

REPORT
of
ARPA MATERIALS RESEARCH COUNCIL
1970

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

INTRODUCTION

This report describes the activities and output of the ARPA Materials Research Council for the year ending December 31, 1970, the third year of operation of the Council.

The idea of a Materials Research Council originated in 1966 when several individuals in materials and material sciences including Dr. Robb Thomson, Director of the Materials Science Office of ARPA, discussed the possibility of bringing together 20-30 outstanding people in the materials field for an extended period each year to examine this area of study and relate their concerns and interests to those of DOD in these fields. The group was to be briefed on the current state of emerging problems and was to be challenged to develop solutions, or a consensus for approaches to the possible solutions of such problems.

Subsequent development of this idea led to the formation of the ARPA Materials Research Council and the bringing together of a group for an extended period of study during the summer of 1968 for the first summer conference. The concept proved to be so fruitful that the Council was continued through 1969, 1970 and plans are currently being projected through 1971.

It has not been the principal purpose of the Council to concentrate on current high-priority and highly-focused materials problems. This type of problem is usually in very competent hands,

and is invariably part of a larger systems problem. The intrusion of the Council into such problems, while possibly of some benefit, would be divisive and cause back-tracking and be wasteful of the efforts of all groups involved. The Council has indeed occasionally worked on such problems and expects to do so in the future, but the real value of the Council lies in using it for its long-range and broad vision. A primary strength of the Council lies in its ability to recognize and work on future critical needs, rather than on current critical problems.

The initial concept that the members of the Council should be among the most able and highly qualified individuals in the country in their respective fields in order to bring their expertise to bear on the complex materials problems of DOD has proved to be a wise decision. The quality of the people in their respective fields has been such that the entire group, physicists, chemists, and engineers, have interacted in such a fashion that they are probably one of the most coherent, versatile and knowledgeable groups working in materials science and materials engineering in the country. It is noteworthy that the group has maintained a high degree of continuity throughout its three-year history.

Since the personnel of the Council 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. Several graduate students are actively pursuing problems first formulated by the Council. They include such topics as surface chemistry, the physics of surfaces, fracture analysis, stress corrosion, plasticity, high-temperature thermodynamics, composite materials, refractory materials, electronic properties, optical properties, etc. The interdisciplinary nature of the group is reflected in the wide range of researches that have been generated as a result of the problems discussed in the Council.

PROJECT ORGANIZATION

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

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

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

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

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

Professor John L. Margrave
Department of Chemistry
Rice University
Houston, Texas 77001

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

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

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

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

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 Chemical 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, 1971.

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

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

Professor Nico Bloembergen
Division of Engineering & Applied Physics
Harvard University
Cambridge, Massachusetts 02138

Professor Bernard Budiansky
Division of Engineering & Applied Science
Harvard University
Cambridge, Massachusetts

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

Professor John D. Ferry
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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

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

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

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

Professor Alan Heeger
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University of Pennsylvania
Philadelphia, Pennsylvania 19104

Professor Robert A. Huggins
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Stanford University
Stanford, California 94305

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

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

Professor Erastus H. Lee
Department of Applied Mechanics
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Professor Donald J. Lyman
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The University of Utah
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Professor William Prager
Division of Engineering
Brown University
Providence, Rhode Island 02912

Professor James Rice
Division of Engineering
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Professor Paul L. Richards
Department of Physics
University of California
Berkeley, California 94720

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

Professor Albert J. Sievers
Physics Department
Stanford University
Stanford, California 94305

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

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

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

PROBLEM SELECTION

In 1968 the Steering Committee, working with the ARPA Materials Science Office, arranged a series of briefings with various DOD agencies to examine those areas which were believed most appropriate for consideration by the Council. As a result

of these meetings and subsequent discussions with the entire Council, four general topics were chosen for detailed examination: composite materials, shock propagation, constitutive relations at high temperatures and pressures and underground sensing. At the 1968 summer conference, consultants and specialists worked with the Council to define more closely the problem areas, and to inform the Council members of related programs and progress. Individual members then worked either independently or in small subgroups on various segments of the problem areas and, after discussion and analysis, issued reports.

While the above procedure was reasonably successful in directing the work of the Council, further improvements were put into effect in the 1969 operation. The original concept of holding a summer conference 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 Council members with representatives of DOD laboratories. The results of this interaction were conveyed to the Steering Committee's May meeting 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.

SUMMER CONFERENCE

The conference was held during the month of July at The Bishop's School in La Jolla, California.

