REPORT

of

THE MATERIALS RESEARCH COUNCIL

December 1973

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INTRODUCTION

This report provides a summary of the activities and output of the Materials Research Council for the year ending December, 1973, the sixth year of operation of the Council. Detailed technical papers and memoranda are in preparation for separate publication.

The Materials Research Council originated in 1966 when the Director of the Materials Sciences Office of ARPA suggested the possibility of assembling 20-30 experts in the materials field for an extended period each year to suggest feasible methods of attack on materials problems anticipated within DoD. 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.

The first study meeting of this group, which became known as the ARPA Materials Research Council (MRC) was held during the summer of 1968. The concept proved to be so fruitful that the MRC meeting was continued each year through 1973, and plans are currently being projected through 1974.

The Council has indeed occasionally worked on current high priority problems and expects to do so in the future, but the real value of the Council lies in its long-range and broad interdisciplinary vision of materials problems. 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 was that MRC membership should be drawn from the most able and highly qualified individuals in the country. The recognized abilities of the Council members 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 knowledgeable groups working in materials science and materials engineering in the country.

Since the MRC membership is drawn largely from the academic community it was felt that exposure to longer range materials problems would have a beneficial influence on research undertakings of Council members and their students. This has indeed been the case. Follow-on work from problems encountered in the Council has emerged at most of the institutions represented by the Council membership. Joint research efforts between faculty members at several institutions have resulted from interests developed from the various study meetings. Many graduate students and post doctoral fellows have actively pursued 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, carbon thermodynamics, etc. The interdis-

ciplinary 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. Even with the breath and quality of talent on the Council it has been necessary and desirable to invite consultants from universities, government, and industry in order to insure that the Council would be kept abreast of the state of the art. A list of those attending the 1973 meeting is included in the Appendix.

PROJECT ORGANIZATION

The technical direction of the ARPA Materials Research Council is delegated to a nine-man Steering Committee, which is 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:

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Professor Michael Tinkham
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To carry out the work of the Council, a contract has been arranged between ARPA and The University of Michigan. The Project Director is Edward E. Hucke, Professor of Materials and Metallurgical Engineering.

The following functions are performed by the University:

a) Coordinating planning, through the Steering Committee.

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

c) Negotiating consulting agreements with the project participants, and handling all administrative and financial affairs.

d) Publishing the reports issued by the Council.

The current contract terminates April 30, 1974.

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

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PROBLEM SELECTION - BACKGROUND

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. Four general topics were chosen for detailed examination:

Composite Materials

Shock Propagation

Constitutive Relations at High Temperatures and Pressures

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.

The original concept of holding a summer conference where the entire Council could devote its concentrated efforts to a few selected issues proved to be fruitful, 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. Consequently, procedures were established for individuals or subgroups of the Council to undertake activities such as visits to DoD installations and DoD contractors or continuing investigations at home institutions in preparation for the following conference.

The technical report of the activities of the 1969 conference stimulated several meetings of the Council members with representatives of DoD laboratories. The results of this interaction were conveyed to the Steering Committee, enabling modification and addition of subject areas for the 1970 conference. Out of this meeting arose the following major areas of investigation:

1) Shock - continuation of efforts were to examine studies of the Grüneisen constant; electrical effects; dispersion by periodic structures; and dislocation structures.

2) Fracture - continuation of efforts to define crack propagation criteria, particularly in multiphased materials; define strain conditions at moving cracks; formulation of dislocation models of fracturing materials undergoing plastic deformation; and examination of surface energy considerations.

3) Composites - continuation of metal matrix composite investigation; examination of gradient composites; study of carbon composites; and analysis of wave propagation in composites.

4) Optics - continuation of analysis of laser glass materials problems; and optical properties of special composites.

5) New Materials - continued examination of materials and property measurements at extreme conditions of temperature; novel chemical combinations; and disordered carbon structures.

6) Stress Corrosion - continuation of survey of the field; examination of specific mechanisms.

7) Materials for Meeting Societal Needs - examination of superconductors for a magnetically suspended transportation system.

8) Bio-Materials - examination of materials compatibility in human bodies; materials problems in artificial organs; blood clotting; biological polymers.

The Steering Committee recommended after the 1970 meeting that the Council conduct more small meetings during the year for the purpose of preparing a given subject area for the summer conference. In this way it would be possible to have the necessary outside consultants contacted early enough to allow them to plan to attend portions of the conference and to identify, secure, and screen the relevant literature. Preconference organizational meetings were held for planning in the subjects of Environmental Degradation of Materials, Amorphous Semiconductors, and Stable Disordered Carbon Systems. It was proposed that aside from

problem areas continuing or arising from previous Council activities, that a closer link be established between the Council and the ARPA Materials Science Director. In this way the talents of the Council could be brought to bear for the purposes of evaluation of future research directions in a particular problem area so as to serve as a long-range advisory group for the ARPA Materials Science Director. This objective was carried forward in the selection of problems for the 1971 summer conference.

In line with the decision of the Steering Committee, several of the subject areas were organized into short meetings of one to three days duration. Considerable use was made of outside consultants with a structured program of presentations and a report of conclusions.

The 1971 activity in the remaining subject areas was carried out in the more traditional means by individuals or two to five man discussion groups. The subject areas are listed below:

Environmental Degradation of Materials
Materials Factors in Design with Brittle Materials
Gradient Materials
Infra-red Transmitting Materials
Amorphous Semiconductors
Stable Disordered Carbon Systems
Amorphous Metals
Applications of Superconductivity
Properties of Non-Biological Polymers
Fracture Mechanics
Materials at High Temperatures
Stress Waves in Composite Solids
Surface Thermodynamic Problems
Irreversible Thermodynamics
Solid Electrolytes

Prior to the 1972 meeting, pre-conference organizational meetings were held for planning in the case of the Environmental Degradation of Materials, Failure Prevention, and Design with Brittle Materials.

The areas of technical activity for the 1972 summer meeting are listed below.

Stress Corrosion Cracking
Surfaces of IR Laser Window Materials
Gradient Materials
Reliability of Brittle Materials
Prevention of Failures from Fracture
Materials Limitation in Advanced Energy Conversion Systems
Structure of Stable Disordered Carbon Systems
Strength Differential Effect
Wave Propagation in Composites
Materials Problems in Applications of Superconductivity
Fracture Mechanics
Structure of Non-Biological Polymers
Thermodynamic Properties of Materials at Very High Temperature
Structure of Amorphous Materials
Solid Electrolytes for Advanced Batteries
Recycling and Waste Disposal of Materials

SUMMER CONFERENCE - 1973

The conference was held during the month of July, 1973, at the Scripps Elementary School in La Jolla, California. A list of invited guests and consultants appears in the Appendix. The Steering Committee selected one or more Council members to plan, organize, and communicate summary reports on each of a group of short meetings held during the month. These meetings, together with the chairman, are listed below and summaries of the deliberations are included in the Appendix. In most cases, these meetings prompted related formal papers, notes and commentary.

Earthquakes and Mechanical Properties of Rock
Professor Rice

Materials Problems in Solar Energy Conversion Systems
Professor Cohen

Scientific Barriers in Battery Systems
Professor Flygare

Superconducting Materials and Long Range Prospects
Professor Duwez

Testing for Brittle Materials Reliability
Dr. Thomson

Materials Problems Related to Transmission and Reflection of Ultra-Violet Radiation
Professor Flygare

A Proposed Stress-Corrosion Cracking Handbook
Professor Cohen

Structure and Properties of Disordered Carbons
Professor Hucke

In addition to the above subjects, individual or small group efforts in the following areas were undertaken.

Characterization of Amorphous Materials
Wave Propagation in Composite Materials
Gradient Materials
Fracture Mechanics
Materials for High Temperature Fuel Cells
Strength Differential Effects
Hydrogen Transportation Systems
Unconventional Materials Processing Schemes
Flywheel Energy Storage
Chemical Theories of Hardness

As in the past, considerable use was made of a computational system utilizing the University of Michigan Computing Center via telephone. Professor B. Carnahan was available to help formulate and solve the member's computational problems.

In addition, representatives of various service and governmental bodies were invited to provide a two-way communi-

cation with the Council. In this manner, the results of the Council's efforts could be more directly communicated to DoD and other government groups working in the materials area. Also, the problem areas most deserving of consideration could be discussed with the Council so that they might be considered as topics at future conferences. The following representatives attended portions of the conference:

R. A. Andrews, Naval Research Laboratory

Frank Baratta, Army Materials & Mechanics Research Center

H. E. Bennett, Naval Weapons Center

M. G. Bowman, Los Alamos Scientific Laboratory

R. G. Brandt, Office of Naval Research

Edward Catalano, Lawrence Livermore Laboratory

A. M. Diness, Office of Naval Research

A. G. Evans, National Bureau of Standards

A. L. Giorgi, Los Alamos Scientific Laboratory

A. J. Glass, Lawrence Livermore Laboratory

William Goldberg, Air Force Materials Laboratory

D. H. Gurinsky, Brookhaven National Laboratory

Marvin Hass, U. S. Naval Research Laboratory

P. W. Hoff, Lawrence Livermore Laboratory

J. R. Huff, U. S. Army Mobility Equipment Research and Development Center

W. R. Hunter, U. S. Naval Research Laboratory

J. C. Hurt, Army Research Office

Alfred Kahan, Air Force Cambridge Research Laboratories

E. M. Lenoe, Army Materials & Mechanics Research Center

H. W. Paxton, National Science Foundation

C. B. Raleigh, National Center for Earthquake Research

Victor Rehn, Naval Weapons Center

Roy Rice, Naval Research Laboratory

L. J. Rogers, U. S. Army Electronics Command

Stanley Ruby, Materials Sciences Office, Advanced Research Projects Agency

Sigmund Schuldiner, Naval Research Laboratory

Paul Shewmon, Argonne National Laboratory

R. R. Smith, Air Force Materials Laboratory

J. L. Stanford, Naval Weapons Center

C. M. Stickley, Director, Materials Sciences Office, Advanced Research Projects Agency

Myron Strongin, Brookhaven National Laboratory

Masaki Suenaga, Brookhaven National Laboratory

Max Swerdlow, Air Force Office of Scientific Research

Alex Tachmindji, Deputy Director, Advanced Research Projects Agency

E. C. van Reuth, Materials Sciences Office, Advanced Research Projects Agency

R. E. Watson, Brookhaven National Laboratory

Sheldon Wiederhorn, National Bureau of Standards

Mark Wilkins, Lawrence Livermore Laboratory

As in prior years, the results of the Council's effort are divided into two broad categories; namely, 1) papers in a state ready for publication, and 2) reports and memoranda for

limited distribution representing work in progress. The former category is available for general distribution and, in most cases, are in the process of publication in the appropriate technical journals. In many instances, the reports arising from the 1973 meeting were the completed forms of work started at earlier conferences. The restricted distribution reports and memoranda represent initial ideas, problem suggestions, position papers, and status reports are aimed primarily to stimulate discussion within the Council and with its various consultants, and as such may not represent unanimous or majority opinions of the MRC. However, they are available by request to the Project Director subject to the author's release.

