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Report of the Materials Research Council (1976)

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INTRODUCTION

This report is a summary of the activities of the Materials Research Council during its annual Summer Conference held in La Jolla, California, during the period July 6-30, 1976. A more complete presentation of the technical papers, workshop reports and memoranda generated by the Council will be prepared and issued later in the contract year.

The Materials Research Council was organized by the Materials Science Office of the Defense Advanced Research Projects Agency to assist them in examining potential future materials problem areas of the Department of Defense. It is not directly concerned with current problems, although it has and will continue to work on these when it can be of assistance. Its primary function is to look beyond the current problems to those of the future and to suggest possible studies that will insure that the necessary science base and preliminary engineering feasibility studies are in place to support later engineering and system development.

The membership of the Council is made up of ceramists, chemists, physicists and engineers whose common interests lie in materials science or materials engineering. This meeting of the Council was the ninth year of operation and over this period this diverse group of scientists and engineers have developed

-1-

into one of the most knowledgeable and versatile consultant groups in the Country.

Since most of the Council membership is drawn from the academic community, their early exposure to emerging materials problems results in their prompt transfer, via their graduate students, into active research programs. Support of these programs comes from several sources, not just the Department of Defense. NSF, ERDA, Industries, Universities and Technical Associations are all represented in the support of these research programs. The range of these programs is very broad since it covers all of the topics that have been examined by the Council over the last several years. Currently work is going on in acoustic scattering, epitaxy, fracture, surface chemistry, nonequilibrium structures, structural ceramics, wear, etc.

While the Council has considerable expertise in many areas, it draws heavily from the science and engineering communities for consultants, assistance and advice. These come from government agencies, industrial laboratories, not-for-profit institutions and from universities. Visitors who have a special interest and capabilities in the areas under consideration by the Council are encouraged to attend and take part in the briefings and discussions that make up part of the Summer Conference of the Council. Visitors have included NSF and NBS personnel, representatives of the basic research offices of the three services; AFOSR, ARO, and ONR and other DoD research and development groups such as NRL, AMMRC, AFML, AFWL, NSRDC, NSWL,

-2-

etc. These service personnel perform a particularly valuable function since they have an intimate knowledge of on-going current research and can relate it to the advanced research concepts under consideration of the Council to the benefit of both groups.

PROJECT ORGANIZATION

The technical direction of the Materials Research Council is delegated to a seven-man Steering Committee chosen to represent the various disciplines of the Council membership. Membership on the Steering Committee is usually for a period of three years with replacements made each year.

The functions of the Steering Committee are:

- a) Work with ARPA-MATS to select problem areas for consideration by the Council.
- b) Select Council members, specialists and consultants to work with the Council.
- c) Structure, direct and evaluate Council activities.
- d) Participate in project management.

The current Steering Committee is as follows:

Professor Willis H. Flygare, Chairman Department of Chemistry University of Illinois Urbana, Illinois 61801

Professor Bernard Budiansky Division of Engineering and Applied Science Harvard University Cambridge, Massachusetts 02138

-3-

Professor Morris Cohen Department of Materials Science and Engineering 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

Professor Amnon Yariv Department of Electrical Engineering California Institute of Technology Pasadena, California 91109

The other members of the Council are:

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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

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There are many people qualified for Council membership but budgetary considerations limits the numbers to 20-25. To obtain a greater flexibility in membership, a recent policy was instituted where some of the Council members are asked to go on an inactive status and new members are added. Some members, because of other commitments, elect to be placed on the inactive list. Inactive members are usually recalled to membership as the Council moves back into their areas of expertise. The current inactive list of Council members is as follows:

Professor Michael B. Bever Dept. of Materials Science and Engineering Massachusetts Inst. of Tech. Cambridge, Massachusetts 02139

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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 Madison, 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 Erastus H. Lee Dept. of Applied Mechanics Stanford University Stanford, California 94305

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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 14950

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

ORGANIZATION OF THE SUMMER CONFERENCES

The principal function of the Materials Research Council is to provide ARPA with a variety of services which bear on the development and use of materials in defense systems. The vehicle for providing these services is the Summer Conference which is a one month summer study meeting.

During the summer meeting the Council not only carries out research of an analytic nature, but also holds conferences and workshops devoted to themes of mutual interest to the Council and ARPA with a balance being sought between themes suggested by ARPA and those suggested by the Council. Position papers are prepared after the conferences and workshops, to aid ARPA in judging the pertinence of new programs, in stimulating the generation of such programs, or in assisting in the evolution of new scientific concepts. A secondary aim is the stimulation

-7-

of the research efforts of individual scientists and engineers who participate in these meetings. Workshops are attended by Council members, who may not be expert in the subject under discussion, and by a core of experts, usually non-Council members, who are selected and invited by the Steering Committee to lead the discussion. The philosophy under which Council members participate in conferences outside their customary interests is based on the idea that highly competent scientists, even if not experts in that field, can bring fresh ideas to that field by virtue of their competence and the fact that they may not be committed to firm and sometimes controversial points of view.

Several techniques for conducting the summer conference have been implemented during its nine years of operation. Initially the entire MRC membership focused on a few problems presented to them via briefings from the various segments of the Services or DoD agencies. Typical topics covered were: Shock Propagation, Constitutive Relations at High Temperature and Pressure, Composite Materials and Underground Sensing. From this the Council evolved a technique whereby individual Council members were given the responsibility of structuring conferences or workshops that would be of interest to different subsets of the Council. Meetings have been held on such topics as Amorphous Semiconductors, Infrared Optics, Materials in Energy Systems, Structural Ceramics, etc.

Because of continuing interest from year to year of the individual members in certain topics, there is a considerable

-8-

carry-over from one conference to the next of the various study areas. Over the nine year period, of the order of twenty major studies have been carried out in areas such as: Composite Materials, Biomaterials, Laser Optics, Superconducting Materials, Solid Electrolytes, Wear, Erosion, Fracture. From these major studies, smaller groups of the Council have nucleated studies in spin-off areas that are more suited to their particular expertise and they regularly report back to the Council the new developments, refinements in theories, experimental studies; new applications, etc.