Since the bio-materials area was chosen as a new topic, rather extensive use of outside consultants was made to brief the Council on the state of the art. The following individuals aided the Council in bio-materials:

Professor J. D. Andrade, University of Utah
Dr. V. Mooney, Ranchos Los Amigos Hospital
Professor Y. C. Fung, University of California,
San Diego
Professor B. W. Zweifach, University of
California, San Diego
Mr. James Benson, Bio-carbon, Inc.
Dr. J. P. Howe, Gulf General Atomic

Since there was considerable experience in industrial laboratories nearby on the status of metal matrix composites, the following were asked to make presentations to the Council:

Dr. A. Hurlich, Convair, San Diego
Dr. J. Christian, Convair, San Diego
Dr. A. Metcalfe, Solar, San Diego

A team from Sandia Laboratories contributed to further discussions on carbon-carbon composites and to the area of shock in various materials. Those taking part were:

Drs. J. B. McDonald, O. E. Jones, A. J. Chabai,
D. S. Munson, D. S. Drumheller, and W. Herrmann

In the areas of shock, spalling, and fracture, Dr. T. Barbee, Stanford Research Institute and Dr. M. Wilkins, University of California, Livermore, made valuable inputs to the Council.

Professor H. W. Staehle, Ohio State University, added outside consultation in the area of stress corrosion, while

Professor M. Pound of Stanford helped formulate some problems in irreversible thermodynamics. Professor J. O. Wilkes, University of Michigan, was available to help Council members in formulating problems for computation via a telephone link to The University of Michigan Computing Center.

In addition, representatives of the various service laboratories were invited to the conference so as to provide a two-way communication between the Council and the respective laboratories. In this manner the results of the Council's efforts could be more directly communicated to the service laboratories. 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 individuals attended portions of the conference:

Dr. W. W. Scanlon, Naval Ordnance Laboratory
Dr. A. J. Schindler, Naval Research Laboratory
Dr. R. A. Weiss, U. S. Army

The interaction proved to be quite valuable to the Council.

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 some cases are in the process of publication in the appropriate technical journals. In many instances, the reports arising from the 1970 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 and are aimed primarily to stimulate discussion within the Council. However, they are available subject to the authors' release by request to the Project Director.

The breadth of activity of the Council during the 1970 conference can be seen from the following list of papers produced. The abstracts are given in the Appendix. Titles marked with an asterisk are reports and memoranda for limited distribution; those marked with (†) are being published.

Fracture

Calculated Peierls Stresses for Iron and Zinc
J. P. Hirth

On Branching Forces on a Fast Crack as it Approaches
an Interface
J. P. Hirth

Outline of a Cracking Problem at a Particle Matrix
Interface in the Microstrain Region
J. P. Hirth

Bond Breaking at Low T
R. M. Thomson

A Question of the Crystallography of Fracture
R. M. Thomson

Fracture Mechanisms and Needed Research
J. P. Hirth and F. A. McClintock

A Criterion of Ductile Fracture for Elastic-Plastic
Finite Element Calculations
F. A. McClintock

*Brittle vs. Ductile Behavior of Crystalline Solids:
Dislocation Nucleation at the Crack Tip
J. Rice and R. M. Thomson

*Separation Forces and Energies in Crack Propagation
from Grain to Grain
D. C. Drucker

*On the Stresses in Hard Inclusions in a Ductile Matrix
D. C. Drucker and J. Rice

*Calculation of Traction-Displacement Relations for
Ductile Fracture Along Grain Boundaries
F. A. McClintock

*Some Viewpoints Concerning the Fracture Problem
M. Cohen

Composites

*On Metal-Matrix Composites
P. E. Duwez and M. B. Bever

*On Gradient Composites
M. B. Bever and P. E. Duwez

Extension of the Theory of Mechanical and Thermoelastic
Properties of Composites into the Plastic Range
G. H. Vineyard

Waves and Transients in Composites
E. H. Lee, J. A. Krumhansl and W. Kohn

Stress Distributions in Plane Waves
in a Periodic Layered Composite
E. H. Lee

Propagation of Transients in Periodic
Composites
J. A. Krumhansl

†Improvement of Rayleigh-Ritz Eigenfunctions
W. Kohn

Optics

†Nonlinear Optical Properties of Periodic Lamellar
Structures
N. Bloembergen and A. J. Sievers

On the Platinum Precipitation Problem in Laser Glass
R. A. Huggins

New Materials

*Approximate LCAO-SCF Calculations Involving Some New
Molecules and New Solids
W. H. Flygare

Lithium-Dihydro-Fluoride--An Approach to Metallic Hydrogen

J. J. Gilman

Electron-excess Compounds

J. L. Margrave

The Impending Revolution in Batteries

R. A. Huggins

Glassy Carbon

E. E. Hucke and P. E. Duwez

New Techniques for Direct Fluorination

J. L. Margrave

Thermodynamic Properties of Liquid Metals

J. L. Margrave

*Bio-Materials

D. J. Lyman

Chemical Thermodynamic Tables - Past, Present and Future

J. L. Margrave

*On the Structure of Glassy Carbon

P. E. Duwez

Stress Corrosion

The Mechanism of Stress Corrosion Cracking

J. J. Gilman

Key Considerations: Stress Corrosion Cracking of High Strength Steels

R. W. Staehle

Societal Materials

Magnetic Suspensions for High Speed Transportation

P. L. Richards and M. Tinkham

Bio-Materials

The Effect of an Electric Field on the Rayleigh Scattered Light from a Solution of Macromolecules

