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REPORT OF THE MATERIALS RESEARCH COUNCIL (1975)

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September 1975

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Report of the Materials Research Council (1975)



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REPORT

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THE MATERIALS RESEARCH COUNCIL

September 1975

ARPA Order Number: 2341/2 Program Code Number: 1D10 Contractor: The Regents of The University of Michigan Effective Date of Contract: 30 April 1975 Contract Expiration Date: 30 June 1976 Amount of Contract: \$265,000 Contract Number: DAHC15-71-C-0253 Principal Investigator: Associate Dean M. J. Sinnott College of Engineering The University of Michigan Ann Arbor, Michigan 48104 (313) 763-0242

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### INTRODUCTION

This report is a summary of the activities of the Materials Research Council for the period 30 April 1975 through September 1, 1975. A more detailed presentation of the technical papers and memoranda generated by the Council is in preparation and will be issued later in the contract year.

The Materials Research Council was organized by the Materials Research Office of the Defense Advanced Research Projects Agency for the purpose of assembling a group of the country's foremost materials science and materials engineers to examine and suggest solutions for anticipated Department of Defense materials problems. It is not primarily concerned with current problems, although it has and will continue to work on these where it can be of assistance. Its primary function is to look beyond current systems and to predict those problem areas that will occur in future systems and to suggest methods whereby the necessary science base and feasibility studies can be in place to support the engineering developments that will follow.

Membership on the Council is drawn from the most able and highly qualified individuals of the Country. It consists of Chemists, Physicists and Engineers from various disciplines whose unifying linkage is their knowledge and expertise in some facet of materials science or engineering. The 1975 meeting

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of the Council was the eighth annual meeting of the group and over these years the group has coalesced into one of the most coherent, versatile and knowledgeable materials science and engineering groups operating as a team anywhere.

One of the significant advantages that occurs to the Defense Department is the early transfer of advanced problem areas to active research programs. The bulk of the Council membership is drawn from the academic community and their early exposure to new problem areas results in new direction of research for them and their graduate students. Support for these subsequent studies comes from a wide variety of sources in addition to the Department of Defense; Government agencies such as NSF, DOT, ERDA; University funding sources from gifts and grants; industrial sources from corporations such as EPRI, AISI, or direct industrial funding. Typical programs initiated by Council members as a result of summer study analysis of problem areas are in surface physics, fracture analysis, amorphous materials, stress-corrosion, optical materials, structural ceramics and many others.

While the Council has considerable expertise in many areas it has been found necessary and very desireable to add to the Council, on a temporary basis, consultants from universities, industries, not-for-profit institutes and members of various agencies of the government to add to the capabilities of the Council. Visitors who have an interest in and special

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capabilities in the areas under consideration by the Council are encouraged to attend and take part in the various briefings and discussions that make up part of the Summer Conference of the Council.

### PROJECT ORGANIZATION

The technical direction of the ARPA Materials Research Council is delegated to a seven-man Steering Committee chosen to represent the various disciplines of the membership on 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 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 Willis H. Flygare Secretary of the Steering Committee Department of Chemistry University of Illinois Urbana, Illinois 61801

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

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

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

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

Dr. Robb M. Thomson National Bureau of Standards Institute for Materials Research Washington, D.C. 20234

To carry out the work of the Council, a contract has been arranged between ARPA and The University of Michigan. The Project Director is Maurice J. Sinnott, Associate Dean, College of 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 June 30, 1976.

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The members of the Council in addition to the members

of the Steering Committee are as follows:

Professor Arthur Bienenstock Materials Science Department Stanford University Stanford, California 94305

Professor Robert Coble Materials Science Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139

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

Dr. Anthony G. Evans Rockwell International Science Center Thousand Oaks, California 91360

Professor Henry Ehrenreich Pierce Hall Harvard University Cambridge, Massachusetts 02138

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

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Professor M. Fred Hawthorne Department of Chemistry University of California Los Angeles, California 90024

Professor Robert A. Huggins Center for Materials Research Stanford University Stanford, California 94305

Professor Gordon S. Kino Department of Electrical Engineering Stanford University Stanford, California 94305 Professor Walter Kohn Department of Physics University of California La Jolla, California 92037

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 Elliott W. Montroll Department of Physics & Astronomy University of Rochester Rochester, New York 14534

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

Professor James Rice Division of Engineering Brown University Providence, Rhode Island 02912

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

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

Professor Ammon Yariv Llectrical Engineering Dept. California Institute of Technology Pasadena, California 91109

### METHOD OF OPERATION

The major technical activity of the Council takes place each year during a one month summer study meeting. The summer meetings are organized so that small groups of two to six within the Council can meet and discuss problems in detail. In addition, somewhat larger group meetings are sometimes organized for briefing purposes. Such meetings are usually more structured, and typically involve three to ten Council members, up to fifty invited consultants, DoD and other agency personnel. After these sessions, the Council members normally continue consideration of various problems raised and publish a meeting summary, and in some cases technical papers dealing very specifically with some of the points raised in the briefing sessions. Often the interest generated is sufficient to warrant follow-up visits by various Council members to DoD installations, and the organization and participation in short meetings covering extensions of the problem In many cases, the Council members maintain an active area. participation in an experimental or testing program which follows the original consideration by several years.

The key to the success of the Summer Conference lies in choosing appropriate Council members and consultants and in finding ways to couple their abilities and ideas to DoD needs. There are many people qualified for Council membership but budgetary considerations limits the numbers to 20-25. To obtain greater flexibility in membership a recent policy was instituted whereby some of the Council members are asked to go on a

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temporary inactive status and new members are added to the roster. Some members, because of prior commitments, also elect to be placed on the inactive list. The current inactive list of MRC members is as follows:

Professor Michael B. Bever Dept. of Metallurgy & Materials Science Massachusetts Inst. of Tech. Cambridge, Massachusetts 02139

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

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

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

Professor Alan J. Heeger Department of Physics University of Pennsylvania Philadelphia, Pennsylvania 19174

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

Professor Erastus H. Lee Dept. of Applied Mechanics Stanford University Stanford, California 94305 Professor Donald J. Lyman Materials Science & Engineering University of Utah Salt Lake City, Utah 84112

Professor Bernd Matthias Department of Physics University of California La Jolla, California 92037

Professor William Prager Dept. of Engineering Mechanics Brown University Providence, Rhode Island 02912

Professor Charles P. Slichter Department of Physics University of Illinois Urbana, Illinois 61001

Professor J. Robert Schrieffer Department of Physics University of Pennsylvania Philadelphia, Pennsylvania 19174

Professor Albert J. Sievers Department of Physics Cornell University Ithaca, New York 14850

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

### PROBLEM SELECTION - BACKGROUND

Various techniques for preparing for and conducting the Materials Summer Conference have evolved in the eight years of its operation. The original concept of devoting the efforts of the entire Council to a few selected topics has proved to be fruitful but somwhat difficult to implement in a satisfactory fashion. Initially the ARPA Materials Science Office and the Steering Committee - ranged for briefings with the Services and various DoD agencies to uncover problem areas that were suitable for the Council consideration. Several topics such as Shock Propagation, Constitutive Relations at High Temperatures and Pressures, Composite Materials and Underground Sensing were chosen and were the subject of continuing analysis over several Summer Conferences. Many reports, memoranda and research programs evolved from the consideration of the problem areas.

The Council felt that better preparation for the Summer Conference could be attained if individuals or groups of the Council and/or the Steering Committee would conduct small preparatory meetings, contact the appropriate consultants and visitors, and identify, secure and screen the relevant literature in the chosen problem areas prior to the conference. Several topics of the Summer Conference such as Amorphous Semiconductors, Infrared Optics, Materials in Energy Systems and Structural Ceramics were organized in such a fashion and proved to be a more efficient way to prepare for the Summer Conference.

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There is a certain amount of carry-over from one conference to the next and this resulted in a proliferation of meetings at the Summer Conference which the Council, while it found them all interesting, felt was somewhat counter productive to their efforts. This has prompted the Steering Committee to limit the major topics to be considered at the Summer Conference but still permitting smaller groups to organize and study whatever areas they consider important.

Over the years an impressive list of problem areas have been examined in depth. A partial listing follows:

> Composite Materials Shock Propagation Underground Sensing Biomaterials Fracture Laser Optics Stress-Corrosion Superconducting Materials Design with Brittle Materials Amorphous Semiconductors Disordered Carbon Systems Solid Electrolytes Materials Limitations in Advanced Energy Systems Scientific Barriers in Battery Systems High Velocity and Low Velocity Erosion

The results of the Council's efforts appear first in this Preliminary Report which summarizes in abbreviated form the results of the Summer Conference. A Final Report is issued later in the contract year and contains all the written output of the Council. In general, this consists of two categories. One is papers in their final state and ready for publication. The second category are preliminary reports and memoranda for limited distribution since it represents work in progress. Those papers in the first category are available for distribution and in most cases are in the process of publication in appropriate technical journals. The second category are more restricted in circulation since they represent initial unrefined ideas, position papers, and status reports generated premarily to stimulate discussion within the Council or with its Consultants and as such they may not represent a unanimous or even a consensus opinion of the Council. These are available on request to the Project Director, subject to the author's release.

### SUMMER CONFERENCE - 1975

The 1975 meeting was held at the Scripps Elementary School in La Jolla, California, during the period June 30 through July 25. In preparation for the meeting, the Steering Committee met in Washington in November 1974 to discuss proposed subject areas for study. As described previously, these suggested areas are proposed by the Materials Science Office, by members of the Steering Committee or by members of the Council. This represents a very large spectrum, some entirely new areas, some that are an outgrowth of previous studies and some that are a re-examination of a topic considered previously. As is usual at this meeting, the difficulty is to narrow the selection of topics to those that can be optimally handled by the Council. It was the consensus of the Steering Committee that there should be four areas examined at the 1975 Conference. They were:

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- 1. Powder Metallurgy and Forming
- 2. One- and Two-Dimensional Conduction
- 3. Optical Electronics
- 4. Wear

Reiss agreed to structure the wear study, Hucke the powder metallurgy study, Flygare the 1- and 2-D conductors, while Bloembergen would structure the optical electronics.

Other possible topics were discussed but no assignments were made to structure these for the 1975 meeting. Many of the members are actively working on programs, papers and concepts developed at prior meetings and it was felt that the number of new topics should be held to a minimum at the 1975 meeting. Possible new members of the Council were discussed including suggestions from ARPA-MATS that experts be added in electronic materials and devices. The Steering Committee agreed to the formation of a sub-committee to review Council membership and to move members to an inactive status in order to accommodate new members. This committee consists of the Chairman of the Steering Committee, the Director of ARPA-MATS and the Project Director.

Normally, a spring meeting of the Steering Committee is held in Washington to finalize the summer program. This proved to be unnecessary this year since the preliminary planning on the above subject areas had proceeded extremely well. Consultants and visitors were contacted, bibliographies and papers were

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circulated and materials ordered for the conference library. Two additional study areas were suggested by ARPA-MATS. One on the Materials-Design Interface and the second on Chemical Feedstocks. By telephone it was agreed by the Steering Committee that small studies would be held on these topics. Hawthorne agreed to set up the structure of the Feedstock program, while Thomson agreed to convene a small group for the Materials-Design study.