The breadth of activity of the Council during the 1973 conference can be seen from the following list of papers produced. Abstracts of many of these papers are given in the Appendix. In most cases where abstracts are not given, the full paper will appear as part of a subsequent report.

Stress Corrosion Cracking and Hydrogen Embrittlement from the Viewpoint of the Defect Solid State
J. P. Hirth

Earthquakes and the Mechanical Behavior of Rock
D. C. Drucker, B. Budiansky and J. R. Rice

Theory of Solution Strengthening of Alkali Halide Crystals
J. J. Gilman

Microwave Conductivity Measurements on Anisotropic Organic Crystals
P. L. Richards

Dynamics of Magnetic Suspensions for High Speed Ground Transportation
M. Tinkham and P. L. Richards

Addendum to AC Losses in Superconducting Magnet Suspensions for High Speed Transportation
M. Tinkham

Comments on Certain Reports of Carbonaceous Linear Polyacetylenes
M. F. Hawthorne

World War II Germany as a Model Fuel-Poor Economy. Synthetic Fuels
M. F. Hawthorne

Hydrogen Transfer by Diffusion Through a Hydrogenation-Dehydrogenation System
M. F. Hawthorne

Phase Transitions and Resistance in Three-Dimensional Arrays of Superconducting Linear Chains
M. Tinkham

Polymeric Entanglement Networks Cross-Linked in States of Strain
J. D. Ferry and S. S. Sternstein

Propagation of Low Frequency Elastic Disturbances in a Three-Dimensional Composite Material
W. Kohn

Hydrogen Storage in Transition Metals
H. Ehrenreich

Dynamics of Electrons in Graded Lattices
H. Reiss

Ductile vs. Brittle Behavior of Crystals
J. R. Rice and R. M. Thomson

Statistics of Brittle Fracture
F. A. McClintock

Resistance of Tsuei's Ductile Composite Superconductors
M. Tinkham

Shielding of the Magnetic Field Onboard Superconducting Trains
P. L. Richards

Structural Characteristics of Amorphous Semiconductors
A. Bienenstock

Decision Analysis Applied to Penetrant Inspection of Ceramic Turbine Blades
F. A. McClintock, R. L. Coble and R. M. Thomson

Interpretive Comments on "Remarks of Giant Conductivity in TTF-TCNQ"
M. Tinkham

Propagation of Transient Elastic Waves in Periodic Composites
J. A. Krumhansl and E. H. Lee

On Waves in Composite Materials with Periodic Structure
E. H. Lee and Wei H. Yang

Elastic Solutions for Imperfections in Brittle Materials
F. A. McClintock

Models of Spall Fracture by Hole Growth
F. A. McClintock

Materials Problems Related to Transmission and Reflection of UV Radiation
M. Sparks, H. Ehrenreich, W. H. Flygare and C. M. Stickley

Workshop on Reliability of Brittle Materials
R. M. Thomson, R. L. Coble and F. A. McClintock

Report on Meeting on Scientific Barriers in Battery Systems
R. A. Huggins, W. H. Flygare, E. J. Cairns and C. W. Tobias

Superconducting Materials and Long Range Prospects
P. E. Duwez

Void Nucleation Via Hyper-Dislocations During Ductile Fracture
J. J. Gilman

Materials Needs for More Efficient Degradation of High-Temperature Energy
J. L. Margrave

Li/CFX Batteries
J. L. Margrave

Light Element Hydrides as Energy Transport Materials
J. L. Margrave

Chemistry Without Containers
J. L. Margrave

On the Scale of Morphological Phenomena in Polymeric Alloys
M. B. Bever and M. Shen

Materials Problems in the Transport and Storage of Hydrogen
M. B. Bever

A Note on Energy Storage
M. B. Bever

Some Comments in Favor of Hydrides Rather Than Hydrogen as an Energy Transport Medium
R. Gomer, M. F. Hawthorne and J. L. Margrave

Comment on a Presentation by Dr. Robert Mehrabian On Casting of Semi-Solid Metals
D. C. Drucker and E. H. Lee

Field Observations on the Deformation of Rocks
F. A. McClintock

On Stress Wave Propagation Differences between Graded and Gradient Materials
E. H. Lee, B. Budiansky and D. C. Drucker

Summary of Discussions on Structure and Properties of Disordered Carbons
E. E. Hucke

Proceedings of the Discussion Group on Solar Energy Conversion
R. Kaplow, A. L. Bement and M. Cohen

An Overview of Some Proposed Solar Energy Conversion Schemes
A. L. Bement

Applications of Solar Energy
M. B. Bever

Comments on Discussion of Solar Energy Conversion
J. J. Gilman

Thermal Insulation of Window Glass
A. J. Sievers

An Alternative to Flat Area Solar Energy Absorption Unit Deployment
J. P. Hirth

Optical Analysis of Thermal Solar Energy Collection
P. L. Richards

Spectral Properties of Small Particle Metallic Coatings
A. J. Sievers

Concentration, Collection and Insulation
R. Kaplow

A Memorandum on the Subject of Photovoltaic Energy Conversion
J. J. Loferski

Photovoltaic Devices: A Discussion Summary
H. Ehrenreich

Photochemical Processes and Solar Energy Utilization
J. C. Light

Photogalvanic Cells
R. Gomer

Apparatus for Converting Solar Energy into Electricity: A Russian Patent by G. A. Korsunovski
Translated by Richard Gomer

Solar Sea Power
C. Zener

On Increasing the Heat Transfer at the Seawater Side of the Boiler in the Sea Thermal Gradient System
J. P. Hirth

Materials Problems in Extracting Power from Ocean Thermal Gradients
R. Bleiden and C. Zener

Energy Storage Via Flywheels
J. J. Gilman

Chemical Systems for Storage of Solar Energy
J. L. Margrave

Materials Problems Relating to High-Temperature Oxide Ion-Conducting Fuel Cells for the Electrochemical Combustion of Hydrogen
R. A. Huggins and R. L. Coble

Comments on the Use of a High Efficiency Solid Electrolyte Thermoelectric Transducer System as a Solar Energy Converter
W. H. Flygare and R. A. Huggins

ARPA Solar Energy Program Proposal

ARPA Stress Corrosion Cracking Handbook Proposal

POST CONFERENCE ACTIVITIES

Shortly after the summer meetings, members were asked to help formulate problem areas for next summer's conference. Final selection awaits action of the ARPA Materials Science Director and the MRC Steering Committee.

Several follow-up activities were requested by ARPA. In the first case the solar energy study task group was asked to prepare a detailed proposal for a broad based research program to demonstrate feasibility of solar energy conversion including its many challenging materials problems. This group, under the leadership of Professor Cohen, successfully prepared such a proposal under some very limiting time requirements.

In addition, a task group on Disordered Carbons was organized to meet in Washington with key experts on carbon materials requirements for DoD applications. Several follow-up discussions have resulted from this meeting.

APPENDIX

GUEST CONSULTANT LIST

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1973 GUEST CONSULTANT LIST

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APPENDIX

ABSTRACTS

STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT FROM THE VIEWPOINT OF THE DEFECT SOLID STATE

J. P. Hirth

Abstract

A Conference on SCC and HE was held in June 1973 at Firminy, France, under the auspices of the U.S. National Association of Corrosion Engineers and of the French Company, Creusot-Loire. Eight guest assessors from outside disciplines were invited to attend, to present a critique of the Conference, and to present a viewpoint of the SCC-HE field. This paper is my critique and assessment, presented from the viewpoint of the defects in solids, dislocation theory area. The first four pages include a number of suggested critical experiments. The remainder is a more detailed commentary on SCC-HE.

EARTHQUAKES AND THE MECHANICAL BEHAVIOR OF ROCK

D. C. Drucker
B. Budiansky
J. R. Rice

Abstract

Earthquakes, spectacular as they may be, are but a minor manifestation of large and continuing motion of the crustal plates and underlying mantle. This relative motion remains essentially steady over times very large in comparison with the intervals between earthquakes. Attention is directed toward regions such as California in which the tectonic plates primarily slide past each other horizontally (strike-slip), as distinguished from thrust fault regions such as Japan, Alaska, and South America, in which crustal slabs are moving deep down into the mantle. Thrust faults do occur in the predominantly strike-slip region as a consequence of geometric mismatch.