W. H. Flygare

†Thermoelastic Properties of Helical Protein Molecules

H. Reiss

Fiber Networks with Controlled Strand Thickness as Biomaterials

J. D. Ferry

Some Comments on the Mechanical Properties of Fibrous Protein Structures

J. D. Ferry

Control of Mechanical Properties of Swollen Hydrophilic Network Polymers; Layer and Gradient Structures

J. D. Ferry

*Questions Concerning the Current State of Biomedical Materials

M. B. Bever

Other Reports

Bulk Stiffness of Metals

J. J. Gilman

Comment on Spinodal Decomposition

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

POST CONFERENCE ACTIVITIES

Many of the Council found that they could take full advantage of the presence of the other Council members by utilizing most of the time during the conference in small group sessions. In this way problems could be formulated and subdivided with maximum effort on interchange of ideas. This resulted in a need to spend considerable time after the conference in writing the results. In addition to report preparation, in some cases it was thought desirable to arrange some additional small meetings between Council members and other individuals. One such meeting was held in San Francisco with Professors Hucke, Huggins and Krumhansl of the Council and a group of researchers known to be active in the area of glassy and CVD carbons. The

others attending were:

Professor R. H. Bragg, University of California,
Berkeley
Professor D. Fischbach, University of Washington
Professor P. L. Walker, Jr., Pennsylvania State
University
Dr. Barry Granoff, Sandia Laboratories
Dr. R. K. Nightengale, Battelle-Northwest Laboratories
Dr. M. C. Smith, Los Alamos Laboratories

The Steering Committee in its fall meeting in Washington recommended 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 contracted early enough to allow them to plan to attend portions of the conference and to identify, secure, and screen the relevant literature. 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. Plans for small preparation meetings were laid and the following subject areas suggested.

Amorphous Semiconductors
Superconductors for Alternating Current
Physical and Mechanical Properties of
Non-biological Polymers
Liquids at High Temperatures
Aspects of Design for Brittle Materials
Stable Disordered Carbons
Stress Corrosion
Biomaterials

APPENDIX

Abstracts

CALCULATED PEIERLS STRESSES FOR IRON AND ZINC

J. P. Hirth

The anisotropy of slip is of interest with regard to crack blunting. A brief note reviews the Peierls estimates of such anisotropy and indicates anisotropies of about a factor of 20 for iron and zinc. Slip on the direction most favoring plastic blunting of a crack is more difficult than slip on the easy glide system by that factor.

ON BRANCHING FORCES ON A FAST CRACK AS IT APPROACHES AN INTERFACE

J. P. Hirth

Dynamic image forces are calculated for a fast climbing dislocation, the analog of a tensile crack, as it approaches a free surface. The image forces are found to stabilize the dislocation against slip out of its climb path and hence should stabilize a tensile crack against branching in the analog. The opposite effect is postulated for a tensile crack in a soft matrix as it approaches a hard imbedded phase.

OUTLINE OF A CRACKING PROBLEM AT A PARTICLE-MATRIX INTERFACE IN THE MICROSTRAIN REGION

J. P. Hirth

The interaction of a matrix and a hard imbedded particle in the microstrain yielding region is considered. The probability of particle cracking versus various plastic relaxations at a dislocation pileup is expressed in terms of pileup theory and the Cottrell-Bilby-Swindon relaxation model. Material parameters are pinpointed which would give numerical estimates of the above probability.

BOND BREAKING AT LOW T

R. M. Thomson

We investigate the possibility of breaking a chain of atoms under a stress by calculating when a fluctuation of sufficient size will occur at the place where the break is to

occur. This calculation is performed in two degrees of sophistication in a semi-classical approximation of rate theory for zero point motion of the atoms. Our results show that the rate of chain breaking is extremely sensitive to the strength of the bond, or equivalently, to the distance to the cut off of the assumed parabolic force law. An estimate of the breaking rate for a carbon-carbon chain suggests that for reasonable stresses, breaking due to zero point fluctuations may be significant.

A QUESTION OF THE CRYSTALLOGRAPHY OF FRACTURE

R. M. Thomson

We work out the simple arithmetic of why a simple cubic crystal with simple bonds prefers to fracture on crystallographic planes. The results show that near the symmetry plane the surface energy increases linearly, while the elastic energy decreases with a higher power of the angle, so that crystallographic fracture is preferred for small angular offset. Anisotropy effects together with the details of the surface energy variation, however may bring in other planes at higher angles between the planes of high symmetry. Hence, when a crack approaches a grain boundary, there will be a force rotating the crack back into the crystallographic plane.