The agenda of the meetings held in La Jolla were as follows:

#### AGENDA

### ARPA-MRC Meeting on

Forming of Advanced Materials from Powders

Objectives of Meeting:

1. To assess the state of the art in forming shapes from powders of advanced materials.

2. To discuss and outline limiting factors in powder production, shape processing, and resulting properties.

3. To assess the potential or powder forming for the next generation of materials.

There will be a minimum of formal structure at the meeting. Each participant should come prepared to present a 30-60 minute discussion of the current state of the field as he sees it.

### LIST OF PARTICIPANTS

Nicholas J. Grant

Director, Center of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139

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Pol E. Duwez	Professor, W. M. Keck Laboratory California Institute of Technology Pasadena, California 91109
Attwell M. Adair	Group Leader, Metals Processing Air Force Materials Laboratory AFML/LLM Wright Patterson Air Force Base Ohio 45433
Harry A. Lipsitt	Air Force Materials Laboratory AFML/LLM Wright Patterson Air Force Base Ohio 45433
Oleg D. Sherby	Professor, Materials Science and Engineering Stanford University Stanford, California 94305
Thomas E. Miles	Director of Marketing Kelsey Hayes Company 7250 Whitmore Lake Road Brighton, Michigan 48116
Arthur R. Cox	Senior Project Metallurgist Pratt & Whitney Aircraft West Palm Beach, Florida
Robert E. Allen	Manager, Alloy Development General Electric Company Evendale, Ohio 45231
Martin J. Blackburn	Supervisor Wrought Alloys Group Pratt & Whitney Aircraft East Hartford, Connecticut 06037
Betzalel Avitzur	Professor, Lehigh University Whitaker Laboratory Bethleham, Pennsylvania 18015
Joe Moore	Chief, Materials Laboratories Pratt & Whitney Aircraft West Palm Beach, Florida

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### Workshop on

### Design-Materials Interface

Upon convening the MRC at La Jolla, we have sharpened the agenda for the workshop. Of course, the design-materials interface is very broad. What we hope to cover is that portion of it which encompasses structural analysis and design in relation to mechanical property characterization of fracture, creep, etc. Our purpose is to explore two related areas:

- I. Institutional Aspects of the Design-Materials Interface.
  - What is the experience in the local situation of each of the participants?
  - What concensus is there in the handling of the interface in major industry? What are the differences?
  - What generic problems remain?
  - What are the important differences between major and small or medium industry? What is the form of spin-off from major industry?
  - What is the role of a materials handbook for designers?
- II. Technical Issues
  - Technical issues which transcend a particular design application. What are the major shortfalls in materials knowledge and presentation?
  - What new technical possibilities exist for making a more efficient match between the design and materials communities, e.g., computer simulation, etc.?
  - What are the practical limits of materials reliability specification? In particular, what developments in materials characterization and structural analysis are needed
    - a. to better implement existing knowledge (e.g., economical computer codes for 3-D K or J)
    - b. to provide new basic (but immediately implementable) knowledge (e.g., theoretical framework for stable crack growth)?

An agenda for the two days follows. Admittedly, we

will not cover every aspect of the issue we have posed. If we can highlight the metals and ceramics mechanical design areas, perhaps the rest can follow at another time. We have not asked all participants to speak formally, but trust that each of you will be prepared at the proper time to make your case informally. On Monday morning, we hope to get the main topics on the table. We will dispose of the institutional situation first, hopefully by early afternoon of Monday, and then turn our attention to Item II. During the second afternoon, we will pull together the concensus and main discussion points of the two days.

### AGENDA

### MRC Design/Materials Workshop

### July 7 8:30-11:30 AM

Ε.	van Reuth		Introduction
W.	Dukes	_	The Design Side
Α.	Hurlich		The Materials Engineering Side
R.	Johnson	-	NASA Experience

July 7 12:30-2:30 PM

Institutional Issues

2:30-3:30 PM

Outline of Technical Issues

July 8 8:30-11:30 AM

Technical Issues

2:00-3:30 PM

Wrap-up

### PARTICIPANTS

Dr. Sumio Yukawa, General Electric Company
Dr. R. Reed, NBS, Boulder
Dr. L. McHenry, NBS, Boulder
Dr. E. T. Wessel, Westinghouse
Dr. W. J. Levedahl, NSRDC-Annapolis
Mr. W. Dukes, Bell Aerospace
Dr. R. DeWit, NBS, Washington
Dr. R. E. Johnson, Johnson Space Flight Center
Mr. A. Hurlich, General Dynamics Convair
Dr. S. Wiederhorn, NBS, Washington

## Conference on

# One- and Two-Dimensional Conductors

Chairman, W. H. Flygare

Thursday, July 10, 1975

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	8:00 AM	G. Stucky, University of Illinois "Some Structural Aspects of One-Dimensional Conductors"
	9:00 AM	A. Heeger, University of Pennsylvania "TTF-TCNQ and Related One-Dimensional Metals: A Status Report"
	10:30 AM	F. DiSalvo, Bell Laboratories, Murray Hill "Electronic Instabilities in Layered Compounds"
	1:00 PM	R. Greene, IBM, San Jose "Polymeric Conductors"
	2:00 PM	T. Garito, University of Pennsylvania "Studies of the Metallic Polymer (SN) <sub>X</sub> "
Friday,	July 11, 19	75
	8:00 AM	A. Bloch, Johns Hopkins University "The Design and Study of New Organic Conductors"
	9:00 AM	B. Scott, IBM, Yorktown "Organic Electronic Materials"
	10:30 AM	L. Roth, Hughes "Polymeric and Organic Conductor Applications"
	1:00 PM	Additional questions, comments, and discussion
Additio	onal Attendee	es: P. Anderson, Bell Labs., Murray Hill C. Elbaum, Brown University W. McMillan, University of Illinois

### WEAR WORKSHOP

DATES: July 15, 16 and 17

FORMAT: Brief talks on various aspects on July 15 followed by discussion and preparation of a position paper during the following two days.

July 15 -- AM

Professor A. H. Shabaik, UCLA "Fundamentals of Wear"

Professor E. Rabinowicz, MIT "Quantitative Aspects of Adhesive Wear"

Professor N. P. Suh, MIT "Myths and Facts Concerning the Wear Mechanisms"

Dr. B. Wescott, Transonics, Inc. "Regimes of Wear"

July 15 -- PM

Professor F. Ling, RPI "Service Mechanisms and Wear"

Dr. J. W. Butler, USNR "Ion Implantation in Wear"

Professor I. Finnie, University of California, Berkeley "Erosion by Solid Particle Impact"

## OPTICAL ELECTRCNICS PROGRAM

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Thursday,	July 17	ů.
8:	:30 AM	Opening Remarks, N. Bloembergen
8 :	:40 AM	ARPA Interest in Optical Electronics, C. M. Stickley
8	:45 AM	"State of the Art of Optical Electronics" A. Javan
10	0:45 AM	"Fundamental Limits to the Sensitivity of High-Frequency Josephson Effect Receivers" P. L. Richards
L	1:30 AM	"Josephson Effect Memories" N. Welker
1	:00 PM	"Frequency Measurements with Tunnel Diodes at the National Bureau of Standards" K. Evenson
2	:00 PM	"IR Detection and Mixing with Heavily Doped Barriers" A. Van der Ziel
2	:45 PM	General Discussion
Friday, J	uly 18	
8	:30 AM	"Quantum Theory of Mixing" T. Tucker
8	:55 AM	"Schottky Barrier Mixing Experiments" A. Silver
9	20 AM	"Tunnel Diodes and Guided Light Waves" S. Wang
1	.0:30 AM	"Nonlinear Characteristics of Tunnel Diodes" K. Gustafson
1	.1:15 AM	"Experimental Configurations of Point Contact Diodes" S. E. Schwartz
1	L:00 PM	General Round Table Discussion "Are Optical Diodes Ripe for Technological Development and Exploitation?"

## Alternate Feedstock Assessment

### AGENDA

Monday, July 14th

9:00	AM	Fred	Steffgan	-	Bureau	of	Mines
		"Coal	Liquefac	ct:	ion"		

10:30 AM Donald Severson - University of North Dakota "Engineering Aspects of Lignite Liquefaction; Lignite Potential as Long Term Fuel Source"

1:15 PM	Irving Goldstein - North Carolina State U	Jniv.
	"Wood as a Renewable Feedstock"	

Tuesday, July 15th

9:00 AM	Bernard Blaustein - Bureau of Mines "Fischer-Tropsch; Chemicals from Coal"
10:30 AM	George Parshall - Dupont Central Research "Novel Chemical Processes; Future Applications"
1:15 PM	Al Schreshiem - Exxon Corporation Research Lab. "Coal as a Petroleum Substitute; Impact on O. Companies"

Wednesday, July 16th

9:00 AM	Heinz Heineman - Mobil Research Corporation "Petrochemicals from Alternate Feedstocks"
10:30 AM	Kenneth Klabunde - University of North Dakota "Catalytic Hydrogenation of Solvent Refined Lignite"
1:15 PM	Henry Grotta - Battelle Memorial Institute "Strategic Importance of Petrochemicals; Alternate Feedstocks"

## VERY HIGH TEMPERATURE MACHINES

Friday, July 25, 1975

8:30 AM P. B. Mohr, Lawrence Livermore Laboratories

High Temperature Topping Cycles using the Lysholm Helical Expander made from Ceramics and Graphite.

9:30 AM Mssrs. Sermka and Stahl, Aeronutronic-Ford

Experience with Very High Temperature Graphite Turbines in Reducing Atmospheres. Turbines for Rocket Valve Actuators.

10:30 AM A. Cohn, EPRI

Materials Problems in a Large Stoichiometric Flame Gas Turbine.

Discussion

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### SUMMARY AND CONCLUSIONS OF WORKSHOPS

As a result of the workshop presentations and the subsequent discussions, several papers and memoranda were generated at the conference and will be listed by title in the next section of the report. This section gives in summary form the highlights and conclusions reached at each session as reported by the Council member or members who had the primary responsibility for its organization and the presentations that were made.

### MATERIALS-DESIGN INTERFACE

R. M. Thomson and M. Cohen

(1) The central conclusion of the workshop is that no major institutional "canyon" exists between the design and materials communities; by and large these two communities have learned to develop a variety of institutional responses which fit the particular circumstances.

(2) Quantitative materials predictability is at the heart of a successful materials interaction at the materials/ design interface in high-technology situations. This principle was most clearly established in recent years through the medium of fracture mechanics, but major challenges remain on other fronts to improve the ability of the materials engineer to perform his function. To this end, materials research is needed toward the applicability of the J-integral for quantifying fracture toughness in service-simulated atmospheres, and under time varying stress. Deeper understanding of the interrelationship

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between J-values and microstructural parameters is urgently needed in this whole context. A special problem exists in bringing the predictability of polymers up to the level of metals as far as the materials/design interface is concerned.