Among the ideas and questions explored are: tectonic stresses; local and average stress drop during earthquakes; differences in the extent of the deformed region in the direction transverse to the fault between strike-slip and an associated thrust fault; creep and small motions due to slip prior to and subsequent to earthquakes; patterns of displacement and of stress

variation through the lower, middle, and upper portion of the crust; possible melting of rock during sliding, healing and weakening of warm rock under pressure in the presence of water; dilatancy in "solid" and jointed rock, its cause, its role as a significant stabilizing factor, and its influence on the speed of stress waves to provide an advance indication of an impending earthquake.

Note: A summary of the meeting held is in the Appendix of this report. A more complete paper has been prepared for publication in a subsequent MRC report.

THEORY OF SOLUTION STRENGTHENING OF ALKALI HALIDE CRYSTALS

J. J. Gilman

Abstract

The solution-strengthening of sodium and potassium halide crystals by dissolved alkaline earth atoms is accounted for quantitatively. Strengthening is associated with the change in electrostatic energy that occurs when a divalent ion-vacancy complex is sheared by a dislocation that passes through it. The model yields a hardening coefficient of 11×10^9 d/cm^2; compared with the experimental value of 9.2×10^9 d/cm^2.

MICROWAVE CONDUCTIVITY MEASUREMENTS ON ANISOTROPIC ORGANIC CRYSTALS

P. L. Richards

Abstract

A microwave technique is described for measuring the electrical conductivity of anisotropic organic materials. This technique is useful in the high conductivity (skin effect) limit which has been encountered in TTF-TCNQ. The sample is placed in the center conductor of a coaxial resonator so that a large microwave current flows through it even when the skin depth is small. Methods for cavity calibration and data analysis are described.

DYNAMICS OF MAGNETIC SUSPENSIONS FOR HIGH SPEED GROUND TRANSPORTATION

M. Tinkham and P. L. Richards

Abstract

This paper discusses the relation between the power spectrum of track roughness and the subjective ride quality of a vehicle traveling over the track. First, we discuss the suspension dynamics with various combinations of springs and dashpots to simulate classes of suspensions. A rather detailed analysis is then given of the effect of a normal conducting screening plate between superconducting suspension magnets and the track. Such a plate both screens AC currents from the magnets to reduce AC losses and damps the vertical motion. It is estimated that a damping time of under one second can be obtained by this passive means, and the high-frequency properties have the favorable characteristics of series dashpot damping. A quantitative discussion is given of the smoothing effect of the finite length of the magnetic "pads", which average out the short wavelength variations in track elevation. A somewhat similar effect arises from the fall-off in subjective sensitivity to accelerations at frequencies above the natural resonance frequencies of the human body. After taking account of all these smoothing effects and integrating over all frequencies, it appears

that there will be no serious problem in obtaining satisfactory subjective ride quality with a high-clearance superconducting magnetic suspension system. An analysis of low-clearance ferromagnetic attractive suspension with feedback stabilization and secondary suspension is also given. This suggests that this system could also give satisfactory performance if the weight of the "magnetic bogie" can be kept small enough compared with the weight of the car.

ADDENDUM TO
AC LOSSES IN SUPERCONDUCTING MAGNET SUSPENSIONS FOR HIGH-SPEED TRANSPORTATION

M. Tinkham

Abstract

An earlier analysis of AC losses in superconducting magnets is extended to include conductors with thick as well as thin filaments. It is shown that thicker filaments may be superior for applications involving small AC fields, while the smallest filaments are best for large AC amplitudes.

COMMENTS ON CERTAIN REPORTS OF CARBONACEOUS LINEAR POLYACETYLENES

M. F. Hawthorne

Abstract

During the past ten years Kasatochkin and coworkers have studied the carbonaceous products obtained by oxidative-polymerization of acetylene.

$$n\ HC{\equiv}CH \xrightarrow[[0]]{Cu^{+2}} H\text{-}(\text{-}C{\equiv}C\text{-})_n\text{-}H$$

Examination of the original literature discloses that no firm basis exists for formulation of the reaction products as a linear, polymeric acetylene ("Carbyne" or "Carbine"). Additional work should be carried out to carefully characterize the reaction products.

WORLD WAR II GERMANY AS A MODEL FUEL-POOR ECONOMY. SYNTHETIC FUELS

M. F. Hawthorne

Abstract

It is suggested that World War II Germany faced an energy crises in fuels not unlike the crisis which faces the U.S. at the present time. The German chemical industry undoubtedly provided large quantities of synthetic fuel prepared from limestone, trees, coke, etc., through acetylene as an intermediate. It is proposed that old reports relating to this subject be reexamined in light of today's available chemical technology and fuel requirements.

HYDROGEN TRANSFER BY DIFFUSION THROUGH A HYDROGENATION-DEHYDROGENATION SYSTEM

M. F. Hawthorne and Howard Reiss

Abstract

Calculations were carried out to explore the feasibility of hydrogen transfer by the following means. Hydrogenation of an alkene, diffusion of the resulting alkane through a pipeline to the delivery point and dehydrogenation of the alkene to produce hydrogen gas. Alkene produced at the delivery point then diffuses through the same pipeline to the hydrogen pickup point. The conclusion is reached that the concept is probably not feasible for long distances (100 miles), but could be used in much shorter lines or by using a two-line pumped flow system to transport alkene to the hydrogenator and alkane to the dehydrogenator delivery point.

PHASE TRANSITIONS AND RESISTANCE IN THREE-DIMENSIONAL ARRAYS OF SUPERCONDUCTING LINEAR CHAINS

M. Tinkham

Abstract

We consider a model solid made up of superconducting unit cells coupled by Josephson coupling energies J_x, J_y, and J_z in the three orthogonal directions. A collection of one-dimensional chains is simulated by making $J_z >> J_\perp \simeq J_x, J_y$. Our model is a generalization of that of Anderson, Lee, and Saitoh, which considers only the intrachain coupling J_z. Short range order gradually develops along the chains as T is lowered below $T_c^* = 2J_z/k$, the approximate mean-field critical temperature, but a true phase transition into a state with long-range order in 3-D does not occur until a much lower temperature $T_c \simeq T_c^* (J_\perp/J_z)^{\frac{1}{2}}$. For TTF-TCNQ, Anderson et al have estimated $T_c^* = 500°K$; if we take $J_\perp/J_z = 10^{-3\pm1}$, as suggested by the conductivity anisotropy, this gives $T_c = 5\text{-}50°K$, a temperature range below the transition to an insulating state which occurs at $\sim 60°K$.

The conductivity of a single chain should rise as $(T/T_c^*)e^{T_c^*/T}$ as T decreases. To reach a value 10^6 times that of room temperature copper from that observed in TTF-TCNQ would

require cooling to ∿20°K if the 3-D superconducting transition to a state of zero resistance did not occur first. In fact, the metal-insulator transition intervenes. It is also shown that the difference in conductivity between the ordinary and special samples of TTF-TCNQ could be roughly accounted for if 1% of the junctions in the ordinary samples were much weaker than the others.

POLYMERIC ENTANGLEMENT NETWORKS CROSS-LINKED IN STATES OF STRAIN

J. D. Ferry and S. S. Sternstein

Abstract

The results of recent experiments on states of ease of amorphous highly entangled polymers which have been cross-linked while strained in simple extension are reviewed, and deviations from the predictions of an earlier report on this subject are examined. In particular, the approach to the state of ease following release of stress after cross-linking is unexpectedly slow, and therefore the kinetics of this process have been treated. With the approximation of linear viscoelasticity, and assuming that the cross-link network is unretarded, it is found that the creep compliance of the entanglement network can be calculated from observations of sample dimensions as a function of time during approach to equilibrium. Further experiments designed to clarify the phenomenon are outlined.

PROPAGATION OF LOW FREQUENCY ELASTIC DISTURBANCES IN A THREE-DIMENSIONAL COMPOSITE MATERIAL

W. Kohn

Abstract

This paper is a generalization to three dimensions of a earlier study for one-dimensional composites. We show here that in the limit of low frequencies the displacement vector $u_i(\underset{\sim}{r},t)$ can be written in the form $u_i(\underset{\sim}{r},t) = \delta_{ij} + v_{ijl}(\underset{\sim}{r})\partial/\partial x_l + \ldots)$ $U_j(\underset{\sim}{r},t)$. Here $U_j(\underset{\sim}{r},t)$ is a slowly varying vector-function of $\underset{\sim}{r}$ and t which describes the mean displacement of each cell of the composite. Its components satisfy a set of three coupled partial differential equations with constant coefficients. These coefficients are obtainable from the three-by-three secular equation which yields the low-lying normal mode frequencies, $\omega(\underset{\sim}{k})$. Information about local strains is contained in the function $v_{ijl}(\underset{\sim}{r})$, which is characteristic of static deformations, and is discussed in detail. Among applications of this method is the structure of the head of a pulse propagating in an arbitrary direction.

HYDROGEN STORAGE IN TRANSITION METALS

H. Ehrenreich

Abstract

Many of the transition metal hydrides contain hydrogen in concentrations comparable to those found in liquid or even solid hydrogen. This fact is of possible technological interest in connection with energy storage: the hydrogen is stored in atomic form and the molecular recombination energy becomes available in a controlled fashion upon moderate heating. This note qualitatively investigates the reasons for the large binding of hydrogen in transition metals in terms of our present understanding of the electronic structure as well as the cohesive energy of these materials. A quantification of these notions may be useful in the search for optimal materials as defined in terms of cost, operating conditions, and storage capacity.