FRACTURE MECHANISMS AND NEEDED RESEARCH

J. P. Hirth
F. A. McClintock

The fracture problem is reviewed and a long list of questions is compiled pertinent to (a) hole growth, (b) cleavage, (c) hydrogen embrittlement and (d) stress corrosion cracking. A need is indicated to select the critical questions in the fracture area. It is proposed that a conference be held to fulfill this need.

A CRITERION FOR DUCTILE FRACTURE FOR ELASTIC-PLASTIC, FINITE-ELEMENT CALCULATIONS

F. A. McClintock

Finite element and finite difference calculations have developed to the point where a local fracture criterion can be incorporated. A preliminary form of such a fracture criterion

is proposed for ductile fracture by hole growth. It includes both the stress and strain history required for localization of flow in a de-cohering zone immediately ahead of the crack and the traction-displacement relation across the zone. The criterion is appropriate only where each element contains one hole. Its most serious approximation is in estimating the growth of the hole as if the element were in an infinite medium without any nearby crack.

BRITTLE VS. DUCTILE BEHAVIOR OF CRYSTALLINE SOLIDS:
DISLOCATION NUCLEATION AT THE CRACK TIP

J. R. Rice
R. M. Thomson

A crack will homogeneously nucleate dislocation loops at its tip at a finite rate. The dislocations thus nucleated blunt the crack on an atomic scale, and the blunting tendency can be used to distinguish truly brittle materials from those which are ductile. The dislocation nucleation rate is estimated by calculating the attractive image force between a dislocation line and the open surface at the crack tip and comparing this with the repulsive force on the dislocation due to the strain field of the crack. A critical dislocation loop energy for nucleation is then estimated, and a critical parameter, $\eta \approx Eb/(1-\nu^2)\gamma$ is obtained where E is Young's Modulus, ν is Poissons ratio and γ is the surface energy. The parameter, η , roughly divides brittle from ductile materials.

SEPARATION FORCES AND ENERGIES
IN CRACK PROPAGATION FROM GRAIN TO GRAIN

D. C. Drucker

Consideration is given to the effect of the change in orientation of the cleavage planes across grain boundaries on the propagation of quasi-brittle fracture in steel. Accommodation by cleavage with steps of atomic dimension increases the surface energy only slightly over the energy for cleavage without such steps. The larger the steps between cleavage planes in the grain ahead, the greater the plastic deformation prior to separation and the greater the equivalent surface energy in a Griffith type approach. However, this mechanism also cannot account for the very large energy dissipation found experimentally in the quasi-brittle fracture of ordinary structural steels at moderate temperatures. It does seem that only the plastic deformation of an appreciable fraction of the grains acting as fully plastic links

can produce the experimentally obtained crack arrest and propagation stress intensity factors. Nevertheless, both true surface energy and steps within grains do play a significant role.

ON THE STRESSES IN HARD INCLUSIONS
IN A DUCTILE MATRIX

D. C. Drucker
J. R. Rice

Questions about the cracking of the larger carbide inclusions in steel, void initiation through decohesion of micron size or larger inclusions in many alloys, and the transverse tensile strength of metal matrix composites motivated this study. For simplicity of description, the matrix is idealized as isotropic, elastic-perfectly plastic, with yield stress σ_0 in simple tension equal to twice the yield stress τ_0 in simple shear. A strong, well-bonded, isolated particle or fiber of any shape, orientation, and properties then cannot increase or decrease the tensile yield strength of the composite (matrix plus inclusion) from the σ_0 of the matrix alone.

Consequently, at an applied tensile stress of σ_0 , one possible solution for an inclusion of arbitrary geometry is a uniform simple tension of σ_0 everywhere in the matrix and the inclusion. This is in fact the correct solution for an initially stress-free system with a strong, bonded inclusion and a matrix having the same elastic constants; and would be a fair approximation for iron carbide in iron. Yet, despite the uniqueness theorem for elastic-perfectly plastic assemblages, the actual state of stress in the inclusion need not be this simple tension σ_0 on each and every plane transverse to the tension. The value σ_0 as an average is a lower bound for almost all geometries; but higher values are permissible for appropriate patterns of initial stress when inclusion and matrix have the same elastic moduli, and are likely when the inclusion is stiffer than the matrix. Stress concentrations at irregularities in the surface of the inclusion then can be very high. Initial stress in the inclusion can be large compared with σ_0 when there is a significant thermal contraction mismatch, as for oxides in a metallic matrix. This stress may increase or decrease as load is applied to the matrix. At yield of the matrix, however, the average stress in the inclusion tends to be moderate for a wide variety of inclusion shapes in two and three dimensions. Upper and lower bounds are obtained to this maximum possible average stress in the inclusion. No matter how mismatched the inclusion and matrix may be elastically and thermally, the average stress in the inclusion cannot exceed $2\sigma_0$ unless the inclusion is fiber-like or sheet-like (major dimension more than 2 to 4 times the minor dimensions).