Output from the Council appears in two publications. The Preliminary Report gives in summary form the results of the Summer Conference. The Final Report, issued later in the year, contains all the written output of the Council. Much of the Final Report consists of technical papers ready for publication in appropriate journals. The balance are preliminary reports and memoranda generated primarily for distribution within the Council and to its consultants. They serve to stimulate discussion since they are initial position papers and present tentative unrefined concepts and ideas. Their distribution is restricted since they do not represent a unanimous or even a consensus opinion of the Council. They are available on request to the Project Director, subject to the author's release.

-9-

SUMMER CONFERENCE - 1976

In preparation for the 1976 Summer Conference, the Steering Committee met in Washington, D.C., on November 21, 1976, with the Staff of ARPA-MATS. Input from the Council was available on possible study topics. Topics were also submitted by ARPA-MATS. From the rather extensive list considered, the following topics were tentatively chosen and a Council member was assigned to structure the program, invite participants, and to collect pertinent publications for distribution to interested Council members.

- Pyroelectric and Piezoelectric Materials Professor Kino
- Non-Destructive Evaluation Dr. Thomson
- Fatigue Crack Growth Professors Budiansky, Rice
- Epitaxial Films Professor Yariv
- 5. Fine Metal Powder Technology Professors Cohen, Hirth, Hucke
- 6. Metallic Glasses Dr. Gilman

It was agreed that the formal presentations of the problems by experts should be restricted to one or two days at most and suitable time left for discussion, argumentation and analysis by Council members.

ARPA-MATS indicated that they would probably schedule a review of potential optical fiber problems in cooperation with the Naval Electronics Laboratory.

-10-

The Steering Committee met again in Washington, D.C., on February 28th with ARPA-MATS personnel to review the plans for the 1976 Summer Conference. The agenda for the six meetings were approved after some rearrangement of timing of the workshops to avoid overlapping of presentations. ARPA-MATS indicated that it would, in addition to the review on optical fibers, probably schedule a one day meeting on metal-matrix composites in cooperation with J. Persh of ODDRE. They also indicated that, if time permitted, they would like the Council to look into the area of high-pressure research.

In March a newsletter was circulated to the entire Council giving the agenda of the summer program. The general policy of the MRC has been to schedule all conferences and workshops into the first two weeks of the Summer Conference in order to give the membership time in the final two weeks to prepare meeting summaries, discuss the presentations with other members and to prepare the papers to be published in the Preliminary and Final Reports of the program. This timing generally produces some overlap in the scheduling of the meetings. ARPA-MATS requested that this policy be relaxed and that some of the meetings be scheduled into the third week to enable their personnel to attend all of the meetings. This was approved, although it was pointed out that this might adversely affect the Council output.

The actual agenda of the 1976 Summer Conference was as follows:

-11-

July	6	Conference opened
July	7-8	Pyro- and piezoelectric materials
July	7-8-9	Fatigue crack growth
July	8-9	ARPA-AFML NDE programs
July	12-13	Epitaxial films
July	12-13-14	Acoustic scatterers, NDE
July	14-15-16	Fine powder technology
July	15-16	Ceramic turbine advisory panel
July	19-20	Metallic glasses
July	21-22	Optical fibers
July	26	Metal matrix composites
July	30	Conference closed

In spite of the prior planning there was considerable overlap on the conferences. This is almost unavoidable since the availability of the experts is the real determining factor in fixing the calendar.

The individual meetings were well attended and quite productive in spite of their large number. Not all of the meetings were attended by all of the MRC members. Each member selects a few in which he has an interest and to which he can contribute. There is probably an optimum in the number of conferences that can be held at the summer meeting. In earlier meetings two or three topics were considered and this was too few; the 1976 meeting probably had too many. The Steering Committee will attempt to find a better balance.

The following pages present the summary of the meetings; the agenda and a listing of the participants and visitors. In some some cases abstracts of the papers presented have been included. The Final Report will include an expanded treatment of this material.

-12-

CONFERENCE ON PYROELECTRIC AND PIEZOELECTRIC MATERIALS

SUMMARY

G. S. Kino

Three classes of materials were reviewed; pyroelectric materials suitable for use in infrared vidicon devices, piezoelectric ceramics and piezoelectric and pyroelectric organic polymers.

Well developed 100-200 line infrared vidicons are now obtainable commercially, and were described by Singer and Helmick. They have a sensitivity of 0.3°C-0.5°C at the target and appear to be operating near their estimated thermodynamic limit for the target materials used. Further improvements depend on the use of thinner retinas and somewhat more sensitive readout techniques. The pyroelectric figure of merit of proper ferroelectrics was shown by Liu and Bell to be near its theoretical limit.

The new pyroelectric and piezoelectric polymers have many potential advantages. They are tough, flexible and cheap. The pyroelectric figure of merit of these materials is a factor of 2 or 3 worse than the more conventional materials. As piezoelectrics, these materials have very desireable characteristics: a good coupling coefficient and a low acoustic impedance near that of water. High quality, broad band acoustic transducers, comparable to the best available commercial ceramic devices were described by Shaw.

-13-

There should be a large class of these materials still to be developed and research on these materials should be encouraged. New device applications as well as the more obvious conventional ones should be studied and developed.

The work on PZT ceramics appears to be at a mature stage. Further improvements are possible but unlikely to be carried out in industry due to the large market in cheap uncritical consumer components. A particular need is better uniformity from sample to sample which could probably be obtained by better processing.

Other applications of ceramics were discussed, in particular the optical memory devices of Land and Fresnel lenses of Auld. The optical memory device work should be continued.

Some attention was paid to the so-called improper ferroelectrics. These materials have a figure of merit which does not obey the same criteria as do the proper ferroelectrics. They might provide some improvement in pyroelectric vidicons. A small effort in this field would be worthwhile.

Abstracts of the individual papers presented at this conference will be published in the Final Report.