(3) NDE, and especially its link to interpretation in terms of materials reliability, merits special emphasis.

(4) The techniques developed in the high-technology industries to cope with materials-critical applications are:
(a) materials sign-off, on design, (b) design-review board participation, (c) preparation of special documents such as materials-design monographs and handbooks, and (d) on-the-job education for both materials and design engineers.

(5) There was somewhat mixed opinions regarding the desireability of new efforts at education and technologytransfer mechanisms for low-technology industries. Desirable activities which might be explored include: (a) traveling "short lecture courses" on the materials aspects of design, perhaps sponsored by technical societies like ASM; (b) selected efforts such as the Stress-Corrosion Handbook being sponsored by ARPA; and (c) articles and case studies in the professional journals relevant to the materials/design interface.

### SUMMARY OF THE MEETING

ON FORMING SHAPES OF ADVANCED MATERIALS FROM POWDERS

### E. E. Hucke

Representatives of the MRC and others from university and industry groups with research and development interest in advanced powder techniques met to discuss the state of the art, identify limiting factors, and assess the future potential of powder forming.

In his introductory remarks Professor Grant set the tone of a recurring theme; namely, that powder metallurgy with very rapidly cooled starting material offers new and exciting potential for alloy development. The more complicated of the modern alloy systems involve many purposeful alloy additions and therefore during solidification inherently produce both macroscopic and microscopic segregations. Since many of these materials can never be plastically deformed significantly, the segregations persist through heat treatment. The mean dendrite arm spacing (DAS) which characterizes the microsegregation, can be taken as a fundamental variable setting the size scale of the structure. The DAS characteristic of ingot processes  $(\geq 10^2 \mu)$  lies at one extreme while at the other is the amorphous state found in splat cooling. Between these lies a very futile area for exploitation where the DAS  $\nu l\mu$  to .01µ. This requires more rapid cooling rates and/or smaller

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particles than currently encountered in the powder industry. Among the possible new effects are 1) existence of different minor phases, i.e., carbides and sulfides, 2) elimination of some usual phases, 3) retention of more uniform solid solutions, 4) very fine grain sizes, 5) the extension of the range of alloying elements previously prevented due to processing difficulties. As an example, 18-18 stainless with 1% S made from powder cooled at  $\sim 10^{2} \circ C/sec$ . formed a very fine  $Cr_2S_3$  phase but was cold workable, where a similar cast alloy would be very brittle. A process involving high speed inert gas atomization through a special nozzle being excited by ultrasonic vibrations was disclosed. The process was reported to have high yield of 3-5µ powder with a present capacity of about 300 KG/hr.

Attwell Adair outlined the Air Force programs now underway toward cost reduction in various air frame and engine parts. The primary problem is one of decreasing the conversion ratio (wt. of primary material to wt. of finished part). Production of various parts from superalloys and Ti alloys has progressed so that shapes are possible that exceed the current capability for ultrasonic inspection. Large scale application of powder formed Ti parts is technically possible but awaits the availability of cheaper powder of the quality now available at v30/#. Programs with Battelle utilizing their spinning process for making fine fibers and powders were described.

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H. Lipsitt described Air Force efforts to meet 1980 high temperature property targets. The approach is through powder forming of  $Ti_3Al$  and TiAl compounds. With various combinations of extrusion and isothermal forging many of the program goals are at hand. Current problems lie in gaining any more than about 2% elongation at room temperature. It was, however, pointed out that some of the best Ni base alloys are now no better than 4-6% elongation.

O. Sherby discussed some interesting preliminary research on superplastic hot pressing of Fe-C alloys ( $\sim 2.6$ %C). Particles of 25µ containing a structure of about 2µ were made superplastic and could easily be fully densified at temperatures far lower than usual sintering temperatures. Controlled heat treatment including malleablization could yield some unique new Fe-C alloys.

Tom Miles described current powder surface characteristics, powder handling and superplastic hot isostatic pressing (HIP) of powder to shapes. Significant advantages were realized from continuous vacuum outgassing, assisted by an electric field. Ordinary powders were rendered superplastic by rolling the powder particles 20-40% and subsequently heat treating for a very fine structure within each particle. The need for careful control of TiC and other reactions at the particle boundaries was emphasized.

A. Cox discussed the status of powder formed parts at Pratt-Whitney, Florida. Nine different parts are in the F-100

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engine and have successful service records of many thousands of hours. They have met and solved the gas contamination problem associated with current powders. This problem is less severe in the Pratt-Whitney approach than in HIP since they extrude with large reduction ratios in order to consolidate and to obtain the necessary fine structure for superplastic hot isothermal forming. This process (gatorizing) using inert atmosphere and TZM dies, gives good definition and tolerance for many complicated shapes, including discs with integral blades, blades with holes, and metal ceramic combinations.

After gatorizing, gradient annealing produced [110] oriented grains comparable in size to those directionally solidified. This material showed creep properties superior to the same alloy directionally solidified. The shapes possible have in general far exceeded those allowed by NDE, however, experimental programs are underway to establish an allowable inspection technique to be used at the extruded billet stage. Cox emphasized the need for a new alloy approach to meet 1985 goals of

> 200°F increased blade temperature 100°F increased disc temperature 100°F increased vane temperature

50% increase in low cycle fatigue life

100% increase in corrosion resistance Rather dramatic immediate savings can result from improvement in fatigue strength.

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R. E. Allen emphasized the need to use powder forming for reduction in cost. At present alloys cost  $\$ ?7-8/# as a rough forging but have a conversion ratio of about 8:1. The removing of this relatively large amount of material costs about \$1-2/#. Limitation on shape in the very highly stressed parts, i.e., discs are now established by NDE and stock requirements for set up in machining. A major area for application that should be pushed is the lower stressed static parts of the engine. Allen felt that powder formed materials would not provide the best answer for the very high temperature regime. The powder formed materials are known to have lower ultrasonic background noise levels. The precise reasons for this behavior are not completely explained.

B. Avitzur discussed powder consolidation and forming under conditions of combined shear and hydrostatic pressure. Optimum combined stress conditions for obtaining sound material exist for a given material. Such conditions can successfully handle many difficult to deform materials including W at room temperature. Methods of obtaining favorable conditions in a completely continuous process called "Extrolling" were described.

M. Blackburn reviewed past alloy development in the superalloy field with reference to the possibilities for powder forming. He cited the need to develop techniques for the more modest priced alloys. From microscopic and mechanical property studies he showed how the A gas problem and the surface carbon reaction problem could be minimized in HIP processed materials.

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An extended group discussion failed to identify any major scientific blind spots limiting engineering development in this field. Possible exceptions to this conclusion are 1) need for a "new" NDE method to allow the full realization of the shaping potential of current processes, and 2) the need for a better understanding of the nature of absorbed and reacted films on fine metallic powders.

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In all other ways the engineering progress seems to be limited only by economic factors such as powder and processing costs. It was a general conclusion that the area of greatest future potential would come from new alloy development through utilization of known ranges of alloy content previously prohibited by processing requirements.

### ONE- AND TWO-DIMENSIONAL CONDUCTORS

W. H. Flygare G. D. Stucky H. Ehrenreich

### Conclusions

1. Since it was last reviewed at an MRC meeting in 1973, the field of organic charge transfer and other onedimensional conductors has made large strides. Materials preparation, the variety of experiments, and the basic physical understanding all have progressed substantially and we now have a fairly good picture of the underlying physics in one-dimensional systems.

2. It now seems unlikely that a high temperature (T>25K) quasi-one-dimensional conducting material will be developed. However, exploration of this frontier of materials science may well lead to new solids with novel and presently unsuspected properties.

3. The practical applications of organic metals at present exploit only the vary large conductivity anisotropies (e.g., infrared polarizers made from  $(SN)_x$ ). The fact that broader technological uses are not yet evident should not be viewed negatively at a time when an entire new class of materials is in the beginning stages of development.

### Recommendations

1. One-dimensional systems

a. The measurement of the complete frequency de-

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pendence (DC-100GHz) of  $\sigma$  in TTF-TCNQ at various temperatures needs further attention in order to help decide among competing theoretical models.

b. Standard synthetic, purification, and characterization techniques should be established in order to achieve agreement on measurements in different laboratories. Exchange of samples among laboratories should be further encouraged.

c. In developing new one-dimensional systems, attention should now be given to the technolgical application and the relationship between structural and mechanical properties.

2. One- and two-dimensional systems

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a. Materials should be prepared, permitting an examination of trends as we proceed from one- to two- to three-dimensional properties and the instabilities in intermediate regimes.

b. Attention should be given to synthesis of organic charge transfer systems with transversely coupled stacks. The conductivity in such systems would be less anisotropic and more nearly three-dimensional. Should such materials be discovered, the incentives for their development as opposed to the use of standard metals should be considered carefully.

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3. The marriage of organic (and inorganic) synthesis and purification techniques with solid state physical methods has led to the development of new materials of high purity and properties. This approach should be exploited further. Specifically:

a. The study of organic photoconductors should be pursued. Although this topic was only mentioned briefly at this meeting, the technological applications are and undoubtedly will remain useful.

b. Of the current one-dimensional anisotropic conductors,  $(SN)_x$  has the most desirable features including epitaxial growth. However, the  $(SN)_x$  polymer spontaneously decompose over a period of weeks in air. Research on new isomorphic variation on the  $(SN)_x$  system should be pursued including (SeN),  $(H-C^*)$ , and others.

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## SUMMARY OF THE MEETING ON OPTICAL ELECTRONICS

#### N. Bloembergen

A two-day meeting was held on the current state-of-the art and the potential of infrared barrier diodes. The nonlinear properties, response time and detection sensitivity of submillimeter and infrared Schottkey-barrier, point-contact and metaloxide-metal devices were reviewed and compared with theoretical predictions. The results are summarized in a number of conclusions and the following recommendation for further research and development: Current activities should receive continued support. Additional support should be provided to encourage groups with broader expertise in engineering and materials science aspects to participate. Micro-engineering of barriers and optimization of devices toward specific applications should be emphasized.