A point of some interest is that in the absence of hardening and of a Bauschinger effect, alternating yielding in tension and compression will reduce the residual stress to zero for the equal elastic moduli case.

Cylinders, spheres, wedges, and other special shapes of inclusions are considered. Calculations and examples of thermal and other initial or residual stress patterns, along with upper and lower bound results, are given in some detail and interpreted in terms of fracture or decohesion of the inclusion.

CALCULATION OF TRACTION-DISPLACEMENT RELATIONS FOR DUCTILE FRACTURE ALONG GRAIN BOUNDARIES

F. A. McClintock

In some alloys at room temperature, such as 7075-T6, and in other alloys in the creep regime, fracture is predominantly intergranular but occurs as the result of holes growing from inclusions along the grain boundary. A plane-strain plasticity model is developed to give the traction-displacement relation expected for such a configuration. The required computer calculations would be of use in other plane-strain, rigid-plastic calculations to determine the coordinates of the slip line field subtended by a given non-characteristic arc and to determine the corresponding displacement fields.

SOME VIEWPOINTS CONCERNING THE FRACTURE PROBLEM

M. Cohen

A description is presented for various stages in the fracturing process, as a basis for establishing models of the individual steps and then deciding on the critical events which control the ultimate fracture under specified conditions. This approach would seem productive inasmuch as no overall theory of fracture is likely to emerge in the foreseeable future. Particular attention is called to the circumstance that fracture initiation, whether fibrous or cleavage, often results from the presence of brittle phases rather than unique dislocation mechanisms.

ON METAL-MATRIX COMPOSITES

P. E. Duwez
M. B. Bever

We consider in this memorandum the current status and future potential of metal-matrix composites and conclude that further efforts should be devoted to their development.

ON GRADIENT COMPOSITES

M. B. Bever
P. E. Duwez

In a gradient composite compositional or structural characteristics vary with position. In such a composite properties sensitive to these characteristics also exhibit gradients. These gradients occur in the local properties and affect the global properties of the composite. Gradient composites, therefore, are of interest for engineering applications.

In this memorandum we shall analyze various types of gradient composites and shall consider some of their properties. We shall then review reported and potential applications of gradient composites.

EXTENSION OF THE THEORY OF MECHANICAL AND THERMOELASTIC PROPERTIES OF COMPOSITES INTO THE PLASTIC RANGE

G. H. Vineyard

The self-consistent method of Budiansky for approximating the mechanical, thermoelastic, and other constants of isotropic composites is extended into the plastic range by introduction of a new approximation. The result reproduces Budiansky's formulas at low stress and becomes the purely hydrostatic approximation at high stress. Results for effective bulk modulus and effective Grüneisen constant of the composite are presented.

WAVES AND TRANSIENTS IN COMPOSITES

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

Stress Distributions in Plane Waves in a Periodic Layered Composite

E. H. Lee

In an earlier report, variational principles were developed to determine the profile of a steady-state oscillatory stress wave propagating through an elastic composite with general periodic structure. Such a wave, known as a Floquet or Bloch type wave, has, on the average, a single direction of propagation, but locally involves refracted and reflected waves. Difficulties in application of the variational principles were anticipated due to the discontinuities in strain which occur at the interfaces between reinforcement and matrix, since the ratio of elastic constants can be of the order 50. In this paper an exact calculation of stress wave profiles is presented for the case of reinforcement in the form of parallel plates, with waves propagated along normals to the plate surfaces. These solutions are compared with stress profiles determined by a Rayleigh-Ritz approximation to the variational principle when smooth test functions were used for the displacement distribution. Shortcomings of this approach are indicated, and means of improvement are suggested. It is important to thus assess the variational approach, since it can be applied to two and three dimensional composite configurations, for which exact comparison solutions will not be available.

Propagation of Transients in Periodic Composites

J. A. Krumhansl

The propagation of transients, particularly impulses, through a periodic medium is discussed in the linear regime. Basically, the method is the generalization of Fourier methods to Fourier-Floquet transient analysis. The "far field" solutions have certain common features, and can be related to "head of the pulse" solutions found by the equivalent of ray tracing.