-14-

CONFERENCE ON PYROELECTRIC AND PIEZOELECTRIC MATERIALS

July 7-8, 1976

AGENDA

Introduction - G. S. Kino Electronic Processes in Pyroelectric Materials - A. Glass Recent Developments in Pyroelectric Vidicon Systems - C. Helmick and W. Woodworth Vidicon Arrays - T. Conklin, G. Loiancono and B. Singer Performance Limitations of Pyroelectric Detectors - S. T. Liu Theory of Pyroelectricity - M. Bell Pyroelectric Polymers - A. Glass and J. B. Lando Study of Ultrasonic Resonance and Broadband Transduction in PVF, Piezoelectric Film - H. J. Shaw Piezoelectric Materials - L. E. Cross Piezoelectric Ceramic Materials and Their Application in Devices -D. Berlincourt Processing of Polycrystalline Piezoelectric Ceramics in the PZT System - R. Fulrath Acoustic Wave Guiding Along Piezoelectric Domain Wall Boundaries -B. A. Auld

PLZT Materials Properties of Importance to Information Storage and Display Applications - C. A. Land

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-16-

WORKSHOP ON THE THEORY OF ULTRASONIC SCATTERING WITH APPLICATION TO ADAPTIVE COMPUTERIZED NDE

R. M. Thomson

SUMMARY

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A week long workshop explained the current prospects for characterization of defects in solids by combining the most advanced features of elastic wave scattering theory, the current experimental capability, and computer adaptive techniques. The current status of these three areas was reviewed and papers were prepared detailing advances, partially worked out at the MRC, which could be made in this direction. The general concensus of the workshop was that the goal was a feasible one for the relatively short term because of the power of present concepts and capabilities in the three areas.

CONFERENCE ON THEORY OF ULTRASONIC SCATTERING

July 12-15, 1976

Comparisons of Theory and Experiment in Ultrasonic Scattering B. Thompson

Ultrasonic Transducers G. Kino

Computer Analysis of Acoustic Signals A. Mucciardi

Review of Theory E. A. Kraut

Review of Gubernatis-Krumhansl Analysis J. E. Gubernatis

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6

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WORKSHOP ON NDE M. Buckley and R. Thomson

SUMMARY

A two-day workship was held at the MRC site to explore issues in the NDE area of potential concern or interest to ARPA. Specific areas studied were NDE for adhesive bonding and composites, NDE for fatigue damage detection, automation in NDE, and the institutional framework of R&D in NDE.

The most significant issue to surface at the workshop was the need to exploit the full physical capability of NDE through an extensive application of computerized automation for overall nondestructive quality evaluation. Without such a development, NDE is likely to remain unreliable, slow, unable to correlate data from a large number of parallel inputs, and expensive. Integration of the NDE community with the electronic and computer communities is an excellent opportunity for promoting further advancements in both fields.

We also found significant R&D technical challenges imbedded in the adhesive bonds, composites and fatigue areas. Specifically, NDE for adhesive handling will require considerable effort to establish practical methods for sensing the adhesive bond strength, but some techniques which are sensitive to the

-19-

cohesive strength of the adhesive already show considerable promise. A big gap appears in the development and application area of NDE for adhesive bonds, especially as it bears on the AF PABST program. (The PABST program is an ambitious attempt on the part of the Air Force to substitute adhesives for mechanical fasteners and rivets in primary aircraft structures.) In order to bring NDE for composites to the level now current in the metals area, considerable research coupling NDE to research on fundamental failure modes in composites will be required. Under institutional issues, the desirability of a centralized NDE center was explored. We conclude that the central issue in this area is to provide sufficient stability for the research community now developing through the auspices of the AF/ARPA program and elsewhere in order for it to gain maturity. A centralized laboratory is one of probably several possible routes for the exploration of this maturity. The development of an integrated NDE service industry was discussed, and is believed sufficiently attractive that we reopen it for further study and consideration, especially as it bears on the automation issue mentioned earlier.

A more complete report on the details of the workshop will appear in the Final Report of the Summer Conference.

-20-

CONFERENCE ON NON-DESTRUCTIVE EVALUATION

PROGRAM SCHEDULE

July 8, 9, 1976

Introductory Remarks - R. Thomson

Current ARPA-AF Program in NDE M. Buckley and D. Thomson

NDE for Adhesive Bonding and Composites W. Yee, J. Florence, D. Hagemaier

Automation in NDE D. Ballard, J. Bushnell, W. Coleman, D. Green

Fatigue Detection W. Reimann, C. Wells, R. Johnson, R. B. Thompson

Institutional Issues in NDE

R. Thomson, D. Thompson, R. Anderson, D. Ballard,

E. Criscuolo, G. Darcy, P. Packman, D. Waidelich,

M. Buckley

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-22-

WORKSHOP ON FATIGUE CRACK GROWTH

B. Budiansky, D. C. Drucker J. W. Hutchinson, J. R. Rice

SUMMARY

Some aspects of fatigue crack growth were discussed at the July 1976 session of the ARPA Materials Research Council.

A focal point of the meeting was the assessment of crack surface closure as a basis for prediction of crack growth under general oscillatory loading histories. In addition, fractographic studies, microstructural effects, and environmental influences on crack growth were aiscussed. The paper attempts to identify critical topics for further research. These relate to the experimental study of closure effects, to the development of predictive crack growth models at the macroscopic level, and to the more detailed understanding of microstructural and environmental influences on the crack growth mechanism.

-23-

MEETING ON FATIGUE CRACK GROWTH

July 7-9, 1976

AGENDA

- P. C. Paris Continuum mechanics aspects of fatigue crack propagation.
- R. M. Pelloux Relationships between Fractography and Microstructure.
- J. P. Gallagher Air Force crack propagation problems and needs.
- W. Elber Comparative discussion of methods of closure observation.

Discussion by D. M. Corbly and O. Buck (ultrasonics), W. Reimann (interferometric), G. R. Chanani and R. P. Wei (electric potential, bridging strain gauge), P. C. Paris (elastic unloading compliance), and others as appropriate on closure observations and relevance to mechanisms and/or models of fatigue.

R. O. Ritchie - Influence of superposed static fracture mechanisms on fatigue.

R. P. Wei - General environmental and temperature effects.

O. Buck - Environmental effects on closure and fracture mode.

Discussion by G. R. Chanani (fractographic features associated with overloads), A. W. Thompson (effect of microstructure in Ti alloys).

- J. W. Hutchinson Closure effects predicted from Dugdale/BCS crack models.
- W. Elber Summary of J. Newman finite-element predictions of crack surface closure effects.

H. Dill - Spectrum crack growth prediction.

A. J. McEvily - Modified COD model.

Discussion: Fatigue detection by NDE, modeling, crack growth prediction.