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#### SUMMARY OF THE WEAR WORKSHOP

A. Bienenstock, B. Budiansky, D. C. Drucker, J. P. Hirth, H. Reiss and J. R. Rice

A workshop on wear was held at La Jolla on July 15, 16 and 17, 1975. Presentations on various basic aspects of the wear phenomenon were presented by eight outside experts, whose own summaries and comments will appear in the final report. The topics discussed ranged widely over descriptive characterizations of the wear process, expositions of old and new wear theories and hypotheses, experimental techniques and results concerned with observations of wear particles, effects of surface ionization, and detailed analyses of erosive wear. However, the MRC participants were rapidly drawn to a focus on some new ideas advanced by N. P. Suh in his so-called "delamination theory" of wear and its challenge to more conventional concepts. The currently widely accepted theory of wear, commonly (if imprecisely) referred to as the "adhesive" theory, contemplates asperities on opposing, sliding surfaces, that meet, adhere, and occasionally break off as chunky particles. In contrast, Suh's proposed mechanism of wear, supported by macroscopic observation, suggests the flaking-off of thin, platelike particles as the primary source of material loss during the process of wear. Considerable controversy surrounds Suh's work, particularly concerning some of its proposed theoretical underpinnings and elaborations. Nevertheless, the challenge Suh's "theory" presents to the established wisdom is

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a powerful one that must be taken seriously. Well-considered research, both experimental and theoretical, is needed to explore the many questions it provokes, establish its possible domains of validity, render it more precise and quantitative, and study its implications with respect to improved control and reduction of wear. The following papers were presented at the workshop by the visiting consultants:

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Fundamentals of Wear A. H. Shabaik

Comparison Between the Adhesive and Fatigue Explanations of Adhesive Wear E. Rabinowicz

On the Delamination Theory of Wear N. P. Suh

Comments on the Bowden and Tabor Asperity Theory of Wear V. Wescott

Surface Mechanics and Wear F. F. Ling

Ion Implantation and Wear J. W. Butler

Erosion by Solid Particles I. Finnie

The Issues of Wear, Particle Size and Structure W. Ruff On a carry-over topic from prior work of the Council dealing with energy problems within DoD, the question was raised by some Council members on the availability of alternate chemical feedstocks for defense needs should petroleum and natural gas supplies become critical. A comprehensive study was directed by Professors Hawthorne and Pittman involving petroleum companies, ERDA, other related agencies, chemical companies and university consultants.

#### MEETING SUMMARY

FUTURE SOURCES OF CHEMICAL FEEDSTOCKS: AN ASSESSMENT

## M. F. Hawthorne

A group of nine consultants met with members of the MRC on July 14 through July 16 to examine future chemical and fuel feedstock problems which face the United States. Organic feedstocks as sources of lubricants, fuel, chemicals and plastics other than oil and natural gas which were considered included coal, lignite and cellulosic materials such as wood. The results of these discussions appear in a report entitled "Future Sources of Chemical Feedstocks and the Probable Impact Upon Military Preparedness." The feedstock of immediate interest is coal and lignite since the conversion of these materials to syngas and synoil was practiced by the Germans in World War II and by the South Africans since 1956. It was recommended that the construction of about five large synthetic oil plants be commenced at once and that the annual rate of

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plant construction be sustained at five plants per year far into the foreseeable future (year 2000).

Wood, which is a constantly renewable resource, appears to be the feedstock of choice following coal and lignite. The conversion of cellulosic materials to synoil is possible with today's technology.

The use of coal and lignite for organic feedstocks was discussed in terms of logistics and the capital investment of plant construction materials and capital. The overview of this requirement was discouraging, but not hopeless. The role which could be played by the DoD in achieving complete independence from foreign feedstock sources was summarized and, in essence, consists of monitoring critical organic materials and, where necessary, encouraging the production of materials critical to transport and weapons for evolving systems.

On July 15-17 an ARPA/AFML "Review of Quantitative Non-Destructive Evaluation" was held at the Science Center of Rockwell International and was attended by several Council members. The NDE problem has surfaced several times at past meetings of the Council and is a critical problem area in many materials based systems such as composites, ceramics, electronic materials, optical materials and laser materials. For that reason the report of that meeting of the Council is presented here.

# THE ARPA/AFML PROGRAM ON NONDESTRUCTIVE EVALUATION

M. Cohen and R. M. Thomson

The current ARPA/AFML Program on NDE is focussed mainly on ultrasonic techniques intended to detect and quantify failure related flaws in structural materials, and is backed up by basic studies of ultrasonic wave scattering in solids as well as by the computer processing of information contained in the resulting signals. Also being developed are nondestructive methods for determining the strength and quality of adhesive bonds, and for measuring residual stresses which may play a role in fracture initiation.

Notable progress is being made (a) in the fundamentals and computer analysis of ultrasonic wave scattering in solids, (b) in the ultrasonic imaging of synthetic flaws with multitransducer systems, and (c) in bringing advanced scientific and engineering techniques to bear on NDE. We also call attention to a number of roadblocks in the overall program: (a) a very large gap still stands in the way of attaining quantitative flaw descriptions by NDE for failure-life predictions based on fracture mechanics, (b) severe difficulties remain in the ultrasonic testing of complex specimen shapes, (c) there is lack of sufficient metallurgical input in the program, (d) the program is still faced with nonavailability of suitable flaw detection standards, and (e) inadequate effort is being directed to understand the poor reliability and reproducibility of commercially available transducers.

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It is suggested that the ARPA/AFML Program on NDE could be usefully reviewed, particularly in the critical areas, by the Materials Research Council next summer.

On the last day of the Conference a session was devoted to an examination of the possibility of operating gas turbines at temperatures approaching the adiabatic stoichiometric temperature in a reducing atmosphere. This is a typical exploratory meeting held to see if further effort should be given to this topic at future meetings.

# FEASIBILITY OF OPERATING OF ENERGY CONVERSION MACHINES UNDER REDUCING CONDITIONS AT VERY HIGH TEMPERATURES

## E. E. Hucke

Discussions with various members of the MRC have been held concerning the idea of a very high temperature energy conversion machine. The basic chemistry of any practical (non-fuel cell) combustion of fossil fuel require that the reaction products have a high activity of carbon, hydrogen and nitrogen, but there is no fundamental reason that the flame have a high oxygen potential. Flames at stoichiometric conditions or slightly fuel rich attain almost the same flame temperature as highly oxidizing flames. In light of this, the inherent properties of the various types of carbon materials have been explored. Such materials have either equal or vastly superior mechanical and thermal properties to any others known. Oxidation resistance is the one limiting feature. In reducing conditions one or more of the carbon materials, which are non-strategic, relatively cheap and formable can easily operate at high stress levels at temperatures exceeding 2000°C. A preliminary discussion session involving members of the Council and representatives from Livermore Laboratories and EPRI has been organized to further analyze the problem areas likely to be encountered in such a very high temperature machine.

Several times over the life of the Council the problem of erosion has been examined and there continues to be interest in this topic on the part of several Council members. The Ceramic Division of the Office of Naval Research is aware of this MRC interest and arranged to schedule their Contractor's Review Meeting at the Summer Conference site the last week of the conference. The agenda of that meeting follows.

#### AGENDA

Impact Response and Erosion Mechanisms for Brittle Materials-ONR Contractors Meeting 23, 24 July 1975

#### 23 July 1975, 0900

R. J. H. S. B.	Rice, NRL Lankford, SwRI Kirchner, CFC Wiederhorn, NBS Hockey, NBS	Compressive Strength of Brittle Materials Flaws in Compressive Failure Strength Degradation from Impact Surface Damage Due to Indentation and Impact Subsurface Damage Due to Indentation
		23 July 1975, 1300
Α.	Evans, Rockwell International	Fracture Mechanics for Impact
R.	Wilshaw, ETI	High Velocity Impact Mechanics
L.	Rubin, Aerospace	
	Corporation	Single Particle Impact on Graphites C-C's
м.	Gulden, Solar	
	Inc.	Overlapping and Adjacent Impacts

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#### 24 July 1975, 0900

₩.	Adler, Bell Aerospace	Erosion Sequences and Mechanisms
м.	Rosenblatt, CaR&T	Analytical Modelling of Erosion
J.	Buch, PDA, Inc.	Modelling for Threshold Effects
с.	Stein, AFWL	Simulation Techniques for Hypersonic Testing of Brittle Materials
т. D.	Peterson, AFML Goldstein, NSWC	In-House Program
	White Oak	RV Nosetip Erosion
		25 July 1975, 1300-1500
F.	McClintock, M.I.T.	Group Discussion - Summary and Perspectives

On July 21 a materials related problem on armor-piercing projectiles was referred to the MRC by the Tactical Technology Office of ARPA. Several members of the Council met with the Contractor and personnel from the Army Materials and Mechanics Center and discussed the problem and possible solutions. A letter report of that meeting and its summary and conclusions has been forwarded to TTO via the ARPA-MATS Director.

The success of the many workshops and meetings held during the Summer Conference is due to the excellent efforts and cooperation received from the many consultants and visitors that attend the meeting. A list of those who attended the 1975 Conference is given in the Appendix to this report.

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#### PAPERS AND MEMORANDA OF 1975 CONFERENCE

The following are the titles of papers produced at the 1975 Summer Conference. Abstracts of many of these papers are given in the Appendix. When the abstract is not given, the full paper will appear in a subsequent report.

> Wear, Polishing and the Study of Surface Layers by X-Ray Diffraction A. Bienenstock

> > Void Collapse in Creep B. Budiansky

Fatigue Analysis of Wear by Delamination B. Budiansky and F. A. McClintock

On the Design of Alloys for High Strength and Fracture Toughness M. Cohen

Quantitative Nondestructive Evaluation M. Cohen and R. Thomson

On the Powder Forming of Advanced Materials M. Cohen

> Design of Materials D. C. Drucker

Elementary Results of Dimensional Analysis For Rates of Wear in Steady State Sliding D. C. Drucker

Rod Penetrating on Oblique Plate at Fairly High Speed D. C. Drucker

Forming Shapes of Advanced Materials from Powder P. E. Duwez

> Materials Design A. G. Evans

Some Problems in the Solid Particle Erosion and Wear of Brittle Materials A. G. Evans

Creep Rates for Concurrent (Linear) Deformation and Crack Propagation A. G. Evans

One- and Two-Dimensional Conductors W. H. Flygare, G. D. Stucky & H. Ehrenreich

> Optical Band-Gaps of Oxides J. J. Gilman

Concentration Fluctuations in Absorbed Layers B. Bell, R. Gomer & H. Reiss

> A Novel Photovoltaic Device R. Gomer

Future Sources of Chemical Feedstocks and Military Preparedness M. F. Hawthorne and C. U. Pittman

The Role of Crystal Plasticity in the Delamination Theory of Wear J. P. Hirth

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Hydrogen Atmospheres in the Elastic Fields of Dislocations and Cracks J. P. Hirth and B. Carnahan

Comments on Superalloy Powder Program J. P. Hirth

Coal Liquefaction as an Intercalation Problem R. A. Huggins

Theoretical Issues Related to Fast Ion Conductors R. A. Huggins

> The Implications of Low Surface Barrier Potential MOM Devices G. S. Kino

Prospects for Nondestructive Flaw Detection in Structural Ceramics G. S. Kino and A. G. Evans

A Review of Acoustic NDE Techniques G. S. Kino Degradation of Photovoltaic Cells W. Kohn

Natural and Anthropogenic Sources of Chlorine in the Atmosphere J. L. Margrave

Some Synthetic Possibilities for Inorganic 1-D and 2-D Conductors J. L. Margrave

> Acid Rainwater J. L. Margrave

Stabilities of Refractory Materials at High Temperatures in the Presence of  $F_2/HF$  Gaseous Mixtures J. L. Margrave

Questions About Erosion. esistant Window Materials F. A. McClintock

A Note on Dynamic Crack Propagation Criteria for Computer Codes F. A. McClintock

A Philosophy of Energy (and Feedstock) Management E. W. Montroll

> An Approach for Preparing Antifouling Concrete for Undersea Use C. U. Pittman, Jr.