DYNAMICS OF ELECTRONS IN GRADED LATTICES

H. Reiss

Abstract

The Wannier functions for the lowest lying band of a one dimensional crystal with delta function potential wells are derived analytically for the tight binding limit. A crystal is then considered whose lattice is nonuniform to the extent that the strength of its potential wells varies linearly with position. Using, as basis set, the Wannier functions corresponding to a uniform lattice whose well strength corresponds to a particular point in this crystal, the differential-difference equations which determine the motion of the envelope vector (wave packet) in the graded lattice are formulated. These equations are then solved analytically for the tight binding case.

These solutions may be of value in examining the roles of "effective" Hamiltonians which "drift" (in the sense that the basis set drifts) with an electron in the lattice. Such "local" Hamiltonians are thought to be of value in understanding the behavior of solid state devices predicted on graded lattices.

DUCTILE VS. BRITTLE BEHAVIOR OF CRYSTALS

J. R. Rice and R. M. Thomson

Abstract

A necessary criterion for brittle fracture in crystals is established in terms of the spontaneous emission of dislocations from an atomically sharp cleavage crack. We have calculated the stability of a sharp crack against emission of a blunting dislocation for a number of crystals and crystal types in two dimensions and the energy to form a stable loop of dislocation from the crack tip in three dimensions. We find that contrary to previous expectations, an atomically sharp cleavage crack is stable in a wide range of crystal types, but that in the face centered cubic investigated, blunting reactions occur spontaneously. Of the body centered metals investigated, iron is an intermediate case between the brittle and ductile cases, and the ionic and covalent crystals investigated are all stable against dislocation emission. Qualitatively, when the dimensionless parameter $\mu b/\gamma$ is larger than about 7.5 - 10, we expect the crystal to support a sharp cleavage crack, though a more precise criterion must include core size of the dislocation and geometrical factors.

STATISTICS OF BRITTLE FRACTURE

F. A. McClintock

Abstract

From a simple statistical model of occasional cracked grain boundaries, a statistical distribution of strength is derived which does not fall into any of the three asymptotic forms of extreme value distributions. The size effects for this new extreme-value distribution are similar to those of the third asymptote with an exponent of about m = 4, but it is necessary to drop 5 or 6 standard deviations below the median in order to reduce the failure probability to 1 in 10^6, which corresponds more to the first asymptote, m = ∞. Stress gradient effects, leading to notch insensitivity, are reviewed for the third asymptotic distribution, and a method for correlating scatter in strength with position of failure in three-point bend specimens is derived and illustrated.

RESISTANCE OF TSUEI'S DUCTILE COMPOSITE SUPERCONDUCTORS

M. Tinkham

Abstract

It is shown that a volume fraction f_s of superconducting filaments of length L and diameter d embedded in a normal metal matrix yields a composite with an effective resistivity $\bar{\rho}_{eff} \simeq (\rho_{matrix}/f_s)(d^2/L^2)$. Since $\bar{\rho}_{eff}/\rho_{matrix}$ may be as small as 10^{-7}, ultrasensitive techniques (such as use of a superconducting voltmeter or decay of persistent currents) may be needed to detect such small resistance in short sample tests. Moreover, this resistance may be low enough for practical applications, even if the matrix is fully normally resistive. The current density in the matrix is less than that in the filaments by a factor of $\sim d/2L$. If this factor is small enough, even the weak "proximity effect" superconductivity between filaments may be able to carry it as a supercurrent, either without resistance or with only flux-flow resistance. Evidently great advantages follow from obtaining the largest possible ratio of L/d (as well as the largest possible superconducting fraction and the lowest possible matrix resistivity) by appropriate development of metallurgical and fabrication techniques.

SHIELDING OF THE MAGNETIC FIELD ONBOARD SUPERCONDUCTING TRAINS

P. L. Richards

Abstract

The problem of shielding passengers from the static magnetic field of a train levitated by superconducting magnets is discussed. A general calculation is presented which shows that iron shielding would be prohibitively heavy. Two dimensional potential calculations are used to estimate the effectiveness of superconducting sheet shields. It is concluded that a combination of iron and superconducting shields is required to achieve satisfactory results. Model experiments are suggested as a method for optimizing specific designs.

STRUCTURAL CHARACTERIZATION OF AMORPHOUS SEMICONDUCTORS*

A. Bienenstock

Abstract

Structural characterization studies of a-Ge and a-Si are reviewed, with particular emphasis on density and void characterization. Systematic studies show that an ideal material is approached through high substrate temperatures, low base pressures, low deposition rates and long substrate to sample distances. The "ideal" films have densities and refractive indices close to crystalline values. It is suggested that a large portion of the apparent discrepancies in existing density, void shape and refractive index data can be rationalized if it is assumed that sputtering or high evaporation rates lead to large numbers of small voids, whereas low evaporation rates lead to smaller numbers of larger voids. In addition, it is assumed that annealing leads to void coalescence and that an important role of oxygen is to decrease the surface mobility of adatoms. Structural studies of amorphous Ge-Chalcogen films are also reviewed, with the tentative conclusion that a structure with fourfold coordinated Ge and twofold coordinated chalcogens is most appropriate for the germanium monochalcogenides.

*An invited paper at the Fifth International Conference on Amorphous and Liquid Semiconductors held in Garmisch-Partenkirchen, Germany, September 1973.

DECISION ANALYSIS APPLIED TO PENETRANT INSPECTION OF CERAMIC TURBINE BLADES

F. A. McClintock, R. L. Coble & R. M. Thomson

Abstract

Decision analysis forces the analyst to express his hunches and insight in a quantitative way. As regards inspection of brittle materials, the very strong dependence of crack growth rate on crack length means that only a very narrow range of cracks need be detected in an inspection scheme. Longer cracks must be removed or prevented in manufacture. Shorter cracks are of no concern. When no hazard to human life is anticipated, even the high cost of failure in terms of reputation and further sales was not enough to justify penetrant inspection of gas turbine blades. This conclusion seemed to hold in spite of a wide variability in expert opinion about the frequency of internal versus external cracks or about the distribution of crack lengths themselves.

INTERPRETIVE COMMENTS ON "REMARKS ON GIANT CONDUCTIVITY IN TTF-TCNQ"

M. Tinkham

Abstract

In a recent preprint, Anderson et al. derived the temperature dependence $\sim T\, e^{T_c/T}$ for the fluctuation-limited conductivity below T_c in a novel model for a superconducting molecular chain. Experimental data on TTF-TCNQ were fitted to this form with $T_c = 500°K$. It is shown here that essentially this same form of temperature dependence is predicted by the conventional theory of thin metallic superconductors, if the diameter is scaled down to the molecular level.

PROPAGATION OF TRANSIENT ELASTIC WAVES IN PERIODIC COMPOSITES

J. A. Krumhansl
E. H. Lee

Abstract

The application of Fourier-Floquet methods to transients in periodic composite media is presented. The head of the wave solutions in the far field are dominated by the maximum group velocity contributions from each frequency band.

In one dimension, the results of the wave front tracing approach for an initial impulse have been recovered from Fourier-Floquet analysis in the case of layers with commensurate transit times.

Motion of a periodic layered medium under applied forces is discussed, including both a formal representation of the response Green's function and the treatment of short pulse pressure loading on a surface.

We conclude that important features of transient elastic wave propagation can be obtained using Fourier-Floquet methods.

ON WAVES IN COMPOSITE MATERIALS WITH PERIODIC STRUCTURE

E. H. Lee
Wei H. Yang*

Abstract

The propagation of waves through non-homogeneous elastic material, with a periodic structure of elastic constants and density variation, can be conveniently treated in terms of Floquet waves. These are quasi-periodic waves, propagating in one direction, the displacement profiles of which change with time, but repeat after the wave has traversed a complete cell of the material. Locally this solution is the superposition of refracted and reflected components. Basic concepts of the theory are presented for a laminated composite material and propagation normal to the laminations. The frequency spectrum has a banded structure, comprising pass or propagating bands and stop bands. It is shown that the frequencies at the boundaries of the bands correspond to wave profiles which are normal modes of vibration of the individual cells with fixed or free surfaces. Both types occur at each limiting frequency. Properties of Floquet waves are interpreted in terms of normal

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mode theory. From these considerations the high frequency limit for Floquet waves is investigated and interpreted in terms of geometrical optics type analysis.

ELASTIC SOLUTIONS FOR IMPERFECTIONS IN BRITTLE MATERIALS

F. A. McClintock

Abstract

An annotated bibliography of 42 references is given to help provide research workers in the field of ceramics and other brittle materials with a collection of the information, especially applicable to their field, which is available from the theory of elasticity. The categories of references include inclusions, corners in inhomogeneous or dissimilar materials, elastic constants of polycrystals, three-dimensional solutions, cracks in dissimilar materials, and arrays of cracks. The author would welcome any additions to this brief collection.

MODELS OF SPALL FRACTURE BY HOLE GROWTH

F. A. McClintock

Abstract

After an introduction to the static fracture of metals by hole growth, the physically possible sources of rate effects are reviewed: those arising from inertia terms as in wave motion; from quantum mechanical tunnelling effects; and from thermal activation. Limitations due to the size of the hole relative to the mean free path of slip lines are also estimated. It is concluded that dislocation viscosity aided by temperature rise, thermal diffusivity and mechanical inertia play markedly different roles in different alloys at different intensities of loading. The largest uncertainty is in the mobile dislocation density of hard alloys. In an extensive author's discussion, it is concluded that inertia effects on hole growth are negligible when the loading time exceeds 20 to 50 nanoseconds for high and low strength alloys, respectively. Otherwise the strength under shock loading is of the order of four times the yield strength.

VOID NUCLEATION VIA HYPER-DISLOCATIONS DURING DUCTILE FRACTURE

J. J. Gilman

Abstract

An outline of a mechanism for void nucleation is presented for the case of pure metals without included particles.