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MEETING ON EPITAXY

N. Bloembergen A. Yariv

SUMMARY

Members of MRC and a group of experts from both the industrial and the university communities met to discuss the state of the art in epitaxial growth of crystalline layers and the variety of applications which depend on them. It was hoped that the meeting would be able to identify and pinpoint serious problem areas where additional work may be required.

The main topics discussed at the meeting were:

 The various techniques used in epitaxial growth-primarily liquid (LPE) and vapor phase (VPE) epitaxy and the recently developed technique of molecular beam epitaxy (MBE).

2. The use of epitaxially grown films in the fabrication of a variety of electronic and electro-optic devices, especially CW injection lasers, light emitting diodes, photodetectors for near visible and infrared applications, impatt diodes and field effect transistors, integrated optics, and magnetic bubbles for computer memories.

 The intriguing possibility of crystal engineering by MBE which makes it possible to grow new crystals with controlled periodicities.

-26-

It became clear from the meeting that epitaxy is playing a key role in a great variety of new technologies of increasing importance to U.S. technology and to DoD. A good example is the GaAs-GaA&As double heterostructure injection laser which is developed intensely in this country and abroad primarily for powering optical fiber communication links.

The meeting convinced us that due to the combined incentive of commercial and military application and of government support the epitaxial technology is pursued vigorously in the U.S. A few areas, however, were identified where additional effort could play an important role in advancing the technology. These are:

1. The development of U.S. sources for high grade InP crystals is recommended. This material is the starting point for growing epitaxial GaInAsP lasers oscillating near 1.25µm a region where the disperison and loss characteristics of silica based optical fibers are optimum.

2. Development of ternary crystals as substrate sources is recommended. All of today's epitaxial technology is based on starting from binary substrates (GaAs, InP, CdTe, etc.) which places a limit on the flexibility and choice of materials available to device designs.

3. Support of research on the use of organo-metallic compounds in vapor phase epitaxy (VPE) is recommended. VPE techniques will be important in large scale fabrication of epitaxial structures. Present VPE techniques cannot handle reactive

-27-

elements such as Al and Sb. Preliminary work in the U.S. and in Japan indicates that VPE using organo-metallic compounds (such as $Al(C_2H_5)_3$), can overcome this problem. It will also be important to develop a supply of high purity organo-metallic reagents.

4. Studies in academic institutions on the detailed <u>kinetics</u> of epitaxial growth are recommended. While the thermodynamic properties are in general, sufficiently well known, basic knowledge on diffusion rates growth habits, sticking coefficients and non-equilibrium growth is inadequate for the systems of III-V and II-VI compounds. The question whether ternary crystals could provide high grade crystals for use as substrates should be addressed.

5. Vapor phase and MBE techniques for InP based systems should be explored. Particular attention should be given to the causes of the generally poorer device performance resulting from these techniques, compared to LPE.

6. The garnet epitaxy technology for magnetic bubble materials appears to be further developed than that of the compound semiconductors. It will be important to determine if this is an inherent property of the different material system, and if the techniques of a high degree of supercooling and liquid motion be successfully transferred to III-V and II-VI systems.

-28-

MEETING ON EPITAXY

July 12, 13, 1976

- A. Yariv Introduction
- M. Panish III-V Liquid Phase Epitaxy From Phase Diagrams to to Devices
- A. J. Strauss Liquid Phase Epitaxial Growth of Lattice Matched GaInAsP-InP for 1+1.3µm Double Heterostructure Laser
- P. Vohl Vapor Phase Epitaxial Growth of $Hg_{1-x}cd_xte$ (0<x<1)
- J. M. Walpole Epitaxial Growth of Pb1-xSnxTe
- A. Cho Preparation and Properties of GaAs Devices by Molecular Beam Epitaxy
- S. Kamath Infinite Melt Liquid Phase Epitaxy of GaAs and GaAlAs for Device Applications
- I. Samid, P. Yeh and A. Yariv Embedded Epitaxy; Distributed Feedback and Distributed Bragg Mirror Lasers Using LPE Grown GaAs-GaAlAs Structures; Optical Properties and Phenomena in Stratified Media
- J. Stringfellow VPE Growth of III-V Materials for Microwave Applications
- A. Gossard Coupled Quantum Wells and Alternation Monolayers of GaAs-AlAs Structures
- J. S. Harris Liquid Phase Epitaxy Growth of Ternary Alloys for Heterojunction Infrared Devices (solar cells and photocathodes)

R. Burmeister - Liquid Phase Epitaxial Growth of Magnetic Garnets

Informal Discussion

MEETING ON EPITAXY

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HIGHLIGHTS OF SESSIONS ON RAPIDLY SOLIDIFIED POWDERS AND RELATED TECHNOLOGY

E. E. Hucke, J. P. Hirth and M. Cohen

The following highlights emerged from the presentations and discussions on "Rapidly Solidified Powders and Related Technology." A more explicit summary of these sessions will be given in the Final Report.

 It is evident that scientific and technological ideas concerning rapidly solidified powders and their products are multiplying in excitement and potential.

2. Further reduction in droplet size appears to be the most effective way to achieve still faster solidification rates, (>10⁶ °C/sec); the capability of forced convection in attaining even greater cooling rates requires more careful definition, particularly since the processing of fine powders becomes much more difficult with decreasing particle size.

3. There are new indications that the progressive decrease in dendritic-arm spacing with increasing solidification rate is interceded by spontaneous nucleation in the supercooled liquid. This is a very significant phenomenon because:

a. The microcrystallites or cells thus formed have a chance to grow just by atom-by-atom jumping across the liquid/

-31-

solid interface without compositional partitioning between the liquid and solid phases. Thus, in the limiting case, the microcrystallites will have exactly the same composition as the liquid, and the resulting grain boundaries can be unusually clean.

b. This prospect shows that it is important to strive for still faster cooling rates or, at least, solidification conditions in which the thermal gradients are large compared to the solid-front growth rate (i.e., without any long-range diffusion).

c. In this new regime, supercooling and nucleation phenomena will play a critical role in the size of the microcrystallites, possibly reaching down to 10-100A.

d. In the light of these factors, the tolerance for impurities as well as for new alloy compositions can be sharply enhanced; indeed, it may well turn out that a quantum-step improvement in properties can be obtained in these highly-supercooled, nondendritic structures.