Improvement of Rayleigh Ritz Eigenfunctions

W. Kohn

A common method of obtaining approximate eigenfunctions of a linear boundary value problem, $H\psi = E\psi$ and homogeneous linear boundary conditions, is the Rayleigh Ritz method. We consider here the case where ψ is expanded as

$$\psi = \sum_1^N C_n w_n \quad ,$$

and the w_n are solutions of a "standard" problem, with the same boundary conditions. The eigenvalue E and coefficients c_n are conveniently determined from the condition $\delta[(\psi, H\psi) - E(\psi, \psi)] = 0$. We show here that, for large N , most of the error of the ν -th Rayleigh Ritz function, ψ_ν , at the point x_1 is removed by the addition of the correction term $\Delta\psi_\nu(x_1) \equiv (\psi_\nu(x), (H-E_\nu)g(x, x_1))$. Here E_ν is the approximate Rayleigh Ritz eigenvalue and $g(x, x_1)$ is a function, largely arbitrary, except for a specified singular behavior at $x = x_1$ (an appropriate cusp in one dimension, a $[4\pi(\tilde{r}-\tilde{r}_1)]^{-1}$ singularity in three dimensions, etc.). Examples are given and possible extensions are discussed.

NONLINEAR OPTICAL PROPERTIES OF LAMINAR COMPOSITE STRUCTURES

N. Bloembergen
A. J. Sievers

Form birefringence and diffraction of light in composite structures is used as a means of phase matching radiation in cubic nonlinear materials. The changes in dispersion characteristics lead to novel phase matching schemes for nonlinear optical processes, including second harmonic generation, parametric down conversion, stimulated polariton scattering and millimeter wave generation.

ON THE PLATINUM PRECIPITATION PROBLEM IN LASER GLASS

R. A. Huggins

Principles developed for the calculation of defect equilibria in crystalline solids are applied to the struction model of vitreous oxides. Attention is focused upon the influence of oxygen partial pressure and a third component under two conditions, a fixed solute concentration, and a solute in equilibrium with an adjacent phase. The influences

of a second solute, the oxygen partial pressure, and the temperature upon a sparingly soluble species are derived, and practical implications related to the problem of platinum precipitation in laser glass are discussed.

APPROXIMATE LCAO-SCF CALCULATIONS INVOLVING
SOME NEW MOLECULES AND NEW SOLIDS

W. H. Flygare

The LCAO-SCF method is applied to several new molecules involving hydrogen, fluorine and lithium. The structure of LiFH_2 is predicted and the approach to a solid LiFH_2 lattice is also attempted.

LITHIUM-DIHYDRO-FLUORIDE--AN APPROACH TO METALLIC HYDROGEN

J. J. Gilman

The possibility of making a form of metallic hydrogen through preparation of the compound LiH_2F is discussed. A proposed structure is specified which is believed to be nearly stable under ambient conditions. The pressures needed to stabilize this compound and to convert it to a metal are estimated. It may have an exceptionally high hydrogen density, high electrical conductivity, high Debye temperature in the hydrogen sub-lattice, and a high superconducting transition temperature.

ELECTRON-EXCESS COMPOUNDS

J. L. Margrave

The concept of multi-center but electron-excess bonding is reviewed and familiar examples cited. Some new and less-familiar examples-- Sn_2F_5^- and Zr_4F_{10} --are also discussed and some possible extensions to new species, as yet unsynthesized, are presented.

THE IMPENDING REVOLUTION IN BATTERIES

R. A. Huggins

The present status of the electrochemical power source field is briefly discussed, with special emphasis upon recent changes, which are causing new attention to be given to the possibility of the development of high energy and power density battery systems for use in applications such as vehicular power.

Results of research on solid electrolytes within the last year or two and the demonstration of the unusually good properties of certain solid electrolyte-mixed conductor interfaces are pointed out. These have led to the recognition that there is ample reason to be quite optimistic about the possibility of highly effective new types of all-solid battery systems.

The structures of several groups of materials that either have, or are expected to have, properties that would make them candidates for use in solid state cells are briefly mentioned.

GLASSY CARBON

E. E. Hucke
P. E. Duwez

The cost and availability of carbon, along with its unusually stable bonding, have given rise to an ever-growing number of engineering applications. This trend should accelerate as the tendency toward extremes in temperature is continued. During the last decade an interesting new form of solid carbon has been introduced. This carbon, called "glassy" or "vitreous" is made by the controlled thermal decomposition of certain highly cross-linked polymers. The resulting materials are isotropic, hard, strong, stiff, relatively stable chemically and thermally, and have unusual electrical properties. The material has a low density but may be made impervious to helium, or in a form with angstrom sized open porosity. The nature of the material suggests still further variations in structure, and properties should be possible through understanding and control of processing.

A limited number of structural studies have failed to fully determine the atomic structure of this carbon. It is not truly amorphous in the usual sense, but possesses a pronounced tendency to order at least in two dimensions over size ranges from 15 to 100 angstroms. However, it should be described as microcrystalline only if it is understood that the degree of perfection of the crystallites, as well as the size and shape, may be variable depending on the details of processing. Glassy

carbon warrants additional intensive study of preparation, structure, and properties as an interesting material in its own right, and to help understand more fully other related materials such as isotropic vapor deposited carbon and the various forms of graphite.