MATERIALS NEEDS FOR MORE EFFICIENT DEGRADATION OF HIGH-TEMPERATURE ENERGY

J. L. Margrave

Abstract

In the current energy crisis the advantages of higher operating temperature are multiple--higher efficiencies, gross conservation of fuel, less pollution, etc.-- but the achievement of these goals is inevitably hampered by the lack of satisfactory high temperature materials. Not only are extended efforts of synthetic chemists and metallurgists required, but measurement of physical and chemical properties at extreme conditions are basic to the development of feasible engineering designs. As an example of the discrepancy between practical developments and the availability of fundamental chemical knowledge, consider the Si_3N_4 program. As of July, 1973, neither the low-temperature heat capacity nor the absolute entropy of this material are known. Within the last year, new gas-phase species have been observed over the heated solid. Coordinated programs in synthesis and property measurement are desirable. Tabulations of basic thermodynamic data are needed.

Li/CFX BATTERIES

J. L. Margrave

Abstract

Thermodynamic data have been obtained for various compounds in the $CF_{0.7-1.2}$ range, including low temperature heat capacities, heats of formation, and thermal stabilities. Theoretical EMF's calculated for $CF_{1.1}$/Li and for C_4F/Li batteries suggest cell voltages close to 5 volts. The basic patents in this area are held by the U.S. Signal Corps (Breuer on C_4F/Li) and by the Japanese (Watanabe on $CF_{1.0}$/Li). Current problem areas are electrolyte stability, electrode construction and a general lack of fundamental knowledge about the electrochemical process at the CF-electrode-electrolyte interface.

LIGHT ELEMENT HYDRIDES AS ENERGY TRANSPORT MATERIALS

J. L. Margrave
M. F. Hawthorne

Abstract

A summary of potential compounds and systems involving lithium and boron mixed hydrides, lithium and boron mixed alkyls, lithium and aluminum hydrides and alkyls will be prepared. Thermodynamic data and preparative chemistry are already available for many of these materials and their large scale use as energy transport materials should be practical from both economic and engineering viewpoints. In simple terms, hydrogen at one of the pipes is converted to a convenient boron compound, e.g., B_2H_6; pumped through existing pipelines; and then the hydrogen and some other boron compound, probably H_3BO_3, are separated by hydrolysis. The boron would be re-cycled.

CHEMISTRY WITHOUT CONTAINERS

J. L. Margrave

Abstract

A review of methods and devices used for levitation of conductors--metals, alloys, carbides, nitrides, certain oxides, etc.--and the application of this approach for the measurement of thermodynamic properties of liquid metals, for metallurgical processing, for chemical synthesis, etc.

ON THE SCALE OF MORPHOLOGICAL PHENOMENA IN POLYMERIC ALLOYS

M. B. Bever and M. Shen

Abstract

The morphological phenomena in polymeric alloys result from the spatial arrangement on a supramolecular scale of assemblies of macromolecules. Their complexity increases rapidly in going from amorphous homogeneous polymers to the various types of heterogeneous polymers.

In this memorandum polymeric alloys are classified by their chain constitution. The major experimental methods for obtaining quantitative morphological data are listed. The size ranges of various morphological features are summarized in a graph and the nature of these features is explained briefly.

MATERIALS PROBLEMS IN THE TRANSPORT AND STORAGE OF HYDROGEN

M. B. Bever

Abstract

This memorandum is concerned with the following questions: If hydrogen is to be transported and stored in large volumes in a routine manner, what materials problems will arise? What information is available regarding these problems? What additional information is required and how can it be obtained?

COMMENT ON A PRESENTATION BY DR. ROBERT MEHRABIAN ON CASTING OF SEMI-SOLID METALS

D. C. Drucker and E. H. Lee

As described, the hot billet in its "solid" form is primarily a viscous metal which surrounds clumps of solid metal. The thixotropy or drop to a very low flow stress following shearing was explained by the speaker to be a consequence of the breaking of contact welds between the solid particles. Although the stresses due to the billet weight alone are low, there is some difficulty with this explanation, even when the viscosity is highly nonlinear, if the fluid has the same low viscosity in the billet that it has when filling the mold after entering a small opening.

An alternative suggestion is that there may be a more complex filamentary or sheet-like reaching out or joining of the solid particles which would drastically constrict any flow at low stress and so cause the billet to behave as a solid under its own weight. This structure would be broken down by strong shearing action and the metal then would behave as a fluid of low viscosity.

Another possible explanation of the thixotropic softening due to deformation is that the effect is associated with dif-

ferent phases of the material in this region of temperature. A simple example of this type of phenomenon for elastic bodies has been studied (E. Varley and Alan Day, "Equilibrium Phases of Elastic Materials at Uniform Temperatures and Pressure" Archive for Rational Mechanics and Analysis 22, 1966, 253-269) which illustrates the essentially free deformation which can occur in such circumstances. The Gibbs free energy is taken to be a function of deformation variables, pressure and temperature which differ for different phases. Entropy balance and deformation compatibility between regions containing different phases, lead to possible equilibrium geometry changes at effectively zero shear stress. It seems possible that the structure of this theory which combines general deformation variables with pressure and temperature in the analysis of phase transformation may be extended to deal with the essentially viscous fluid or plastic characteristics of a metal near its melting point.

ON STRESS WAVE PROPAGATION DIFFERENCES BETWEEN GRADED AND GRADIENT MATERIALS*

E. H. Lee, B. Budiansky and D. C. Drucker

Abstract

This work contains a comparison of the resistance to impact of built-up plates with stepped mechanical properties (such as density and elastic constant) with plates having a similar range of properties distributed continuously. Marked differences arise in the stress generated in such types of plates under the same impact loading. In particular, the tendency to spall can be quite different in the two cases.

This work continues an initial effort last year for which the computing was then not completed. We now have the solution to a much more meaningful problem, for which we can vary the width of transition zone between homogeneous regions with different properties, and so assess in detail the change from continuous variation to discontinuous steps in properties.

This problem arose from a discussion with visitors from AMMRAC in the sessions on gradient materials arranged by Professor Bever.

Note: Full paper will be included in a later report.

COMMENTS ON DISCUSSION OF SOLAR ENERGY CONVERSION

J. J. Gilman

1. The analysis of realistic and complete systems is receiving too little attention. The analysis that is being done (and published) is the work of proponents of particular conversion systems. These analyses are often incomplete.

Total capital costs are being underestimated as are operating costs such as maintenance and storage. Present values (cash flow analyses) for various projects are not commonly computed for comparison with other options.

Cost reductions are being anticipated for components based on past experience. In a rapidly changing world economic structure, this method is not a realistic basis for justifying spending budgets at rates as high as tens of millions of dollars per year. In some cases the present "applications" work is based on subsystems that are known to be inadequate because of poor performance or high cost.

2. Since incoming terrestial solar power is intermittent and often aperiodic it is clear that sophisticated storage systems are crucial to any substantial solar energy system. Also, such systems will make major contributions to overall system capital and maintenance costs. Far too little attention is being given to them. In fact, my analysis of the FY73 - NSF Budget indicates

that zero attention is being paid by this organization. If an economically and technically adequate storage system is not available there is little point in developing large scale collecting systems.

3. More research attention should be given to photochemical conversion techniques because they are relatively unexplored and therefore have the greatest potential for novel discoveries as a result of exploration. These techniques include:

a. bio-conversion - use of algae-bacterial systems to perform the overall reaction:

$$2H_2O + CO_2 \xrightarrow{h\nu} CH_4 + 2O_2$$

b. photogalvanic action at membranes - this is the ionic analog of the electronic photovoltaic cell.

c. photo-assisted electrolysis of water or other substances to produce fuels.

d. photo-activated adsorption for separations of mixtures of phases.

e. artificial photosynthesis of hydrocarbons.

f. photo-activated catalysis.

g. long-lived excitonic storage of photons for activating selected chemical reactions.

h. resonant two photon up converters for skewing solar frequency distribution toward higher frequencies.

i. phosphors for concentrating broad-band incident

radiation into a desirable narrow band.

j. photo-activated permeation through membranes.

THERMAL INSULATION OF WINDOW GLASS

A. J. Sievers

Abstract

The thermal insulation of window glass is increased by a factor of two with a simple spray-on conductive coating.

OPTICAL ANALYSIS OF SOLAR-THERMAL ENERGY COLLECTION

P. L. Richards

Abstract

A brief analysis is presented which illustrates how design parameters such as the concentration factor and the operating temperature interact with the optical parameters of materials in the system design of thermal solar energy collectors. The use of wedge concentrators is suggested as an economical way to achieve large concentration factors. A schematic system design is given to illustrate the use of such concentrators.

SPECTRAL PROPERTIES OF SMALL PARTICLE METALLIC COATINGS, I. General Considerations

A. J. Sievers

Abstract

We find that in the free electron approximation, the plasma resonance for small metallic particles can be adjusted to occur near the center of the solar spectrum. A metallic particulate coating is expected to be temperature independent because the Fermi temperature of the electrons is extremely large and the electron mean free path is determined by the small particle size. A bright metal surface coated with this material can provide a nearly temperature independent wavelength selective coating for collectors of solar energy.

PHOTOGALVANIC CELLS

R. Gomer

Abstract

An analysis of photogalvanic cells is carried out and applied to a specific system, iron-thionine, with only slight simplifications. The criteria for successful cell design are given and discussed. It is concluded that many formidable obstacles to practical application exist. The principal difficulties are the following: 1) Diffusion to the electrodes and reaction there must be sufficiently rapid to make bulk back reactions unimportant. 2) A means for keeping at least one active species from reaching one electrode must be found. 3) A sufficient range of the solar spectrum must be exploited without increasing the rate of photon absorption to the point where bulk back reaction becomes important. These problems are discussed in some detail and quantitative criteria are presented in terms of absorbed photon flux, cell size parameters, chemical rate constants, exchange current densities, overvoltages and diffusion coefficients.