4. Skin-melting of bulk alloys by high-intensity laserbeam heating, together with conductive quenching by the metallic substrate, provides an excellent research tool for producing and studying the above-type of highly supercooled, nondendritic solidification and its competition with dendritic solidification. The inhibition of secondary-phase precipitation on solidification as well as the kinetics and morphology of the precipitation on reheating can also be investigated via this technique, comparing both dendritic and nondendritic structures in the skin-melted zone.

-32-

5. Consideration should be given to model alloy systems (such as Pd-Si and Pd-Si-Cu) which, even at conveniently accessible cooling rates applied to a given composition, will exhibit the complete range of processes from dendritic segregation to microcrystalline solidification to amorphous-glass formation.

6. It appears that an electrostatic field tends (a) to stabilize a stream of liquid metal against break-up into droplets, and (b) to damp out oscillations once the droplets are formed. These phenomena should be examined as to origin and possible application to atomization processes.

7. Particular attention should now be given to the powderconsolidation steps and their role in the resulting structure/ property relationships. Very little systematic information is available on what happens to the grain size, dendritic structure, and secondary-phase morphology as a function of the processing and heat-treatment variables. These interactions also point up the need (and opportunity) to optimize compositions and treatments in order to take full advantage of the small-particle approach to materials technology.

8. The wide-scale exploitation of rapidly-solidified powder processing will require multi-faceted structure/property research programs on numerous alloy systems. To that end, there is urgent need for flexible, small-lot (½ to 10 lbs.) powder-making facilities which will permit the detailed study of compositional and structural variables. The availability of such equipment will probably do as much as anything to expand the understanding and

-33-
applicability of the resulting materials.

9. Although glassy-metal powders can be produced in some alloy systems, it is still not known whether these powders can be consolidated without degradation of the glassy state. Such experiments might be tried on the Pd-Si and Pd-Si-Cu prototype alloys mentioned in Item 5.

10. Results to date on the powder-processed intermetallics TiAl and Ti₃Al look encouraging; substantial progress has been made during the past year toward achieving some ductility and good fatigue strength along with noteworthy creep resistance.

11. There is increasing evidence that powder processed aluminum alloys exhibit improved resistance to stress-corrosion cracking and to corrosion fatigue, compared to the conventional wrought alloys. This finding has major implications from the standpoint of extending the mechanically-useful range of highperformance materials in typical environments.

12. A promising approach to the ultrasonic nondestructive testing of powder-processed bodies with curved surfaces has been described, based on the use of appropriately-shaped adapters between the transducer and the curved surface.

13. It appears that, in order to take advantage of the expected 100°F improvement in operating temperature for powderprocessed jet-engine turbine blades, the development of a protective coating for the state-of-the-art superalloys will become mandatory.

14. Fe-Al-Si alloys look attractive for reasons of special

-34-

magnetic properties as well as oxidation and corrosion resistance, without requiring any potentially strategic metals. However, the development of such alloys has been blocked by brittleness problems, which may now be circumvented by powder processing. This means that the stable and metastable phase relationships in the ternary Fe-Al-Si system should now be roughed out by computational methods.

15. There are good prospects for substantial advances in titanium alloy formability and properties through the RSP approach. However, less expensive methods are needed for producing high quality titanium powders.

SMALL-PARTICLE PHENOMENA AND TECHNOLOGIES MEETING

July 14-15, 1976

First Session - Morris Cohen, Chairman

E. C. van Reuth - ARPA Program in Small-Particle Processing

*Alan Lawley - Overview of Advanced Powder-Making Processes; Fundamentals of Droplet Formation

*M. C. Flemings - Theory of Dendritic Solidification During Very Rapid Cooling

**J. B. Moore and A. R. Cox - Progress in the P&W Rapid Solidification Program

Second Session - E. E. Hucke, Chairman

*N. G. Grant - Special Methods of Achieving Rapid Solidification in Fine Particles

- E. J. Dulis Inert Gas Atomization and Shape Consolidation of Commercial Alloys
- *O. D. Sherby Fundamentals of Superplasticity; Extension to Refractory Metals

*A. G. Evans - Prospects for Attaining Superplasticity in Intermetallic and Ceramic Materials

Third Session - J. P. Hirth, Chairman

*Larry Kaufman - Calculation of Metastable Phase Relationships

R. E. Maringer - Survey of Microcrystalline - and Amorphous - Metal Technologies

***Five-minute presentations on new ideas relative to processing, structural control, novel properties, and applications; preparation of brief memoranda

Fourth Session - Morris Cohen, Chairman

Identification of important research opportunities and potential applications

Recommendations to ARPA

- * A more complete written account is to be published in the final report of the Materials Research Council Meeting for 1976, ARPA contract MDA903-76-C-0250.
- ** Written reports are issued under ARPA contract F33615-76-C-5136.
- ***Brief notes to be published in the final report of the Materials Research Council Meeting for 1976, ARPA contract MDA903-76-C-0250.

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SUMMARY OF THE CONFERENCE ON THE STRENGTH OF OPTICAL FIBERS

A. G. Evans

The intent of this meeting was to discuss the fracture of large lengths (~lkm) of optical fibers, in order to identify methods for assessing the structural reliability of these fibers in a variety of applications.

A presentation of the potential Navy utilization of optical fibers by G. A. Wilkins of the Naval Undersea Center, indicated that cable design considerations require that the fiber be able to withstand relatively long time axial tensile stresses of at least 100 Ksi and larger localized tensile stresses (up to 500 Ksi) induced by fiber bending.

It has been well established that optical fibers in short lengths (~lm) are capable of withstanding short time axial tensile stress in excess of 500 Ksi. However, the statistical nature of the fiber fracture process and the occurrence of slow crack growth generally results in a much lower long term strength capabilities when the fibers are fabricated in very large lengths. The long time structural reliability of long fibers then requires an understanding of the time dependence and statistical character of the fracture strength, the development of techniques that eliminate the fibers at the low strength extreme of the distribution and,

-39-

if possible, the utilization of fiber strengthening processes. Each of these issues was addressed by a series of four speakers.

The time dependence of fracture strength was discussed by R. H. Doremus. He emphasized the use of delayed failure data on fibers to determine empirical relations (between the failure time and the normalized stress) that provide a good description of the data over the widest possible range of stress. The rationale being that the use of such relations should enhance the confidence in the extrapolation of test data to large times.