> > Molecular Rectifiers C. U. Pittman, Jr.

Chemical Anchoring of Mildewcides in Paints C. U. Pittman, Jr.

Comments on Synthetic Approaches to One-Dimensional Conductors C. U. Pittman, Jr.

A Qualitative Approach to Anisotropic Semiconducting Polymeric Materials C. U. Pittman, Jr.

Research on Material Characterization for Structural Reliability and Design J. R. Rice Notes on the Mechanics and Thermodynamics of Brittle Interfacial Failure in the Presence of a Mobile Species (Hydrogen) J. R. Rice

Sources of Shear and Localization J. R. Rice

Antennae and Matching Structures for Infrared Diodes P. L. Richards

Atmosphere Assisted Fracture in Semi-Brittle and Brittle Materials R. M. Thomson

Threshold for Hydrogen Embrittlement R. M. Thomson

Analysis of the Duwez Splat-Cooling Process M. Tinkham

Fundamental Considerations Limiting Tunnel Diode Mixers and Detectors M. Tinkham

Frequency Response Limitations in Tunnel Diode Mixers A. Yariv APPENDIX

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# WEAR, POLISHING AND THE STUDY OF SURFACE LAYERS BY X-RAY DIFFRACTION

A. Bienenstock

#### ABSTRACT

In this note, the determination of surface layer characterization parameters, crystallite size and average strain, through the use of X-ray diffraction with wavelengths just below absorption edges is discussed. The note begins with calculations of penetration depths at these wavelengths and an analysis of the contribution of surface layers to the measured diffracted intensities. After some comments on experimental techniques, applications of high absorption diffraction techniques to the study of worn metal surfaces and to quality control of molybdenum high power infrared laser mirror surfaces are proposed.

# VOID COLLAPSE IN CREEP

B. Budiansky

### ABSTRACT

On the basis of the classical Eshelby solution for ellipsoidal inhomogeneities, it is possible to study the collapse of an isolated ellipsoidal cavity in an infinite, linearly viscoelastic material subjected to arbitrary stress histories. The appropriate analytical procedure has been implemented for an initially spherical cavity, for the following loading cases: (a) uniaxial compression, with superposed transverse pressure, and (b) transverse pressure, with superposed longitudinal tension. The first case models, roughly, the process of direct compaction; the second, extrusion. It is found that under uniaxial compression, a length reduction of about 50% is needed to completely flatten out a spherical void. Under transverse pressure alone, an overall area reduction ratio of 12:1 is needed to squeeze the void into a needle-shaped cavity having 1/10% of its original spherical volume.

### FATIGUE ANALYSIS OF WEAR BY DELAMINATION

B. Budiansky and F. A. McClintock

### ABSTRACT

There appears to be a moderate amount of credence in the validity of Archard's adhesive wear formula

$$\left(\frac{\text{Wear Volume}}{\text{Sliding Distance}}\right) = \frac{k}{3} \left(\frac{\text{Normal Force}}{\text{Hardness}}\right)$$
(1)

in which the factor k, to be determined experimentally, is described as a rip-off probability associated with an adhesive encounter of opposing asperities. Suh's delamination theory of wear rejects the notion that wear occurs by the knockingoff of asperities, but rather results from successive delamination of thin sheets of material. In the present, admittedly crude, analysis we reconcile Archard's formula with Suh's mechanism, and discover that k can then be interpreted as a number inversely proportional to the number of cycles of sliding contact load needed to produce a fatigue fracture just below the surface of the material, in the vicinity of an asperity.

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## ON THE DESIGN OF ALLOYS FOR STRENGTH AND FRACTURE TOUGHNESS

M. Cohen

#### ABSTRACT

It is postulated that fracture toughness increases with the energy that is absorbed in the plastic zone at the tip of a moving crack, and that this absorbed energy increases with the strain-hardening rate  $(d\sigma/d\epsilon)$ . When the yield strength is raised, as in the martensitic strengthening of steel, the energy absorbed by the plastic zone is decreased because the critical size of the plastic zone and the strain hardening within it are reduced. However, by starting with metastable medium-carbon austenitic steels (intiially warm worked to provide high yield strength), the base composition can be chosen to favor a strain-induced martensitic transformation in the plastic zone at a crack tip; and inasmuch as the martensite thus generated is significantly stronger than the parent austenite, the effective strain-hardening rate is very high. TRIP steels make use of this phenomenon, and the observed combinations of strength and toughness are probably the best that have been attained in any material to date (Y.S.  $\simeq 250$  ksi and  $K_{1c} \simeq 100$  ksi/inch).

Unfortunately, the strain-induced nucleation of martensite is usually quite temperature-sensitive, and adiabatic heating due to high strain rates raises the temperature

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sufficiently to render inoperative this special mode of strain hardening. We then inquire into the possibility of avoiding the latter undesirable feature by alloy design.

Recent work has shown (G. B. Olson and Morris Cohen, "Kinetics of Strain-Induced Martensitic Nucleation," Met. Trans. <u>6A</u> (April 1975) 791-795) that, based on a shear-band intersection mechanism, the volume fraction of martensite (f<sup>M</sup>) resulting from strain-induced nucleation at such intersection sites can be expressed as:

 $\mathbf{f}^{\mathsf{M}} = 1 - \exp\{-\beta \left[1 - \exp\left(-\alpha \varepsilon\right)\right]^{\mathsf{n}}\}$ 

where  $\varepsilon$  is the plastic strain, n is a fixed exponent  $\simeq 2$  for randomly oriented shear bands,  $\alpha$  is a physical parameter depending on the stacking-fault energy ( $\Delta G^{fcc+hcp}$ ) and measures the propensity to form shear bands during plastic deformation, and  $\beta$  is a physical parameter depending on the driving force for the martensitic transformation ( $\Delta G^{fcc+bcc}$ ). Since both  $\Delta G$ 's are known as a function of composition and temperature, it becomes possible to choose compositions which will not only keep f<sup>M</sup> vs.  $\varepsilon$  in the right regime, but will also minimize the temperature-dependence of this functional relationship. The indications are that the replacement of nickel by manganese in the steels under consideration will meet the necessary conditions.

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# DESIGN OF MATERIALS D. C. Drucker

### ABSTRACT

A program of exciting promise utilizing research efforts in chemistry, mechanics, metallurgy, and physics now can begin which will place the design of metals on the same firm footing as the design of electronic materials and the design of engineering structures and machines. Design carries the implication of ability to specify, control, and to vary as needed.

The recent advance in ability to produce appreciable quantities of very small diameter, very rapidly cooled powders of many metals and alloys without significant surface contamination opens a radically new dimension for the design of materials. These controlled powders can be made into complex shapes without altering their character appreciably. More important for the research proposed they can be made easily into test specimens for the careful study of mechanical properties.

Techniques to mix two or more metallic and ceramic powders or to add particular chemical constituents in a controlled manner are available. Those that do not already exist could be developed. Tailored microstructures could be prepared to aid in the development of and to test reasonably incisively many key

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concepts of the mechanical, chemical, and physical design of microstructure and chemistry. Idealized materials could be given reality and the validity of the idealizations determined as is now commonplace for electronic materials.

# ELEMENTARY RESULTS OF DIMENSIONAL ANALYSIS FOR RATES OF WEAR IN STEADY STATE SLIDING

D. C. Drucker

#### ABSTRACT

When the independent variables governing the rate of wear in steady state sliding are assumed to be only the speed of sliding v, the nominal or average normal pressure on the surface of sliding and the macroscopic elastic and plastic time-independent properties of the materials, no natural length or time appears. Consequently, the simplest or the most elaborate theory constructed on this basis must predict that the rate of wear is linear in v and all the dimensions of the asperities of the sliding surfaces or of the wear particles are zero or indeterminate. A natural length is introduced when either an interfacial surface energy  $\gamma^{A}$  or a fracture parameter  $K_{c}$  is added to the list of independent variables. Dimensions of asperities or wear particles then must be predicted to be proportional to  $\gamma^{A}$ or  $K_c^2$  respectively. If both  $\gamma^A$  and  $K_c$  are included this proportionality no longer needs to hold but rate of wear still must be linear in v. Nonlinearity in v is likely for a time-dependent (creep and relaxation) material as it is for a time-independent one when the mechanical properties vary with temperature and the heat conductivity is taken into account.

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# ROD PENETRATING AN OBLIQUE PLATE AT FAIRLY HIGH SPEED

D. C. Drucker

#### ABSTRACT

The range of interest here is a speed, v, at which the rod of density  $\rho$ , length L, diameter D, slows down only a little and does not change its direction of flight appreciably. Penetration of an oblique target plate of density  $\rho_t$ , thickness h, and flow stress in shear  $\tau_t^Y$  then is equivalent to normal penetration of a thicker plate  $h_t = h/\cos\theta$ . The lower speed range in which the rod penetrates completely but is almost stopped is fully as important and has been treated by J. Awerbuch and S. R. Bodner in a recent series of papers and reports (see Interational Journal of Solids and Structures, vol. 10, 1974).

Success in penetration with only moderate loss of speed and rod material requires  $\rho L/\rho_t h_t$  to be much greater than unity,  $\frac{\rho v^2}{\tau_t Y} \frac{DL}{h_t^2}$  to be much greater than 10 and the tensile impact

strength of the rod penetrator to be greater than the compressive flow strength at the enormously high strain rates of impact.

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# EROSION AND WEAR IN BRITTLE MATERIALS

A. G. Evans

## ABSTRACT

Prior studies of fracture from quasi-static plastic indentation in brittle materials have indicated that the crack lengths, c, can be characterized by the relation; c  $\propto$  (H/K)<sup> $\alpha$ </sup>a<sup> $\beta$ </sup>, where H is the hardness,  $K_{C}$  is the fracture toughness, a is the impression radius and  $\alpha$  and  $\beta$  are constants. This basic relation, as specifically determined for sub-surface (lateral) fracture, can be used as the basis for estimating material removal rates, due to machining, wear, solid particle erosion (at low velocities) etc. Such estimates are made in this paper. Firstly, the role of interactions between adjacent indents on the lateral crack extension is evaluated to determine the volume of material removed in terms of the applied force, the hardness and the fracture toughness. This relation can be used directly to estimate abrasive wear (or machining) rates, which may be compared with available data for ceramic materials. Finally, the force exerted by a projectile on a plastically deformable target is determined (in terms of the projectile and target properties) to enable material removal rates under conditions of low velocity solid particle impingement to be estimated. These estimates can again be compared with available data for ceramic materials.