ENERGY STORAGE VIA FLYWHEELS

J. J. Gilman

Abstract

A method for energy storage that has considerable versatility is the flywheel. The elements of flywheel energy storage are discussed and the pros and cons are discussed in terms of specific idealized configurations. An expression for the maximum power output is derived which shows that flywheels are capable of delivering approximately 10^6 times as much power as very good batteries. Because of this and other features, flywheels complement the performances of batteries. This makes hybrid battery-flywheel systems attractive for energy storage.

CHEMICAL SYSTEMS FOR STORAGE OF SOLAR ENERGY

J. L. Margrave

Abstract

Thermodynamic data are being reviewed for some simple systems of energy storage, including the possibility of using a water-sulfuric acid working fluid from which water is removed by daytime evaporation to produce concentrated sulfuric acid and then, heat is recovered by dilution of the concentrated H_2SO_4, a process which is exothermic by 15-23 KPM, depending on dilution. Other suitable chemical reactions or phase transformations will be considered.

MATERIALS PROBLEMS RELATING TO HIGH TEMPERATURE OXIDE ION CONDUCTING FUEL CELLS FOR THE ELECTROCHEMICAL COMBUSTION OF HYDROGEN

R. A. Huggins and R. L. Coble

Abstract

The current status of the development of high temperature fuel cells utilizing solid electrolytes for the electrochemical combustion of gaseous fuels is reviewed. Special attention is given to the materials problems relating to cells employing doped ZrO_2 as the electrolyte. Also included are comments relating to cost estimates for such systems. It is concluded that oxide ion-conducting solid electrolyte fuel cells might be particularly attractive for the combustion of hydrogen, but that there are still serious problems relating to the development of adequate materials to use as interconnectors and for the electrode on the oxidizing side. In addition, costs will be critically dependent upon the development of inexpensive ceramic fabrication methods.

COMMENTS ON THE USE OF A HIGH EFFICIENCY SOLID ELECTROLYTE THERMOELECTRIC TRANSDUCER SYSTEM AS A SOLAR ENERGY CONVERTER

W. H. Flygare
R. A. Huggins

Abstract

It is proposed that consideration be given to the use of a thermoelectric device involving the use of a solid electrolyte and isothermal expansion of sodium for solar energy conversion.

The theoretical principles involved in such a device have been discussed, and the theoretical efficiency calculated. It has been shown that the theoretical efficiency in such a system is much higher than that of conventional thermoelectric devices, closely approaching the Carnot limit.

Because of its inherent simplicity and low materials cost, major practical limitations or disadvantages do not appear likely.

APPENDIX

MEETING SUMMARIES

(A more detailed discussion and related papers are in the process of publication in a later report.)

SUMMARY OF DISCUSSIONS ON EARTH FAULTING MECHANISMS

J. R. Rice, B. Budiansky and D. C. Drucker

The discussions focused on identifying key problems of material behavior for developing a description of earth faulting mechanisms. Special emphasis was given to material characteristics relevant to earthquake prediction and control, including the role of stress-induced dilatancy and of pore-water pressure variations. Such dilatancy provides a mechanism for seismic and other anomalies observed prior to earthquakes, whereas pore suctions and pressures seem to be factors in the inhibition and initiation of faulting.

Much uncertainty as to the operative mechanisms, and to the identification of problems for study, arises from the lack of knowledge of stress levels and properties of rock in-situ. This includes the difficulty of unambiguously translating laboratory measurements on essentially coherent rock specimens to the enormously larger size scales of faulting, particularly when it is uncertain as to whether the proper picture is one of coherent rock vs. rocks with large joints vs. perhaps a highly fissured compact rubble or possibly a well ground clay-like gauge on fault surfaces from previous sliding.

Nevertheless, some tentative conclusions were reached on tectonic stress levels, and a number of important problem areas

were identified and analyzed at least in part. These include:

1. The development of constitutive models for pre-failure deformation of rock including mechanisms of fissure opening, effects of pore-fluid pressure alterations, and the coupling between overall dilatancy and permeability of rocks in the description of pore fluid transport.

2. Formulation of conditions for deformation localization into fault planes, including the possibility of widespread stable failure through dilatant strengthening.

3. Description of the resisting shear tractions on a propagating fault, including strength degradation with on-going sliding, stick-slip phenomena, and the possibility of local melting.

4. Processes of strength recovery after faulting, through sintering and possible cement-like reactions between pore-water and freshly fractured rock.

5. Identification of the role of pore-water in hydroxide reactions with rock, with resulting effects on ductility and crack resistance, and the possibility of instabilities generated by the dehydration of serpentine.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON MATERIALS PROBLEMS IN SOME SOLAR-RELATED ENERGY-CONVERSION SYSTEMS

M. Cohen and R. Kaplow

The following items are highlights of presentations, discussions, and studies that took place during the MRC meeting in La Jolla, and will be amplified in the forthcoming proceedings. For the most part, these points deal only with the materials problems in various solar-related systems.

General

1. Solar energy can contribute a significant part of the energy requirements of the United States on a reasonable time scale, both as a basic and a marginal source.

2. Relatively simple low-temperature applications, such as water heating, space conditioning, and treatment of brackish water and sewage, are now technologically feasible, and hold promise of becoming economically feasible in the near term depending on the locality. These applications are also of military as well as environmental interest, and could furnish an increasing portion of the energy consumed in the nation.

3. Special attention must be directed to energy-storage systems, which are a common requirement for virtually all means of solar energy conversion. The development of improved thermal-insulation materials for both high and low temperatures would also be beneficial.

Concentration and Collection of Sunlight for Thermal Systems

1. A three-pronged search for surfaces with special optical properties for radiative insulation should be pursued. Each of the three aspects may be realized in the near future; indeed, adequate materials may already exist.

a. A surface material that is stable for long periods ($\sim$20 years) at high temperatures ($\sim$500°C) is needed for high light-concentration systems; for this purpose, a sunlight-absorption/infrared emission ratio (α/ε) as low as 2 may be acceptable.

b. A heat-mirror surface with high transparency for sunlight and high reflectivity for infrared will prove useful for supplementing or replacing low ε coatings in the absorbing surface, and will also find application in general insulation against infrared radiation (windows, light bulbs, searchlights, etc.).

c. A surface material with very high α/ε for use in low-temperature systems ($\sim$250°C) without light concentration should be sought; the low operating temperature will lessen the problem of thermal degradation. A new concept based on the use of small metal particles ($\sim$100Å) should be explored.

2. Calculations have been made which illustrate the relationship between the geometry, the light-concentration factor and the optical properties of materials used for solar thermal energy collectors. A wedge-shaped mirror geometry has been suggested for high-concentration systems.

Photovoltaic Cells

1. New emphasis should be placed on terrestrial operations without the special requirements of outerspace applications, the latter having hitherto dominated the field. Emphasis should be placed on low cost and durability; standards of reliability can be lowered, and lower efficiencies (∿5-10%) should be regarded as acceptable.

2. The physics and metallurgy of heterojunctions need to be better understood, especially the degradation processes in otherwise economical materials, such as Cu-Cd-S.

3. Improved techniques for characterizing surfaces and interfaces during the fabrication of cells are necessary.

4. The role of grain boundaries in photovoltaic cells requires elucidation, inasmuch as polycrystalline materials are much less expensive than the currently used single crystals.

5. The possibility of developing low-cost fabrication techniques for stacked photocells, with graded energy gaps which will effectively utilize a greater portion of the sunlight wavelength distribution, should be examined.

6. Materials for photovoltaics should be considered in terms of their own requirements since these may be different than for semiconductors used in other electronic devices.

Photochemical and Photogalvanic Conversion

1. Although endo-energetic photochemical reactions and direct photogalvanic conversion to electricity do not look promising now for storing or utilizing solar energy, more research

on these processes may be warranted because of their potential low cost.

Hydrogen Storage and Transport

1. Hydrogen embrittlement in gaseous H_2 requires careful consideration and further experimental work to guard against this potential hazard since current knowledge is inadequate and extrapolations from seemingly relevant experience may be misleading.

2. Materials problems for the handling of liquid hydrogen are those of cryogenic technology; they have largely been solved for small installations but probably not for large ones.

Hydrogen Fuel Cells

1. High temperature fuel cells involving the use of oxide ion-conducting solid electrolytes present an attractive method for the conversion of hydrogen to electrical energy. The capital cost and overall efficiency of this type of electrochemical conversion appear to be potentially competitive with other methods. Because of operation at elevated temperatures, there are no catalytic problems in such cells.

Ocean Thermal Gradients*

1. Low-cost methods of fabricating the required high heat-transfer boiling and condensation exchanger surfaces will be one of the necessary steps in demonstrating economic feasibility for this type of energy system.

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*This subject was presented by Clarence Zener, but was not studied critically by the Council members.

2. It will be necessary to develop methods for preventing biological fouling on exchangers.

3. The rate of heat transfer on the sea-water side of the heat exchangers has to be increased; ideas for doing this include roughening surfaces, production of small ridges on surfaces, and discharging hydrogen gas cathodically (the latter may be coupled with Cl discharge to control biological growth).

4. There is an important need for efficient and low-cost hydrolysis cells in case hydrogen and oxygen turn out to be the most economic way of transporting the energy produced from ocean thermal gradients.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON SCIENTIFIC BARRIERS IN BATTERY SYSTEMS

R. A. Huggins
W. H. Flygare

Approximately 10 people from industry, government labs, and universities met with members of the Materials Research Council to discuss recent developments and materials problems which are limiting the effective use of batteries as energy storage systems. Indeed, it is evident that materials problems constitute the major stumbling blocks in developing high energy density and power density batteries.