The statistical aspects of fiber fracture were described by A. G. Evans. He indicated how recently developed statistical analyses could be used to characterize basic strength distributions from tensile data on relatively small samples, and then those distributions might be used to predict the strength of much larger samples in the presence of both axial strains and bending moments. He also discussed the role of strength distribution analysis for identifying the source of most deleterious flaws.

The strengthening of fibers by the development of surface compressive stress was discussed by P. Macedo. He showed how compressive surface zones can be tailored by utilizing a molecular shifting process and demonstrated the development of 20 Ksi stresses. He also indicated that much larger stresses (>100 Ksi) might be developed by depressing the glass transition temperature of the inner zone relative to the outer zone. Such a strengthening process would be invaluable if the internal defects of the fiber can be removed by more diligent fabrication controls.

-40-

The development of techniques for assessing the structural reliability of fibers was addressed by J. E. Ritter. He emphasized the use of proof testing, but cautioned that the effectiveness of the proof test is strongly dependent on the proof conditions when slow crack growth does not occur; and one such possibility for the fiber is to insure that the proof stress is only applied at temperatures of approximately 100°C. Alternatively, if proof testing has to be conducted at standard room temperature conditions, the deleterious effects of the slow crack growth that occurs while unloading from the proof stress must be taken into account. These effects are not readily derived from available theory and Ritter. proposed the use of laboratory scale testing to identify the cost effective proof cycle.

STRONG OPTICAL FIBERS

July 21, 22, 1976

AGENDA

G.	Wilkins - Navy Requirements for Strong Optical Fibers
R.	H. Doremus - Delayed Failure of Glass
J.	E. Ritter - Engineering Design and Fatigue Failure of Fused Silica Fibers
Α.	G. Evans - Failure Statistics
D.	Kalish - Fatigue Failure in Optical Fibers

Discussions

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CONFERENCE ON METALLIC GLASSES

J. J. Gilman

SUMMARY

To review the present state of knowledge about metallic glasses, a brief conference was held during the annual meeting of the Materials Research Council. This conference had the purposes of informing interested members of the MRC about metallic glasses, and of identifying the research approaches toward the study of these materials that might be most fruitful in generating fresh understanding.

Some of the questions that arose during the conference on structure, mechanical behavior, corrosion resistance electrical properties and the magnetic properties were addressed and suggestions were made for finding the answer.

1

METALLIC GLASSES

July 19, 20, 1976

AGENDA

- J. Gilman A Technological Overview
- D. Turnbull Genesis and Structure
- R. Hasegawa Electrical Properties
- H. Ehrenreich Round Table Discussion
- L. David Mechanical Behavior
- R. Staehle Corrosion Resistance
- C. Graham Magnetic Behavior
- J. Hirth Round Table Discussion

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David Turnbull Harvard University Pierce Hall Cambridge, Massachusetts 02138 The following pages list abstracts of memoranda, position papers and technical papers that were developed at the 1976 Materials Research Conference. Most of these, as technical papers, will appear in the Final Report of the meeting to be published before the termination of the current contract.

A listing of these is as follows:

Metallic Glass Structures - J. J. Gilman On the Mechanism of Shear of an Amorphous Metal - J. P. Hirth A New Approach to Radial Distribution Functions of Glassy Metals - H. Reiss and G. H. Vineyard Electrical Properties and Metastability of Metallic Glasses -H. Ehrenreich Prospects for Improved Flaw Detection by Acoustic Emission -F. A. McClintock and G. S. Kino Prospects for NDE of Powdered Metals - G. S. Kino Interpretation of Ultrasonic Scattering Theory for Analysis and Design of Flaw Detection Experiments - J. E. Gubernatis, J. A. Krumhansl and R. M. Thomson Experimental Characterization of Defects with Elastic Waves -L. Adler, G. S. Kino, R. B. Thomson, B. R. Tittman Variational Techniques for Scattering and Other Problems -G. S. Kino Discrete Model for Elastic Wave Scattering by Defects in Elastic Materials - E. W. Montroll Molecular Dipolar Pyroelectricity - W. H. Flygare The Use of Bubble Domain Materials for Submillimeter Wave Magnetic Devices - P. L. Richards Heating Effects in High-Frequency Metallic Josephson Devices: Voltage Limit, Bolometric Mixing, and Noise - M. Tinkham Mechanistic Limitations on the Speed of Response of Electrochromic Optical Devices - R. A. Huggins Fundamental Limitations on Performance of Pyroelectric Vidicon Detectors - M. Tinkham and A. Yariv Closure Analysis in Fatigue Crack Growth - B. Budiansky, J. W. Hutchinson, J. R. Rice Dynamic Elastic Crack Tip Stresses and Displacements for Fracture Criteria - F. A. McClintock Computational Needs for Predicting Plane Strain Fracture -F. A. McClintock Fatigue Crack Growth - P. C. Paris On the Ratio of Tensile Strength to Modulus of Rupture of Ceramics - D. C. Drucker High Strength Optical Fiber - R. L. Coble High Strength Optical Fiber - A. G. Evans, F. A. McClintock,