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# CREEP RATES FOR CONCURRENT (LINEAR) DEFORMATION AND CRACK PROPAGATION

A. G. Evans

## ABSTRACT

In many ceramic materials (e.g., silicon nitride, magnesium oxide, refractories) high temperature deformation is accompanied by the growth of many small cracks. This crack growth can constitute to the measured deformation rate when the crack densities are sufficiently large. The contribution of this crack growth to the total deformation is analyzed herein for a linear material. The analysis shows that, when the crack growth contribution is significant, the deformation rate is time dependent; but a 'pseudo-steady state' may be obtained at small times. Within this range the stress exponent n is not limited, but 1 < n < n + 1 (where n is the slow crack growth exponent). This possibility of 'anomalous' stress exponents for creep suggest that some caution be injected into the direct use of stress exponents for creep characterization and analysis.

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# CONCENTRATION FLUCTUATIONS IN ADSORBED LAYERS

Brian Bell\*, R. Gomer and H. Reiss

### ABSTRACT

The temperature and coverage dependence of the mean square concentration fluctuations in a small open domain of an adsorbed layer is discussed for various situations. It is shown that fluctuations decrease with increasing temperature and reach a limiting value when attractive interactions predominate, if a single non-ideal two-dimensional phase exists. Deviations from ideal gas behavior are strongest at half coverage. At very low coverage (low particle concentration) and very high coverage (low hole concentration) ideal behavior is approached.

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If the layer consists of a two phase system, for instance a two-dimensional liquid or solid in equilibrium with a two-dimensional gas, fluctuations far below the critical temperature are dominated by fluctuations in the partition between phases. As the critical temperature is approached fluctuations first decrease because the mean concentrations in the two phases approach each other, and then increase very sharply near  $T_c$ . Detailed calculations for the single phase situation are given for several approximations: a dilute gas;

\*The James Franck Institute, The University of Chicago.

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a mean field approximation; a lattice gas in both the Bragg-Williams and the Bethe-Peierls-Weiss approximations. The latter which takes some account of correlations between adsorbate particle positions seems to explain reasonably the presently available experimental observations on chemisorbed layers.

#### A NOVEL PHOTOVOLTAIC DEVICE

R. Gomer

#### ABSTRACT

A classical vacuum photocell consists of a light absorbing metallic photocathode and a metallic collector. The open circuit voltage of such a device is  $h\nu-\phi_c$ ,  $\phi_c$  being <u>collector</u> work function. Such a cell will work if photoelectron emission from the emitter exceeds that from the collector whether this is achieved by masking the latter, making its area smaller, or constructing it from a material with intrinsically smaller photoelectron production cross section.

It is proposed that a solid state analogue of this device can be built by thin film technology, with (for instance) an oxide layer replacing the vacuum. In this device the vacuum work function is replaced by the Fermi level bottom of conduction band separation, thus lowering the effective  $\phi_c$ . The width of the oxide film must only be enough to prevent tunneling, i.e., 100-200A. In principle emitter and collector can be made from the same material if light absorption in the emitter section is nearly complete, or if electron production in it is much larger than in the collector section. This could be achieved by making the emitter film (on the photon receiving side of the device) thicker than the collector.

A problem, which must be more fully assessed arises

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because the optical absorption length may exceed the mean escape depth of even low energy electrons in metals. For applications where maximum efficiency is sought this would require construction as a stack, with emitter sections of a thickness comparable to the escape depth, cells being hooked up in parallel.

Because of its inherent simplicity and potentially low cost the device might be useful both for solar power generation and as light active circuit element in various electronic and communications applications. FUTURE SOURCES OF CHEMICAL FEEDSTOCKS AND THE PROBABLE IMPACT UPON MILITARY PREPAREDNESS

M. F. Hawthorne and C. U. Pittman, Jr.

### ABSTRACT

The increasing dependence of the United States upon foreign oil may in the future present unique problems of procurement of organic materials used by the Department of Defense. Consequently, an analysis of Defense Department needs and the needs of the civilian population has been made and cast in terms of future options and possible opportunities to develop alternate feedstocks for fuels and organic materials.

Included in this study are the following items: An analysis of the organic materials necessary for the construction of a typical sophisticated weapon system, the Navy F-14 Tomcat Fighter. A description of the source of organic chemicals and plastics and the nature of the prerequisite feedstocks. An assessment of alternate chemical feedstocks based upon coal, lignite and wood and the development of German synthetic fuel and chemical processes during World War II. The South African synthesis fuel plants which are now producing synthetic fuels and chemicals from coal are described in terms of their usefulness as prototypes for U.S. plants of the future. The difficulties to be overcome and the vast capital investment

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of materials and money needed to eventually replace oil and natural gas feedstocks by coal or lignite are presented in terms of 1974 dollars and industrial production of such items as steel.

The conclusions and recommendations which were obtained point up the need for the construction of about five large synthetic fuel and chemical feedstock plants per year and continuing this construction program well into the future. The recommendation is also made that some segment of the Defense Department continuously monitor the availability and prices of critical organic materials and that the future needs of the DoD be clearly delineated with respect to new weapon and transportation systems.

# THE ROLE OF CRYSTAL PLASTICITY IN THE DELAMINATION THEORY OF WEAR

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J. P. Hirth

## ABSTRACT

Some implications of crystal plasticity effects with respect to the delamination theory of wear are discussed. Critical experiments to decide the soft versus hard surface question, of interest both with respect to wear and to deformation in general, are suggested. A specific dislocation model for ncp metals under wear conditions is proposed.
# HYDROGEN ATMOSPHERES IN THE ELASTIC FIELDS OF DISLOCATIONS AND CRACKS J. P. Hirth and B. Carnahan

### ABSTRACT

Explicit finite sum solutions are obtained for the integral amount of hydrogen absorbed into the elastic fields of dislocations and cracks in both and Boltzmann and the Fermi distribution models. Predictions are made of the hydrogen permeability in metals as a fraction of dislocation density, a problem of interest in the hydrogen embrittlement of high strength steels. The results indicate that the hydride model of hydrogen embrittlement, considered to apply to Ti, Ta, Zr and Hf, also applies to iron and iron-based alloys.

# COAL LIQUIFACTION AS AN INTERCALATION PROBLEM

R. A. Huggins

### ABSTRACT

Some of the experimental information on the structure and the liquifaction of coals is reviewed. This is discussed in the light of current knowledge of the intercalation of species between the carbon sheets in graphite and other groups of materials with layer structures.

Interaction between intercalated species and the host layers, structural changes, exfoliation, and some unique properties of intercalated layer structures are also mentioned. THEORETICAL ISSUES RELATED TO SOLIDS CONTAINING HIGHLY MOBILE ATOMS OR IONS

R. A. Huggins

### ABSTRACT

Solids containing highly mobile atomic species have received greatly increasing attention recently, due at least partly to their potential practical use in battery and fuel cell systems, or as electrochemical transducers in a variety of other types of applications.

Theoretical understanding in this area is currently quite immature. As a guide to the development of useful theoretical efforts in this area, some of the important experimental facts that distinguish these materials will be reviewed.

Similarities between fast ionic conductors and interstitial diffusion of hydrogen in certain metals will be shown. Misconceptions concerning the existence of a "superionictransition" will also be discussed.

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# THE IMPLICATIONS OF LOW SURFACE BARRIER POTENTIAL MOM DEVICES

G. S. Kino

### ABSTRACT

The properties of point contact MOM devices are examined. It is shown that the point contact devices are operating very near to the limit of their thermal capacity and the yield strength of the materials. The mixer conversion efficiencies are extremely low both because of inefficient coupling and the weak nonlinearity of the device.

It would be desirable to employ vapor deposition techniques to construct these devices. This is extremely difficult to do if one requires an oxide 7-10Å thick and at the same time a barrier area of the order of  $10^{-2}\mu m^2$  in order to keep the capacity low. Thus a prime requirement for fabrication of a practical device is to increase the barrier thickness and area, which in turn could increase the limits on lower dissipation and hence the local oscillator voltage amplitude and conversion efficiency.

The only way to increase the thickness of the function is to lower the barrier potential from its present level of 3-4 volts. It is known that the barrier potential between a metal and a semiconductor is of the order of 0.5-1 volt. Thus by using semiconductor layers instead of insulating layers it should be possible to increase the thickness of the barrier layer to at least  $50\text{\AA}$ .

In this report the implications of such low barrier potential devices are examined. The ideally matched mixer conversion efficiency is estimated still to be poor of the order of 20db. The implications of these results to the design arrays and holographic imagery devices is discussed.

# PROSPECTS FOR NON-DESTRUCTIVE FLAW DETECTION STRUCTURAL CERAMICS

Statement of the statement

G. S. Kino and A. G. Evans

## ABSTRACT

The prospects for detecting critical flaws in structural ceramic materials (such as silicon nitride and silicon carbide) in the size range, 50 to  $100\mu$ m, are discussed on the premise that acoustic techniques will be the most pertinent for these materials. The optimum frequency range and transducer characteristics for detection are evaluated, and possible attenuation and microstructural scattering problems are discussed. Then, estimates of the flaw types that are capable of detection are made, and characterized in terms of their detection difficulty. Finally, configurational limitations on detection are assessed.

#### A REVIEW OF ACOUSTIC NDE TECHNIQUES

G. S. Kino

### ABSTRACT

This report discusses the requirements for acoustic NDE techniques, and the present state of the art. It is, in part, a review of the ARPA sponsored meeting on Non Destructive Evaluation at the Science Center of North American Rockwell.

The different theoretical and experimental approaches for determining by acoustic techniques the location, orientation and size of flaws either smaller or larger than the wavelength will be reviewed critically. The practicality of employing these techniques eventually in rapid measurement systems will be discussed. Some possible new approaches for quantitative measurement of such parameters as residual stress and bond strength will be reviewed. These include phase contrast techniques, rotation of the plane of polarization of shear waves, nonlinear techniques and acoustically stimulated acoustic emission.

The requirements of the measuring systems themselves will also be discussed. Standardized transducers must be developed, cheap flexible arrays of electric transducers would be useful, as are EM non-contacting transducers. Signal processing techniques to provide visual images, signature analysis and improved sensitivity are needed.

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### DEGRADATION OF PHOTOVOLTAIC CELLS

W. Kohn

## ABSTRACT

This is a short report on a one-half day workshop on degradation of  $CdS/Cu_xS$  and similar photo-cells. For these systems, which can be very inexpensively prepared, the short operating life-time is the chief obstacle to large scale use. The present status of understanding of the degradation mechanism is briefly reviewed. It is noted that very little is firmly established and some suggestions for further research are made.

# NATURAL AND ANTHROPOGENIC SOURCES OF CHLORINE IN THE ATMOSPHERE

J. L. Margrave

### ABSTRACT

In order to evaluate the potential effects of chlorinecontaining molecules being introduced by man into the atmosphere there is a need for extensive sampling data at various levels to establish the concentrations of  $CCl_4$ ,  $CCl_2F_2$ ,  $CCl_3F$ , HCl, etc.

There is some evidence for both a natural origin and a natural sink for CCl<sub>4</sub>. Also, HCl and CCl<sub>4</sub> can result from high temperature reactions in fumaroles and volcanos. There seems to be a lack of information about possible interactions of CO and  $CO_2$  with HCl. The importance of carbenes in the upper atmosphere is unknown.