NEW TECHNIQUES FOR DIRECT FLUORINATION

J. L. Margrave

Broad new techniques for the fluorination of graphite and carbon to yield "CFX", a lubricant powder, and for the fluorination of various organic and inorganic species including plastics, polymers and elastics are reported. "Fluoro-diamonds" and various "Fluoro-Koted" materials have been prepared.

THERMODYNAMIC PROPERTIES OF LIQUID METALS

J. L. Margrave

Although liquids are susceptible to statistical mechanical description, current theory does not provide quantitative values for either heats of fusion or heat capacities of liquid metals at high temperatures. Only recently has a generally applicable experimental technique--levitation calorimetry--become available. At the moment, the very crude estimation rules

$$\Delta S_{\text{fus}} \approx 2.2 - 2.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$C_p(\text{liq}) \approx 7 - 8 \text{ cal deg}^{-1} \text{ gram-atom}^{-1}$$

are as good as the data and the theory. A table of consistent thermodynamic data for liquid metals has been assembled, including estimates for the many high-melting transition metals which have not yet been studied.

BIO-MATERIALS

D. J. Lyman

Two major areas of importance in bio-material research are in the area of: (1) non-thrombogenic surfaces, (2) orthopedic joint reconstruction materials.

The proteinated surface appears to be one appropriate to a non-thrombogenic surface, however, the technique to coat surfaces with protein can have limitations. It is of interest, therefore, to determine the chemical and physical nature of this surface so it can be duplicated synthetically.

At the present state of the art, we do not have suitable chemical techniques for determining adsorbed monolayer structures. Work is needed in this basic area if progress is to be made.

Current ceramic materials have not shown suitability for bone replacement. However, preliminary work has indicated that several new ceramic materials and ceramic/polymer composites appear to approach the needed properties for bone replacement (in terms of mechanical strength and brittleness). More work is needed on determining the performance of these materials in vivo. This includes degradation of the composite as well as any adverse tissue or fluid reactions.

CHEMICAL THERMODYNAMIC TABLES - PAST, PRESENT AND FUTURE

J. L. Margrave

A critical discussion is presented to explain the problems currently faced by scientists and engineers when they turn to the literature for thermodynamic data. The format and philosophy behind the very useful JANAF Tables are described. Special emphasis is given to the need for not just continuing but for expanding the coverage of thermodynamic data. An adequate set of thermodynamic tables could minimize redundant thermodynamic research and provide real guidelines for the evaluation of new theoretical approaches to the calculation of thermodynamic quantities.

ON THE STRUCTURE OF GLASSY CARBON

P. E. Duwez

Technical memoranda - no abstract available.

THE MECHANISM OF STRESS CORROSION CRACKING

J. J. Gilman

Small changes in surface environments can change the energy needed to create a surface shear step. Increases in this energy tend to shift a delicate balance between glide and cleavage initiation at a crack tip. By inhibiting plastic deformation this causes an increased tendency for cleavage. Thus a material that is ductile in a vacuum can become quite brittle in the presence of certain surface active environments.

KEY CONSIDERATIONS: STRESS CORROSION CRACKING OF HIGH STRENGTH STEELS

R. W. Staehle

Memoranda - no abstract available.

MAGNETIC SUSPENSIONS FOR HIGH SPEED TRANSPORTATION

P. L. Richards
M. Tinkham

A rather general analysis is given of the physical principles governing the performance of magnetic suspension systems for high speed transportation. Presumably superconducting magnets would be used in such a system, but the analysis is equally applicable for any magnetic source. Two complementary idealizations are treated: a periodic magnetic field represented by a single Fourier component, and a lumped parameter analysis based on mutual inductance. The first idealization is useful in dealing with a passive structureless track (or ground plane), whereas the second is more useful in dealing with a structured track (using coils) such as the "null-flux" suspension proposed by Powell and Danby. The generality of both methods allows an overview to be obtained which clarifies the strengths and weaknesses of various possible systems. It is shown that suitably phased ac excitation of the magnets at a controlled variable frequency can provide levitation at rest as well as propulsion and levitation at speed, an

attractive possibility if ac losses in the superconducting magnets can be made small enough. In order to make quantitative experimental tests of such systems, a modeling scheme is proposed using a "magnetic windtunnel" with normal metals cooled to liquid nitrogen temperature to maintain the same magnetic Reynolds number as in the full scale system. Finally, proposals are made for more efficient mechanical support of the train by the magnets, making use of high-strength composite materials.

THE EFFECT OF AN ELECTRIC FIELD ON THE RAYLEIGH SCATTERED LIGHT FROM A SOLUTION OF MACROMOLECULES

W. H. Flygare

The hydrodynamic properties of macromolecules in solution are reviewed in an attempt to suggest better methods of analyzing the plasma proteins. Better analysis of plasma proteins will lead to a better method of interpreting the effects of biomaterials on a biological system. A method combining electrophoresis and laser beat frequency spectroscopy is suggested as a new approach to this old problem.