R. L. Coble

-47-

Structural Reliability of Optical Fibers - A. G. Evans and F. A. McClintock Ultrasonic Flaw Detection in Ceramic Turbine Components -G. S. Kino and A. G. Evans Prospects for Superplasticity in Ceramics - A. G. Evans and R. L. Coble Ceramic Turbine Program - R. L. Coble Fracture Mechanics and the Static Fatigue of Strong Silica Fibers - D. C. Drucker Thermal Stability of CFX in Fluorine - P. Kamarchik and J. L. Margrave Reactions of Li Atoms in Low Temperature Matrices - C. Krishnan, P. Kamarchik, P. Meier, R. Hauge and J. L. Margrave ESCA Studies of Fluorinated PVC and CFX - G. Parks and J. L. Margrave Chlorofluorocarbon Update, 1976 - J. L. Margrave Solid Sources of Elemental Fluorine. I. Thermal Stabilities of Solid Perfluorides and Superfluorides - J. L. Margrave Solid Sources of Elemental Fluorine. II. Thermal Stabilities of Ternary Fluorides - J. L. Margrave Very Rapid Quenching with Thermal Spikes - G. H. Vineyard Nucleation, Undercooling and Homogeneous Structures in Rapidly Solidified Powders - J. P. Hirth Curvature Effects in the Thermodynamics of Multicomponent Systems: Possible Effect on Dendrite Spacing in Rapidly Cooled Small Liquid Metal Drops - H. Reiss Rapid-Solidification Processing (RSP) of Thermoelastic Alloys -M. Cohen A Key Bottleneck in the Exploitation of Rapid-Solidification Processing (RSP) - M. Cohen Comments on Alternative Methods that Might Be Used to Prepare Superhomogeneous-Fine Particles of Metals - R. A. Huggins Small Particle Technology - R. L. Coble Theory of Dendrite Solidification During Very Rapid Cooling -M. C. Flemings Pressure in a Spherical Cavity or On a Solid Sphere is Limited by Instability - D. C. Drucker A Fluid Thermal Switch - H. Reiss Tight Binding Theory of Metallic Adhesion - W. Kohn and R. Gomer Effect of Electrolyte on Dipole Layer Potentials at a Liquid-Solid or Liquid-Air Interface - R. Gomer and H. Reiss A Mechanism for Liquid Phase Epitaxial Growth of Nonequilibrium Compositions Producing a Coherent Interface - J. P. Hirth and G. B. Stringfellow

METALLIC GLASS STRUCTURES

J. J. Gilman

ABSTRACT

A model for the structures of transition metal-metalloid liquids and the glasses that derive from them is proposed. Existing models are based on dense-random-packing of the metal atoms with the interstices filled by metalloid atoms. The proposed model consists of the dense random packing of specific metal-metalloid clusters immersed in a sea of conduction electrons. It is believed that such a model can better explain: the composition of the eutectic liquid; the relative stability of the liquid; the viscosity minimum at the eutectic composition; and other physical properties.

ON THE MECHANISM OF SHEAR OF AN AMORPHOUS METAL

J. P. Hirth

ABSTRACT

Several mechanisms have been proposed for the shear flow of metallic glasses. These models are shown to give explicit predictions of both the flow stress and the strengthdifferential effect where the flow stress varies with the total external stress tensor. Comparison of results for these quantities show that the best overall correlation is with a dislocation-type flow model proposed by Gilman. A complete rationalization of data, however, requires a contribution of a plastic-type dissipative term to the flow resistance.

A NEW APPROACH TO RADIAL DISTRIBUTION FUNCTIONS OF GLASSY METALS

H. Reiss and G. H. Vineyard

ABSTRACT

We suggest a novel way of writing approximate equations which determine the radial distribution functions of multicomponent amorphous systems, including their time dependence in non-equilibrium situations. Applications to the structure of glassy metals are being worked out.

ELECTRICAL PROPERTIES AND METASTABILITY OF METALLIC GLASSES

H. Ehrenreich

ABSTRACT

The electrical properties and the metastability of metallic glasses, and their relationship is discussed on the basis of a "frozen liquid" model with a view of exploring the general applicability of that model. Several questions concerning the transport theory of metallic liquids are for the most part resolved. These are:

1. The applicability of a theory based on independent and strong scatterers (e.g., the transition metal constituents) whose coordination is specified by the radial distribution function.

2. The long standing puzzle concerning the effective valence Z_{eff} for transition metal liquids which falls in the range $1 < Z_{eff} < 2$ independently of the liquid under consideration.

3. The role of the metalloid constituent in electronic transport. Recent speculations by Tauc and Nagel concerning the metastability of metallic glasses are examined using the same viewpoint. These considerations are shown to be consistent with those concerning the electrical properties in accounting for the negative temperature coefficient of the

-52-

resistivity ρ observed in many metallic glasses and why this type of behavior is found in glasses having large ρ , whereas for intermediate values ρ is either temperature independent or increases with temperature.

PROSPECTS FOR IMPROVED FLAW DETECTION BY ACOUSTIC EMISSION F. A. McClintock and G. S. Kino

ABSTRACT

A brief review of increasing needs for flaw detection, the coming use of finer grained materials, and developments in transducers and signal processing resulting from the current work on ultrasonic inspection are all factors indicating bright promise for improvements in flaw detection by acoustic emission, especially by distinguishing between shear and dilatational sources.

PROSPECTS FOR NDE OF POWDERED METALS

G. S. Kino

ABSTRACT

A discussion of possible NDE techniques for cast powdered metal structure is given. It is concluded that contacting of curved surface using a mating curved part should not provide a major problem. Detection of small flaws in the $10-50\,\mu\text{m}$ size range and comparable to the grain size should be very difficult at distances more than a few millimeters from the surface. The use of focused transducers could help in this respect. Surface waves could be used to detect small flaws near the surface of the order of $\lambda/4$ deep and λ in diameter where λ is the acoustic wavelength. Initially measurements of attenuation in these new materials must be carried out before good estimates of the resolution capabilities of NDE can be made.

-55-

INTERPRETATION OF ULTRASONIC SCATTERING THEORY FOR ANALYSIS AND DESIGN OF FLAW DETECTION EXPERIMENTS

I. LONG WAVE LIMIT

J. E. Gubernatis, J. A. Krumhansl, R. M. Thomson

SUMMARY

Recently¹ it has been shown that the results of the general theory of ultrasonic scattering, in the far field region, can be compactly represented by a vector \underline{f} . The experimental dependence on incident mode, scattering angle change in properties, and shape can be systemized thereby. In the long wave limit \underline{f} may be determined exactly, and significant features of the flaw are to be found therein. We discuss this case for both volume flaws and flat cracks. Comparison is made with some of the results of the Born (Rayleigh-Gans) approximation² which has been compared to experiment in some cases.³ The high frequency limit will be discussed elsewhere.

¹J. E. Gubernatis, E. Domany, J. A. Krumhansl (to be published).
²J. E. Gubernatis, E. Domany, J. A. Krumhansl and M. Huberman, Report #2654, Cornell Materials Science Center, also listed as ERDA #C00-3161-42.