Until data of this sort become available and are inserted into ozone layer calculations, it is not possible to make definitive statements about the relative effects of natural and anthropogenic chlorine on the ozone layer thickness.

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# SOME SYNTHETIC POSSIBILITIES FOR INORGANIC 1-D AND 2-D CONDUCTORS

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J. L. Margrave

### ABSTRACT

Isoelectronic analogies, coupled with the experience of inorganic chemists, allow one to suggest several systems which are closely related to the  $-(SN)_{x}$  polymer and, therefore, may have interesting and useful electrical properties. Co-condensation of atoms, matrix syntheses and high temperature studies are needed to establish the conditions of preparing these materials.

### ACID RAINWATER

J. L. Margrave

### ABSTRACT

Weather reports which recorded the pH of rainwater are scarce, but in the limited number of cases for which data are available, there is a large apparent trend toward increasing acidity in rainwater. For example, pH $\circ$ 6 in the 1930's but pH  $\sim$ 4-5 now in New Hampshire/Upper New York State. The bio-effects are unknown. Weathering of rocks, soil and buildings will be accelerated. SO<sub>2</sub>/SO<sub>3</sub> from fossil fuels react to yield H<sub>2</sub>SO<sub>4</sub>; there is some HNO<sub>3</sub>, too. This problem could get worse as coal/ lignite/shale based fuels are used more extensively for energy generation, unless sulfur is removed.

Among the potential solutions to this problem considered are (a) The complete removal of sulfur from fuels; (b) The use of neutralizing additives to form sulfates which can be precipitated; (c) The use of photo-excitation (UV lamps/lasers) to activate  $SO_2$ , and accelerate oxidation to  $SO_3$  and nucleation of  $H_2SO_V$  before release of stack gases.

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# STABILITIES OF REFRACTORY MATERIALS AT HIGH TEMPERATURES IN THE PRESENCE OF $F_2/HF$ GASEOUS MIXTURES

J. L. Margrave

### ABSTRACT

The known thermodynamic and kinetic behavior of various refractory elements and compounds are reviewed and the use of MgO or  $Al_2O_3$  as oxide refractories in the presence of  $F/F_2/HF$  mixtures is recorthered. Graphite is useful at temperatures near 1000°C and Cu or Ni are satisfactory for temperatures for temperatures up to ~800°C. At room temperature and up to 200-300°C, one can use Al or Mg-metals or Teflon or polyethylene or polypropylene or polystyrene which have a thin fluoro-coating applied by careful direct fluorination.

# QUESTIONS ABOUT EROSION RESISTANT WINDOW MATERIALS

F. A. McClintock

### ABSTRACT

### I. System Needs

- A. Altitudes, velocities, rain, fog, hail, dust, wave lengths, size of window and acceptable costs? Assume threshold damage in rain; contained damage in dust?
- B. Thermal stress or gas force cracking of windows imminent?

### II. Erosion

- A. <u>Linear</u> stress waves from drop deformation. Similarity between dynamic and static fields?
- B. Oblique drop mechanics. Shear stress?
- C. Compressive yield of candidate materials as functions of T,  $\dot{\epsilon}$ .
- D. Grain boundary strength under combined stress for candidate materials? (Possibly obtained from spall fracture studies.)
- E. Dynamic crack growth from defects.
- F. Mechanism from crater character just above threshold (i.e., sled, flight, whirling arm)?
- G. Residual strength after cratering. (Chip rather than break.)

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H. In lieu of above, data on rain erosion thresholds for diamond cubic BN, SiC,  $Al_2O_3$ ,  $SiO_2$ ,  $Si_3N_4$ ?

### III. Physical Limitations

- A. Theoretical strength of candidate materials under combined stress? Ideal, grain boundary, K<sub>I</sub>d, dislocation initiated.
- B. Reduced thermal expansion for candidate materials, viz. titanium doped SiO,?
- C. Improved oxidation resistance of diamond.
- D. Transmission data, particularly for CVD candidate materials?
- IV. Manufacturing Technology
  - A. Availability of single crystals?
  - B. Availability of highly sintered polycrystals? Transparency?
- V. Promising Materials

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- A. Complete missing data on transmissibility, fracture.
- B. Suitability of  $Al_2O_3$  coatings on SiC,  $Si_2N_3$ ; also what coatings for BN?
- VI. Possible Design Improvements
  - A. Graded materials (ZnS, ZnSe) for strengthening by differential expansion?
  - B. Thermal quenching.
  - C. Chemical stressing (i.e., ion exchange).
  - D. Fiber optics (i.e., composites).

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E. Spikes, screens, etc.; shielding approaches for aerothermodynamics improvements? -

F. Aerodynamic window.

# A NOTE ON DYNAMIC CRACK PROPAGATION CRITERIA FOR COMPUTER CODES

F. A. McClintock

# ABSTRACT

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For dynamic crack growth calculations the fracture criterion cannot consist solely of the critical stress in an element, because the critical stress intensity factor would then depend on element size. Rather, the crack velocity should be taken to be a function of the dynamic stress singularity. Equations for the necessary stress and displacement fields are gathered from the literature and plotted to show the very marked distortion that occurs at speeds approaching the Rayleigh wave velocity. The crack openings between elements near the crack tip can be used with these results to obtain the dynamic stress singularity, and hence, from test data, the current crack velocity.

# A PHILOSOPHY OF ENERGY (AND FEEDSTOCK) MANAGEMENT E. W. Montroll

#### ABSTRACT

A common attitude of the professionals who discussed feedstock matters was that if the energy problem is kept under control through the use of coal and available oil, including shale oil, then the feedstock problem would also be kept under control.

There are several points about energy management and distribution which I wish to emphasize.

- I. There is no one solution to the energy problem
- II. As energy costs increase, less energy should be dissipated through transport of energy sources.

It has been estimated that the energy required to put a gallon of gaspline into ones automobile (if the gasoline was derived from Middle East oil) might be five times as much as the energy available in the gasoline. While some of this is the energy cost of refining the oil, most is used in transport of the oil to storage stations, from storage stations to refinery, from refinery to distribution centers, and from distribution centers to service stations. If coal is transported across the country to cities for power generation and the electricity generated is carried over long distance cables suffering resistance losses similar transport losses are suffered.

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As long as the price of gasoline is less than that of milk and about the same as bottled water, the reduction of transport costs will not be a major issue. However, with increasing costs one should be more concerned with regional "Projects Independence" so that each region of the country can satisfy its energy requirements with a minimum of energy transport. The map below indicates some likely regional sources in the U.S. Programs should be organized to develop a scientific and economic basis for local independence.



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The regions rich in coal, oil, sunlight, etc., are evident to the reader and projects are being well financed for the exploitation of these resources. Important resources which are not being given sufficient attention are sewage and manure. It is highly likely that the time is not too far off when we will no longer be rich enough to, at considerable expense in antipolution measures, to discard our night soil.

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Sewage might be considered to be young petroleum. Two methods are available for its decomposition



U.S. Bureau of Mines Process



Two cities, one in California and another in England run generators on sewage methane. A California city has contracted with an engineering firm to design a plant for the conversion of sewage into oil.

Large feed lots in which cattle can be concentrated are expected to reduce beef costs significantly, but have not yet been constructed because of EPA's concern with the pollution handling problem. Since such feed lots would furnish easily collectable manure the possible engineering of the following flow chart should be investigated more vigorously.



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It has been estimated (Science, Nov. 1972, p. 599) that with present collection systems for garbage, sewage, agriculture waste, etc., enough oil could be produced per year by process (b) to satisfy ten day's U.S. gasoline requirement. With the present movement toward small cars with higher mileage per gallon, this might become 20 day's demand; and with the oil being produced where the need is greatest, the saving of transportation losses might raise this figure to 40 days demand or about 10% of the U.S. annual requirement, a significant production. The development of a more effective collection system as would result from proper feedlot engineering might raise this contribution by another factor of two.

Two attractive features of this almost untapped resource is that it scales with the number of people, and no expensive security measures are required to keep it from being stolen by the enemy.

We close with the expectation that

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III. In the sophisticated technological society of the

future a minimum of organic waste will be discarded.

Economics will determine when stage III of social development is achieved.

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# AN APPROACH FOR PREPARING ANTIFOULING CONCRETE FOR UNDERSEA USE

C. U. Pittman, Jr.

#### ABSTRACT

Currently, antifouling concrete is made by impregnating porous shale with creasote oil and tin compounds followed by mixing with portland cement. It is fairly weak and is used for compressive loads up to 3000 psi and uses large amounts of biocide. Polymer impregnated concrete (PIC) made by impregnating mature concrete with a liquid monomer, which is then polymerized in-situ, develops compressive strengths greater than 20,000 psi and shows good durability against chemical attack and excellent impermeability. It is proposed that liquid monomers, which contain functions biocidal to the fouling community, be mixed with the monomers used in the polymer impregnating process. Then a PIC which is antifouling should result having high compressive strengths. Similarly, the use of biocidal monomers in the area of polymer strengthened concrete (PSC) should also be investigated.

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### MOLECULAR RECTIFIERS?

C. U. Pittman, Jr.

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#### ABSTRACT

The synthesis of donor acceptor molecules (such as 1) with an insulating connecting group between them might be useful as rectifiers. Thus, current flow from donor to acceptor is much easier than the reverse case. By orienting such molecules





between "plates" or contacts one can envision building a "molecular" rectifier such as that shown below which contains three donor-acceptor molecules at the interface:

Calculations were performed on an example molecule of the TTF-TCNQ type, using net polarizabilities estimated for the molecule, to obtain  $I_{\rm R}/I_{\rm Rc}$  as a function of  $\rho_{\chi}$ ,  $\omega$ , and M. The frequency is  $\omega$  the number of molecules of type <u>1</u> was M, and  $\rho_{\chi}$  is the resistivity of the array in the direction of the donor to acceptor axis. It was shown that as long a M is kept small, such rectifiers could be useful for fairly low frequency applications.

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CHEMICAL ANCHORING OF MILDEWCIDES IN PAINTS: AN ANALYSIS AND DISCUSSION OF ITS FEASIBILITY

C. U. Pittman, Jr.

### ABSTRACT

Mildew defacement of organic coatings is a serious, wide ranging problem which has received exhaustive industrial attention. A wide variety of mildewcides have been used in paint systems. However, biocides have not been chemically attached to the paint's polymer system. By anchoring biocides to the polymer system of paint in a way that it may later be cleaved under biological (bacteria, fungi, etc.) attack, a paint that "fights back" might be prepared. A comprehensive literature survey was performed to assess the state of anchoring biocides in paints. Surprisingly, this has not been reported for paints used above ground. A critical review of the feasibility of this approach to the mildew defacement of organic coatings problem (MIDOC) was written. Experimental approaches for achieving this objective were outlined.