The formal presentations began by a discussion of the principles of electrochemical systems, electrodes, electrolytes, and enclosure materials by C. Tobias. The remaining presentations by S. Mitoff, E. Cairns, B. Owens, C. Liang, M. Eisenberg, and G. Kugler, outlined recent developments, prospects, and applications of advanced battery systems. Materials problems were discussed in several specific areas:

1. Problems with Solid Electrolytes
2. Problems with Liquid Electrolytes
3. Problems with Electrodes
4. Problems with Electrode-Electrolyte Interfaces

Following the formal presentations and discussion sessions, several general observations became apparent and we were able

to identify a group of specific areas of materials study which should lead to a more rapid development of high performance battery systems.

General Observations

1. Li is generally chosen as the alkali metal for ambient T use because it is readily available in a variety of forms, is easy to handle (MP = 180.5°C), and it is safe in the presence of H_2O because the heat of hydration is not sufficient to melt the Li metal. Li metal also forms a passive layer of oxide (or nitride). It is the most electro-positive metal with the highest emf to equivalent weight ratio.

2. Li is normally also chosen for molten alkali halide systems because it is relatively insoluble in its own alkali salts and thereby reduces the possibility of internal shorting. The other alkali metals are generally more soluble in their own salts.

3. Dendrite formation is still a major problem in several solid-electrode systems, particularly with Zn electrodes in alkaline batteries and Li anodes in ambient temperature non-aqueous electrolyte systems; however, there are no serious dendrite problems in the Pb-acid system.

4. β-alumina is currently the best solid electrolyte; this limits present solid state batteries of high energy density to the use of Na anodes and β-alumina electrolytes. Problems with electrolyte fabrication and the polysulfide cathode dominate

the performance of such cells.

5. It is too early to define specific problems in the non-aqueous (Li anode) inorganic electrolyte systems, but they appear promising.

6. The greatest payoff is to be expected from work on non-aqueous liquid and solid electrolyte systems because of the inherent thermodynamic limitations of aqueous systems.

Problem Areas for Study

1. More effort is needed to search for new elevated temperature liquid electrolytes, particularly those with anions inert to alkali metals and low melting points.

2. More research into the measurement of the transport properties of alkali metal ions in various solids (including glasses) in the hopes of finding good Li^+ ion conductors is necessary. Basic problems such as the influence of purity and microstructure are also important.

3. There are serious problems of charge retention in Ni electrode (alkaline electrolyte) systems. More research is needed on Ni electrode chemistry.

4. More work is needed on understanding polyphase air electrodes in order to inhibit the flooding problem, and allow the development of rechargeable systems.

5. Currently platinum is the best electrocatalytic electrode for H_2, air, carbonaceous fuels, and NH_3. A less expensive substitute is needed, and fundamental guidance is critical.

6. More effort should be expended in finding new non-aqueous ambient temperature electrolytes, both organic and inorganic.

7. Seals and joining materials for both ambient temperature and high temperature use in highly reactive environments deserve more effort.

8. Other electronically conducting current collector materials for use with highly oxidizing molten electrodes should be explored. The presently used carbon felt is very expensive and mechanically fragile.

9. Porous polyphase electrodes are utilized in many battery systems, and wettability (either too much or too little) is often a serious problem, sometimes sharply changing with time. Fundamental understanding of wetting and its control would be very desirable.

10. What is the nature of passive layers on Li, Mg, and other very electropositive anode materials?

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON SUPERCONDUCTING MATERIALS AND LONG-RANGE PROSPECTS

P. E. Duwez

The three main subjects discussed at this meeting were 1) Superconducting metallic alloys and the chances of increasing their transition temperatures; 2) The present state of development of copper-stabilized superconductors; and 3) The possibility of achieving a true superconducting state in organic solids.

The best superconducting alloys at present have a transition temperature between 20 and 21°K, at zero field and zero current, and the practical temperature range for these materials would be 16 to 17°K. In order to use hydrogen instead of helium (which may not be available in sufficient quantities within 10 to 20 years), the transition temperature should be raised to about 25°K. Several participants were optimistic that this goal could be met within about 10 years; others were skeptical. The approach suggested by Matthias, Giorgi and others is to extend the study of alloys to include other elements than Nb, V, etc., and include ternary and even quaternary alloys with crystal structures other than the A15 structure. Obtaining reliable data on thermodynamic properties and phase stability of ternary alloys was mentioned in the discussion as an important problem in this general field.

In spite of their limitations, the presently known superconducting alloys would meet the requirements for certain applications providing they can be processed into useful shapes such

as wires, cables or tapes. Progress in this direction has been rapid and the results are encouraging. It appears that within less than five years the feasibility of superconducting transmission lines, electric generators and motors will be demonstrated. The project at the NSRDL is of particular importance because it is the first attempt to use superconductors in an integrated engineering system.

The presentations on organic materials raised a great deal of interest from all participants. The prospect of achieving superconductivity at room temperature (or even at 60°K) is fascinating and seems to be out of reach with metallic superconductors. However, the materials studied so far show a relatively high conductivity (comparable to that of copper) within a rather narrow range of temperatures, and a truly superconducting state has not yet been found. The lack of reproducibility of measurements (resistivity, magnetic susceptibility, etc.) is a serious problem, especially since it also exists for materials prepared and measured in the same laboratory. This is an important materials problem showing that the properties are extremely sensitive to the purity and the structural perfection of the organic crystals. There is no doubt that these problems can be solved by an increased effort (and funding) in this general field. It is also essential to encourage a better cooperation between the scientists involved and promote a free exchange of samples for physical properties determinations in several laboratories.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON THE BRITTLE MATERIALS WORKSHOP

R. M. Thomson, R. L. Coble and F. A. McClintock

Techniques were reviewed for assuring mechanical reliability in ceramic structural applications. Generally speaking, the state of the art in flaw control of ceramics is much less well-developed than in metals.

The flaw control problem seems to center around

(1) laws for slow crack growth

(2) starting material quality

(3) available NDE techniques, and physical or economic constraints on their use

It appears at this point that no one technique will do the complete job. We have found that decision analysis is a promising tool in making these choices, and more important, in forcing one to think quantitatively about the problem.

Methods which seem to have important potential are:

(1) Proof testing; perhaps in conjunction with acousitc emission. (Problems arise with this method in simulating the thermal shock situation). The high value of n in the crack growth law, $v = \alpha\sigma^n$ means that more dependence will be placed on initial quality control and less on maintenance vis a vis metals. Likewise, prooftesting will be a more critical test for

ceramics than for metals. Finally, since only a narrow range of crack size will grow to critical size within the design life, it will not be necessary to detect extremely small cracks (in the range of $\sim$1-10μ).

(2) Liquid penetrant, or future developments of the same. (Problems in application arise because internal flaws are not perceived, because of tightly closed cracks, and because present techniques are developed for metallic applications).

(3) Radiography - useful for gross survey and inclusion detection, but will not detect the small critical flaws.

(4) Ultrasonics - present techniques will not observe critical sized flaws, but is potentially a powerful technique.

(5) New techniques and development of old ones for the ceramic application will be important because the ceramic regime is sufficiently different from metals that traditional methods are not likely to be optimum in their present forms. Examples of new possibilities are the use of corona discharge in connection with a conducting penetrant, laser microstrain techniques, thermography, dielectric loss, etc.

Internal flaws in the material are primarily associated with either voids which are left over from the sintering process

or are formed around precipitate particles which have a different thermal expansion from the matrix material and which break away from the matrix in a crescent shaped crack around the precipitate at the lower temperatures. A pore or precipitate situated on a grain boundary will tend to form a crack running the full length of the grain boundary on either side of the pore to the point where the grain boundary branches. According to this picture the material, as grown, will then possess numerous cracks associated with aglomerates and voids where the size of the crack is approximately given by the grain size of the material. Thus uniformity in grain structure will be very important since any large grain is a likely site for a crack.

A considerable difference of opinion developed in the workshop relative to the importance of surface versus internal cracks. Present commercial material appears not be be sufficiently good relative to grain size distribution and aglomerate particles so that internal cracks are common. On the other hand, the General Electric group has been successful in consistently preparing sintered silicon carbide with a very small and very uniform grain size so that no internal flaws larger than 10 microns are observed. The G.E. experience is that the major problem rests with surface flaws which are formed during various processing procedures, especially at corners and fillets of the specimen. One hopes that the G.E. experience in silicon carbide gives one a glimpse of the kind of ceramic material one can eventually hope to obtain for practical applications. If so, one can hope to

have very high strengths and the problem will then shift to controlling the damage to the surface during manufacture and operation.

In conclusion, we are still too deeply involved with important materials improvements and even with design concept changes to be able to develop an exact picture of what the reliability requirements will be for ceramics, and what techniques will be most effective in assuring this reliability. However, certain broad generalizations appear to be possible. Briefly, these are

1. So far as previously existing cracks are concerned, the extreme sensitivity of slow crack growth to either temperature or stress indicates that it will be relatively easy to operate on a safe life principle. Since decreasing the largest flaw size in the material by a factor of two increases the safe life by a factor of ten, no advantage accrues to monitoring slow crack growth during the service life of the ceramic part. (The creation of new flaws by surface damage in service or long term corrosion is, of course, a different matter).

