density, and u_o the sound velocity. In the case of strong shocks in solids, the applicability of this formula is questionable because of the atomic character of the medium, but the formula is the only simple guide to shock thickness that is available. Uncertainty about the proper value of η to employ allows a wide range of values of h to be about equally plausible.

Evidence of thicknesses from experiments and from machine calculations on atomic models is reviewed briefly. The results are conflicting and lead to the conclusion that the front of a strong shock ($\sim$100 kb) may be a few tens of angstroms thick, or may be as much as several orders of magnitude thicker than this. Recent experimental evidence for polycrystalline aluminum presents an upper limit of about 5×10^{-4} cm for the front of a 90 kb shock.

THE PRODUCTION OF PHASE TRANSFORMATIONS BY SHOCK WAVES

G. H. Vineyard

A simple criterion is given for determining whether a phase transformation will be produced by a shock wave in a solid. The criterion is that the time for the transformation to occur, assuming certain general features of the transformation kinetics and assuming that the driving force for the transformation can be computed as if the transformation did not occur, is shorter than the time presented by the shock pulse. A discussion of the reverse transformation that may occur on unloading is given, and dynamic effects which alter the simple criterion are briefly considered. The basic factors that determine whether a transformation occurs are emphasized.

REMARK ABOUT LARGE TRANSVERSE ELECTRIC FIELDS AND TEMPERATURE GRADIENTS IN TILTED METAL-INSULATOR COMPOSITES

W. Kohn

Flow of electric or heat current through a slightly tilted insulator-metal fiber composite can produce very large transverse electric fields or temperature gradients.

NEW MATERIALS SUMMARY

J. L. Margrave

One of the areas to which science and technology are most sensitive is that of New Materials, since a truly new compound or alloy or polymer may open up many new pathways and lead to applications far from those envisioned by the discoverer or developer. It is the purpose of this summary to outline some of the general kinds of chemical and physical considerations which enter into the generation of ideas about hypothetical new materials, to cite some examples from current pioneering research activities which seem destined to lead to important materials developments and finally to explore some particular developments which have obvious potential applications. A possible outline for future activities is also included to provide a starting point for development of the 1970 program in this area.

A BRIEF ON THE CORROSION OF ENGINEERING MATERIALS IN THE UNITED STATES

Nature of the Problem and a Plan for Action

R. W. Staehle

This report was prepared for the Council by Professor Staehle and does not represent the considered views of the Council as a whole. It describes the nature of the problem of corrosion of engineering materials and presents a plan for approaching the problem on a natural and organized basis.

CORROSION PERSPECTIVE

W. A. Tiller
M. B. Bever
H. Reiss

This is a report of the subgroup assigned to examine the field of corrosion for the Council and presents their perspective of the field.