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# COMMENTS ON SYNTHETIC APPROACHES TO ONE-DIMENSIONAL CONDUCTORS

C. U. Pittman, Jr.

### ABSTRACT

The drop in conductivity exhibited by tetrathiafulvalenetetracyanoquinodimethane (TTF-TCNQ) complexes below T<sub>C</sub> appears, at least in part, to be a result of Peierls instability. This might be avoided by increasing interstack interactions or by locking the TTF-TCNQ stacks into a "super lattice" similar to graphite. Specific synthetic ideas along these lines are mentioned.

# A QUALITATIVE APPROACH TO ANISOTROPIC SEMICONDUCTING POLYMERIC MATERIALS

C. U. Pittman, Jr.

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### ABSTRACT

Anisotropic electrical properties are needed for a variety of electrical devices. Block copolymers of a semiconducting (or conducting monomer), A, and an insulating monomer, B, could be prepared where phase separation in a regular array occurs to generate cylinders of A-domains in a matrix of B. This material should be semiconducting along the direction of the cylinder axis but insulating perpendicular to this axis. The longest cylinders which could be expected would be 10µ. Similarly, interphase polymerizations can result in A-domains dispersed in a B matrix. In these polymers the A-domains could be much larger than those in block copolymers. This material could be cut or rolled into films or sheets which could be used as a one-dimensional semiconductor. Thus, the bulk film is a one-dimensional semiconductor, while the polymer which constitutes the A-domains may be a three-dimensional semiconductor. The possible synthesis of organic semiconductors from complexes found in "organic metals" is commented on. Three reports currently exist in the literature. Can improved semiconducting polymers be prepared using mixed valence complexes currently being studied for their mecallic properties?

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# RESEARCH ON MATERIAL CHARACTERIZATION FOR STRUCTURAL RELIABILITY AND DESIGN

J. R. Rice

### ABSTRACT

As an outgrowth of MRC discussions on the Design/ Materials Interface, some areas of materials research, mostly in fracture mechanics, are identified which would seem to have direct relevance to needs in structural reliability and design.

# NOTES ON THE MECHANICS AND THERMODYNAMICS OF BRITTLE INTERFACIAL FAILURE IN PRESENCE OF A MOBILE SPECIES (HYDROGEN)

J. R. Rice

### ABSTRACT

The thermodynamics of interface separation in presence of a mobile species (H) is discussed. It is argued that low pressure hydrogen in steels involves the weakening of internal interfaces. In some cases these can be grain boundaries and the mode of fracture is then predominantly intergranular; in other cases the critical interfaces are those of inclusions or precipitates, and the role of H is then simply to allow the early nucleation of voids, which spread by conventional transgranular ductile rupture. Attention in the thermodynamic discussion is directed to the limiting cases of separation at constant potential of the solute, and of separation at constant surface concentration. Effects on both the separation energy and the maximum cohesive strength are discussed.

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### SOURCES OF SHEAR BAND LOCALIZATION

J. R. Rice

### ABSTRACT

The localization of plastic flow into a shear band is widely observed as a precursor to ductile fracture. It seems to set a limit to the achievable fracture toughness of ductile alloys when all impurities, serving as void nucleating sites, are removed. Also, shear localization is a critical part of the newly proposed delamination theory of wear.

There are many possible explanations for such localizations, ranging from bifurcations of deformation at a continuum scale to the speading of flaw-like imperfections on the microscale. Also, they may result from instabilities in plastic flow which, once localized, lead to ductile fracture, or they may result from the destabilization of fracture-inprogress, by the nucleation and growth of voids.

Possible mechanisms have been cataloged and some preliminary analysis has been done on several of these, with an aim toward trying to limit or eliminate possibilities and settle on localization mechanisms in various materials.

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# ANTENNA AND MATCHING STRUCTURES FOR INFRARED DIODES

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P. L. Richards

#### ABSTRACT

The problem of efficiently compling the energy from a free space infrared beam to a diode with dimensions less than one wavelength has been studied. Contributions under the subject of optimizing the feed structures for high gain antennas include:

 Estimates of the efficiency of presently used schemes.

2. Suggestions of improved single antenna structures.

3. Analysis of array feed structures.

Contributions under the subject of impedance matching include:

1. Fundamental limits to impedance matching.

2. Effect of antenna resistance, transmission line

resistance, and diode series resistance on impedance matching and speed of response.

3. Use of arrays for impedance matching.

It appears that the techniques now generally used to couple to MOM diodes can easily be improved by about one order of magnitude even at low infrared frequencies. A second order of magnitude might be available with a carefully optimized array.

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#### THRESHOLD FOR HYDROGEN EMBRITTLEMENT

R. M. Thomson

#### ABSTRACT

Recent experimental results show a generally logarithmic dependence between the pressure of atmospheric hydrogen and the stress intensity factor, K. We show that the experimental results can be rationalized in terms of the decrease of surface energy by adsorbed hydrogen. Theoretical expressions for the effect on surface energy are given. Quantitative comparison, however, must await working out the functional relationship between the true surface energy and the effective surface energy which includes effects of the plastic zone surrounding the crack.

# ANALYSIS OF THE DUWEZ SPLAT-COOLING PROCESS M. Tinkham

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#### ABSTRACT

In the Duwez drop smasher, a molten metal drop is frozen very rapidly by being compressed between two pistons driven together by compressed air. The very high cooling rate obtained in this way enables creation of solids with amorphous and unstable structures.

In this note we give an elementary analysis of the cooling and viscous effects which determine the thickness of the final disc. The analysis also gives insight about the time-dependent cooling rate, which may be useful in interpreting the structures which are obtained. Our primary conclusion is that the thermal diffusivity is the key material parameter, unless thermal boundary resistance dominates the cooling; viscosity effects are expected to be unimportant unless the viscosity is several orders of magnitude larger than the usual values of about  $10^{-2}$  poise.

## FUNDAMENTAL CONSIDERATIONS LIMITING TUNNEL DIODE MIXERS AND DETECTORS

M. Tinkham

#### ABSTRACT

Fundamental physical principles limit the degree to which one can simultaneously achieve high speed (or maximum useable frequency), high sensitivity, and high temperature of operation of tunnel diode detectors. In the context of a voltage-controlled mixer or square-law detector, a useful figure of merit is the logarithmic derivative  $S = \frac{d}{dv} \ln \frac{dI}{dv} =$  $(d^2I/dV^2)/(dI/dV)$ , which has the dimensions of volts<sup>-1</sup>. In a classical Schottky diode, for example, S = e/kT, so that sensitivity apparently can be increased without limit by lowering the temperature. In fact, this increase reaches a limit when thermal electron currents drop below the tunneling current. Moreover, as shown by Tucker, the improvement which can be obtained in this way is also limited by quantum effects as soon as  $kT \sim \hbar\omega$ ; specifically, S approaches  $2e/\hbar\omega$  for  $(kT/\hbar\omega)$ << 1, corresponding to a single extra electron of current per photon absorbed. None the less, further cooling below T = hw/k may be needed to reduce background current. By contrast, in the MOM tunnel diode there is no sharp feature in the density of electronic states on the energy scale of kT (such as the semiconductor or superconductor gap edge), and so S

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must be of the order of the inverse of the barrier height V,, in volts. Thus, S = 1 volt<sup>-1</sup>, compared to  $\approx 40$  volt<sup>-1</sup> for a room temperature Schottky diode, or ~12,000 volt-1 for a super-Schottky at 1°K. This comparison explains the poor sensitivity of the MOM diode detector or mixer; but it also provides the basis for the MOM's remarkable frequency response, which is flat out to photon energies  $\hbar\omega \approx eV_{b} \approx 1 eV$ . In fact, we argue that there is a quantum limit on the nonlinearity-bandwidth product of the form S Aw < 2e/h, where S is the low-frequency value of S and Aw is the bandwidth. That is, it is not possible to obtain the fast response of a MOM diode except at the expense of low sensitivity, even if one allowed operation at low temperatures. For example, it appears that such sharp features as the zero-bias anomaly in the I-V curve can not be effective in giving a sensitive and fast response. However, it may be possible to make considerable improvement in existing diodes by optimizing the barrier design tradeoffs for a given speed, frequency, and temperature of operation. Specifically, it appears that there is no fundamental reason to prevent development of a Schottky tunnel diode using heavily doped material (such that the plasma frequency is comparable to the frequency to be detected), operating at room temperature, which will require local oscillator power of no more than 10<sup>-4</sup> Watts to approach the quantum limit for heterodyne detection sensitivity at 10µm. Such a device would clearly be of great practical value for heterodyne systems using CO, laser radiation.

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## FREQUENCY RESPONSE LIMITATIONS IN TUNNEL DIODE M'XERS

A. Yariv

#### ABSTRACT

Frequency Response Limitations due to high order mixing processes in tunnel diode mixers.

In addition to frequency response limitations inherent to quantum mechanical tunneling which are reviewed by M. Tinkham we find a new limitation which is peculiar to the interaction between the quantum mechanical tunneling and the circuit frequency response. If as an example we are interested in the process whereby the frequency  $lw_1 tmw_2 tnw_3$  is generated by mixing the fields  $v_1 e^{iw_1 t}, v_2 e^{iw_2 t}, v_3 e^{iw_3 t}$  then the actual fields appearing across the junction will be

 $\frac{\mathbf{v}_1}{(\mathbf{l}+\mathbf{i}\mathbf{w}_1\mathbf{t}_1)}, \frac{\mathbf{v}_2}{(\mathbf{l}+\mathbf{i}\mathbf{w}_2\mathbf{t}_2)}, \frac{\mathbf{v}_3}{(\mathbf{l}+\mathbf{i}\mathbf{w}_3\mathbf{t}_3)}$ 

where  $t_1$ ,  $t_2$ ,  $t_3$  are effective circuit RC time constants as discussed by Richards which in Javan devices are  $\sim 10^{-14}$  sec.

When this fact is incorporated into the basic tunneling expression one finds that the power generated at  $lw_1 \pm mw_2 \pm nw_3$ is reduced by

 $\frac{1}{(1+w_1^2t_1^2)^{\ell}(1+w_2^2t_2^2)^m(1+w_3^2t_3^2)^n}$ 

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This would predict a steep penalty for high order processes beyond w  $\sim 1/t$ .

Considerations of Coupling Efficiency from electromagnetic modes to diode antennas.

Basic electromagnetic considerations applied to the problem of coupling losses radiation into the MOM antennas reveal that in general the received power  $P_r$  is related to the incident power  $P_\ell$  or

$$P_{r} = P_{\ell}G_{a}P_{\ell}\frac{\Omega_{\ell}}{4\pi} = P G_{a}\frac{\lambda^{2}}{4\pi^{2}w_{o}^{2}}$$

where  $G_a$  is the antenna gain,  $w_o$  is the minimum radius (waist) of the focused laser beam and  $\Omega_{\ell}$  is the solid angle of the laser beam. For the ordinary experiments reported, it is estimated that the coupling efficiency varied between 0.1% and 1%. The answer to increased coupling efficiency seems to be in increasing the antenna gain  $G_a$  and some means for achieving it will be discussed.