THERMOELASTIC PROPERTIES OF HELICAL PROTEIN MOLECULES

H. Reiss

The effect of stress on the helix-coil transition in a protein or polypeptide is investigated using the methods of statistical mechanics. A case is treated in which the helical sections are regarded as flexible chains with very long, freely "orienting" segments and another in which they are considered to be rigid rods.

Thermoelastic relations are derived; and it turns out that, depending upon conditions, stress can induce the helix-coil transition in one or another direction or do nothing at all. The most probable situations either involve stress applied to a molecule initially helical, in which case the helix is stabilized, or stress applied to the coil form, in which case transformation to the helical form is induced.

The helical form exhibits a very low modulus of elasticity (which we also compute), and it is speculated that preservation of, or transition to, the helical form under stress aids in the protection of living tissue from disruption when subjected to large applied strain.

Real tissues involve highly organized or quasi-random networks of protein chains. The results of this analysis suggest that insofar as the mechanical properties of the networks are concerned, the chains be treated as quasi-harmonic strings whose configurations (weighed by potential energy) can be enumerated in order to include entropy effects in the calculation of the network modulus.

FIBER NETWORKS WITH CONTROLLED STRAND THICKNESS AS BIOMATERIALS

J. D. Ferry

Fibrous networks with controlled coarseness of structure can be formed from solutions of cellulose nitrate, fibrin, and probably collagen by regulating the degree of lateral aggregation of the macromolecules during phase separation (cellulose nitrate) or polymerization (fibrin, collagen). For biomedical applications, the mechanical characteristics and permeability of water-equilibrated network structures must depend critically on strand thickness. Possible methods for regulating coarseness in networks formed from synthetic polymers are discussed.

SOME COMMENTS ON THE MECHANICAL PROPERTIES OF FIBROUS PROTEIN STRUCTURES

J. D. Ferry

Collagen fibers, with triple helices at the molecular level, have very high modulus and low extensibility; the properties of softer, more extensible connective tissues cannot be explained in terms of collagen fibers alone. Fibrin clots and films, whose molecules involve some single helical structure within a complicated external geometry, have properties which superficially appear rubbery but cannot be explained in terms of rubberlike elasticity. Both collagen and fibrin undergo helix-coil transitions under non-biological conditions (elevated temperature, certain reagents) and develop elasticity which is primarily rubber-like, but this phenomenon is not applicable to natural structures or reprocessed biomaterials. The mechanical behavior of fibrin under biological conditions may be related to a helix-coil transition induced by tensile stress, treated theoretically for the first time by Reiss.

CONTROL OF MECHANICAL PROPERTIES OF
SWOLLEN HYDROPHILIC NETWORK POLYMERS;
LAYER AND GRADIENT STRUCTURES

J. D. Ferry

The equilibrium swelling, in excess aqueous solvent, of a cross-linked hydrophilic gel depends on the moles of network strands per cc. (v), the volume fraction of polymer at the time of cross-linking (v_0), and the thermodynamic interaction coefficient of the polymer with the swelling solvent (χ_1). The shear modulus of the swollen gel depends on the volume fraction of polymer at equilibrium (v_r) and v and v_0 . For applications as biomaterials, it is important that there be no volume change when such a gel is placed in contact with excess solvent, i.e., $v_0 = v_r = v_0^c$. Numerical evaluations from a theory of Flory have been made to examine the conditions for this requirement. It is particularly important in designing layered or gradient structures in which the modulus changes either discontinuously or continuously. Possible methods for preparing gradient structures are discussed.

QUESTIONS CONCERNING THE CURRENT STATE
OF BIOMEDICAL MATERIALS

M. B. Bever

Technical memoranda - no abstract available.

BULK STIFFNESS OF METALS

J. J. Gilman

A simple application of the Uncertainty Theorem is used to calculate the bulk moduli of the alkali metals and some transition metals. The results approximate the measured values and the observed dependences on atomic size and d-electron concentration. The simplicity of the method is attractive for pedagogical purposes.

COMMENT ON SPINODAL DECOMPOSITION

W. A. Tiller

G. M. Pound

J. P. Hirth

Cahn and Hilliard have developed a theory for the thermodynamics of inhomogeneous media, similar to that of Landau, and have applied the theory to spinodal decomposition. The present authors have suggested a modification of the theory to include odd order terms in a Taylor's series expansion of the free energy in terms of gradients of various potentials. Cahn and Hilliard more recently responded to the modified theory by extensively discussing anomalies that arise from three sample diffusion equations that contain an inadvertently introduced form of the chemical potential, and then, by implication, dismiss the modified treatment altogether. The present paper clarifies differences in viewpoint in the two approaches and corrects the anomalies. Criticisms by Cahn and Hilliard are shown to be inapplicable to our earlier work because we use imbedded, Eulerian coordinates while they use Lagrangian ones.