2. Materials development is moving in the direction that one may be able to eliminate internal flaws as a serious problem with surface damage emerging as the primary flaw control problem. Under these conditions, penetrants and proof testing (possibly in combination with acoustic emission) were the techniques which appeared to the working group to have the greatest potential.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON MATERIALS PROBLEMS RELATED TO TRANSMISSION AND REFLECTION OF UV RADIATION

(Preliminary Report)

M. Sparks, H. Ehrenreich, W. Flygare, M. Stickley

Approximately 15 outside users and developers of UV lasers and materials met with several Materials Research Council members to examine the nature of materials limitations as related to high power UV generation and transmission. The schedule of formal presentation attempted to cover four general areas:

(1) Fundamental Principles of Reflection and Transmission of UV Radiation; H. Ehrenreich, F. C. Brown, J. Stafford, and A. Glass.

(2) Current Materials Problems in UV Lasers; P. Hoff.

(3) Materials Selection, Preparation, Polishing and Characterization of Bulk Materials and Surfaces; H. Bennett, W. Plummer, W. Hunter, V. Rehn, and E. Catalano.

(4) Methods of Generation of Fundamental Optical Constants in Materials in the UV and Soft X-ray Regions; F. Brown, W. Spicer, and H. Ehrenreich.

In addition to the above, R. Andrews discussed the prospects of X-ray lasers but the associated materials problems were not discussed extensively.

The principal points that emerged from the discussion following the conference based on information supplied by the speakers, focused on (1) the fundamental limitations of the materials used for UV mirrors and windows and (2) recommendations for future research.

A. Fundamental Limitations

1. Al appears to be the mirror material that comes closest to having ideal properties. Its reflectivity cut-off lies beyond 15 eV; still, in pure Al above about 1 eV, 8% of the incident photon flex is absorbed. The interband mechanism responsible for this is also present in polyvalent metals that might be alternate candidates.

2. All insulators have gaps smaller than about 12 eV. This limitation is imposed by the fact that the spacing of adjacent atomic energy levels are usually of the order of, or smaller than, 1 Rydberg. LiF and MgF_2 appear to be prime candidates since their band gaps are larger than 10 eV. The number of materials is limited, the band gap sequence being $LiF > BeO > NaF > MgF_2 > Al_2O_3 > SiO_2$.

3. The extent of non-linear absorption mechanisms in the UV is only incompletely understood at the present time. Present estimates of the power density limits for both windows and mirrors pertaining to Xe lasers are $\sim$1 megawatt/cm^2.

4. The role of imperfections is also incompletely understood. The failure mechanisms in laser glasses considered by

Bloembergen are applicable here. In addition, the formation of such imperfections, as well as color centers (in UV windows) with time must be considered.

5. The mechanical properties of windows must be such that they can withstand appreciable pressure differentials and shock waves (30-40 atm.). Unhardened LiF may be poor for that reason.

B. Recommendations

1. The non-linear optical constants should be measured through the UV region. These would include: (a) $\chi^{(2)}(\omega)$ in crystals lacking inversion symmetry; in this case a 2ω photon is generated and absorbed by a single step mechanism: (b) $\chi^{(3)}(\omega)$ which involves two photon absorptions, simulated Raman and Brillomin scattering, as well as the non-linear index. This might be accomplished by using SLAC UV photons together with a coherent source (say, a ruby laser).

2. Lower energy UV lasers ($h\nu$ = 3-4 eV) should be seriously considered since windows can be chosen for which the disipative part of χ^{NL} vanishes to third order. It is not clear whether the mirror problem would be resolved by this expedient although a phased array of insulating partial reflectors (like LiF) followed by an Al-MgF_2 mirror could be visualized.

3. UV mirror technology should be developed along the following lines: (a) use of sputtering techniques to make curved self-sustaining mirrors; (b) use of combined mechanical polishing and chemical etching, the former to produce correct curvature,

the latter to remove surface damage; (c) the development of other techniques such as ion polishing.

4. High purity LiF and MgF_2 should be prepared and their optical and mechanical properties, as well as resistance to radiation damage and tendency to form color centers should be investigated more thoroughly than heretofore.

In addition, the controlled addition of impurities such as Mg which may harden LiF (pure LiF is very soft and therefore difficult to polish) should be investigated.

5. The use of SLAC for some of the foregoing experiments should be investigated. At $h\nu$ = 10 eV, there are $\sim 10^{13}$ photons/Angstrom-mr-sec. For $\Delta\lambda \sim 10^2$Å and 10 mv this would lead to 10^{16} photons/sec and an energy flux of 10^5 watts/cm^2 which is only an order of magnitude smaller than the presently achievable power limit of 10^6 watt/cm^2 (this is strictly a materials limit). It is estimated that a factor of 10 scale up would be possible with the presently available system, were it not for this limitation.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS OF THE TASK GROUP ON STRESS-CORROSION CRACKING

M. Cohen

The SCC Task Group (consisting of B. F. Brown, M. Cohen, J. P. Hirth, H. H. Johnson, H. W. Paxton, and R. W. Staehle) has concluded that an urgent need exists for a handbook on stress-corrosion cracking in order to meet the growing stress-corrosion threat in advanced technologies. To be effective, it is essential that this effort be directed toward design and operating engineers, and we have prepared an editorial and organizational plan with that audience in mind.

Our proposal envisions a two-volume handbook to be produced over a three-year period under the leadership of B. F. Brown(Vol. I - Control of Stress-Corrosion Cracking), R. W. Staehle (Vol. II - Engineering Design Data on Stress-Corrosion Cracking), and H. W. Paxton (Advisory and Publication Board). We have also estimated an appropriate funding schedule for this handbook program, and the proposal has been submitted to ARPA for consideration.

Note: A more detailed discussion and related papers are in the process of publication in a later report.

SUMMARY OF DISCUSSIONS ON STRUCTURE AND PROPERTIES OF DISORDERED CARBONS

E. E. Hucke

Representatives of the four ARPA contractors investigating various aspects of disordered carbons met July 23 and 24 with interested members of the MRC and guests. Those present for all or a portion of the meeting were E. E. Hucke, University of Michigan; P. L. Walker, Pennsylvania State; J. C. Bokros, Gulf Medical Products Division; G. Tingey, Battelle Northwest; M. Stickley, ARPA; A. Bienenstock, Stanford; M. Cohen, MIT; Frank McClintock, MIT; H. Reiss, UCLA; J. Hirth, Ohio State; F. Hawthorne, UCLA; H. Paxton, Carnegie-Mellon; P. Shewmon, National Science Foundation and J. J. Gilman, Allied Chemical Corporation.

The purpose of the meeting was fourfold:

1. To appraise MRC members of progress and gain ideas for solutions of the outstanding problems of understanding the evolution of the various structures and the resulting properties of the disordered carbons ("glassy carbons").

2. To allow review of the major findings of the first two years work by each of the contractors.

3. To map out the third year's effort for each contractor and provide a coordination in sample exchange and property determination.

4. To discuss potential applications to DoD problems of some of the materials produced and characterized during the past two years.

A short introductory presentation was given by E. Hucke in which he discussed the broad range of structures obtainable in the non-crystalline forms of carbon. It was pointed out that solid carbons are always formed from molecular decompositions with loss of mass which in most cases gives considerable void space within the structure of the remaining high carbon polymers and therefore is importantly influenced by the temperature, pressure and time sequence occurring in the pyrolysis. While this behavior allows a very wide range in properties to be produced by varying processing it becomes difficult to either reproduce or characterize different disordered carbons. This behavior is in sharp contrast to the crystalline metals and ceramics and other amorphous materials where structural changes occur at constant mass.

The major findings of the various groups is summarized below:

University of Michigan

1. Thick sections of sound material with controllable porosity can be reproducibly achieved in short processing times.

2. Structural variations induced by processing changes can alter every property measured over wide ranges, often several orders of magnitude.

3. A comparatively simple thermodynamic measurement can differentiate the structural differences in various disordered carbons according to their enthalpy and entropy of disorder and yield information on the occupation of active surface sites.

Gulf Medical Products Division

1. High strength, fatigue and wear resistant carbons can be produced in both batch and steady-state pyrolytic beds.

2. The mechanical properties of the low temperature isotropic carbons can be well-correlated to their microstructures and can be varied over wide ranges with process parameters.

3. Alloy additions of Si and Ti can significantly improve mechanical properties, especially wear resistance.

Pennsylvania State

1. Fine dispersions of large amounts of Fe can be incorporated into carbons by way of organometal additions to organic precursors.

2. High pressure during pyrolysis significantly affects the structure of the carbon residue.

3. Useful molecular sieve carbons can be produced in open pored structures by suspension polymerization, pressing, and pyrolysis.

4. Novel carbon-metal structures can be produced by sputtering.

Battelle-Northwest

1. Some disordered carbons have significantly greater oxidation resistance per unit area than the best graphites.

2. Processing changes can improve oxidation resistance by several orders of magnitude.

3. Strength properties can be improved over commercial glassy carbon by controlling processing variables.

4. Toughness can be improved by several orders of magnitude by proper incorporation of carbon fibers.

It was decided that the third year's effort would concentrate on each laboratory following and extending the major result areas summarized above. Considerably more sample exchange between laboratories was recommended.

It was agreed that a meeting would be set up with Bob Meyers of Aerospace Corporation to discuss details of carbon materials requirements in certain nozzle and heat shield applications.

Martin Stickley will endeavor to appraise the group of any potential ways that materials developed by the ARPA contractors can be of use in the NOL re-entry vehicle program.

Considerable discussion of unique properties of disordered carbons led to the conclusions that:

1. Some unusually difficult seal and bearing problems would be solved with disordered carbons.

2. That carbon materials including those in a low pyrolysis state offer a solution to several problems as insulators, current collectors, and catalyst supports in advanced electrical cell systems for direct conversion, including high energy density batteries, fuel cells, and concentration cells.

3. Disordered carbons now offer the only satisfactory materials for many biomedical devices.

4. The inherent corrosion resistance of carbon for acids molten salts, H_2, Cl_2 offers potential solution to several difficult materials problems in solar energy storage and conversion systems.