³B. Thompson, B. Tittman: Rockwell Report

EXPERIMENTAL CHARACTERIZATION OF DEFECTS WITH ELASTIC WAVES

L. Adler, G. S. Kino, R. B. Thompson, B. R. Tittman

SUMMARY

Experimental limitations on the information available in an ultrasonic scattering experiment are summarized. Included are effects due to component geometry, material attenuation, critical flaw sizes, and wave polarizations. Within the experimentally accessible regime, the ability of existing scattering models to describe measurement regions where further work is needed are identified. Needs and some approaches towards the inverse problem, wherein defeat characteristics are estimated from measured data, are emphasized.

VARIATIONAL TECHNIQUES FOR SCATTERING AND OTHER PROBLEMS

G. S. Kino

ABSTRACT

The reaction principle of electro-magnetic theory has been used to develop new variational techniques for acoustic wave problems. This has enabled us to obtain relations similar to those of Kohn and Krumhansl, and to Nemat-Nasser for Eigen value problems.

By using this reaction principle we have derived a new type of formalism for scattering of acoustic waves from flaws in materials. The great advantage of this scattering formalism is that it makes it very clear which stress terms and displacement terms contribute to the scattering. It does not require the direct use of a Green's function technique. By simplifying the mathematics, following established principles, we can reduce the formula to a Born scattering theory, and have used it to obtain a scattering formula for the scattering of Rayleigh wave from a cylindrical hole drilled perpendicular to the surface of a metal. This formula, in the range where it should be valid appears to be in reasonable agreement with experimental results obtained by Viktorov.

-58-

We have then gone on to use the reaction principle to derive general variational formulae for scattering from arbitrary defects. These formulae are complicated. So it remains to be seen how useful they will be in their quantitative application to practical problems. However, they may be extremely useful for obtaining a qualitative feel for scattering effects.

DISCRETE MODEL FOR ELASTIC WAVE SCATTERING BY DEFECTS IN ELASTIC MATERIALS

E. W. Montroll

ABSTRACT

The development of ultrasonic flaw detection methods requires mathematical formulae for scattering of acoustical waves by the flaws in the material being examined. It is well known that the application of traditional scattering theory to scattering by defects has certain limitations. If one requires accurate expressions in the case in which the scattering center is characterized by propagation parameters far different from the normal materials, one is restricted to certain geometrical shapes of the scatterer (spheres, ellipsoids, and cylinders) for which it is possible to find a coordinate system in which the wave equation is separable. While the Rayleigh-Gans-Born approximation is applicable for any shape, it is accurate only in the limit in which the scatterer is acoustically very similar to the normal material and has dimensions which are not large compared with the acoustical wavelength.

We have developed a form of scattering theory from which computer algorithms can be prepared which yield scattering cross sections valid for unusual shaped scatterers and for scattering centers whose acoustical characteristics are far different from those of the normal material.

-60-

MOLECULAR DIPOLAR PYROELECTRICITY

W. H. Flygare

ABSTRACT

The polarization of a liquid (or solution) of cylindrically symmetric dipolar molecules is calculated according to the Onsager theory of electric moments of molecules in liquids. Then, assuming the liquid structure can be rapidly solidified (fast freezing, or matrix technique) in the presence of the electric field, the polarization is frozen in. The pyroelectric effect is then estimated on the basis of the temperature dependence of the polarization. The molecular model for the temperature dependence involves the fluctuation in orientation of the cylindrically symmetric molecule in a cylindrical potential in the solid. Quite large pyroelectric coefficients are estimated for simple dipolar molecules.

-61-

THE USE OF BUBBLE DOMAIN MATERIALS FOR SUBMILLIMETER WAVE MAGNETIC DEVICES

P. L. Richards

ABSTRACT

Several classes of magnetic materials are considered which may prove useful for submillimeter wave magnetic devices. Progress has been made recently in the preparation of large high quality crystals of two of these classes, the orthoferrites and the garnets, because of their use in bubble domain devices.

The magnetic resonance properties required for these applications include narrow resonance linewidths, and the ability to tune the resonance to the required frequency by means of changes in composition or by a magnetic field of moderate strength. These properties are difficult to achieve simultaneously, but some useful cases may be found among the rare earth substituted orthoferrites and compensated garnets. The S-state antiferromagnet M_nF_2 also has useful properties.

The use of a tuneable magnetic resonance absorption as an order sorter for a submillimeter Fabry Perot interferemeter or as a selective absorber for a thermal submillimeter wave detector is suggested. In this way it should be possible to make a magnetic field tuned spectrometer that is simple, more efficient, has higher throughput, and higher resolution than currently used tuneable submillimeter spectrometers.

-62-

HEATING EFFECTS IN HIGH-FREQUENCY METALLIC JOSEPHSON DEVICES: VOLTAGE LIMIT, BOLOMETRIC MIXING, AND NOISE

M. Tinkham

ABSTRACT

In this paper, we analyze nonequilibrium effects within a simple heating approximation for the case of metallic Josephson weak links which have a favorable three-dimensional cooling geometry. Our principal conclusions are: (1) The temperature in the center of the junction with voltage V applied is $T_m =$ $[T_b^2 + 3(eV/2\pi k)^2]^{\frac{1}{2}}$ where T_b is the bath temperature, e is the electronic charge, and k is Boltzmann's constant. This T_m can be as high as 70 K in Nb point contacts on a high Josephson step; thus the device noise temperature $T_{N} \approx \frac{1}{2}(T_{h}+T_{m})$ can greatly exceed T_{b} . (2) The critical current falls approximately as $e^{-P/P_{O}}$, where P is the power dissipated in the junction and P is typically 10 µW for Al, Sn, Pb, and Nb, but much smaller for Nb₃Sn. This leads to a decrease in the amplitude of Josephson steps at high voltages which is in good agreement with data on the best Sn variable-thickness microbridges and Nb point contacts. In a junction of optimized resistance level, the overall maximum voltage at which microwave-induced steps can still exceed the noise is predicted to be proportional to $T_{c}[\Omega\xi(0)/\rho_{o}]^{2/7}(v_{1}/T_{c})^{1/7}$, where Ω is the solid angle of the

-63-

three-dimensional cooling, $\xi(0)$ is the extrapolated coherence length at T = 0, ρ_0 is the residual resistivity of the metal, and v_1 is the microwave frequency. (3) The thermal response should be fast enough $(\sim \tau_{\rm GL})$ to allow detection (heterodyne or square-law) with bandwidth as large as the energy gap frequency; it is estimated that this bolometric detection effect will dominate true Josephson detection for carrier frequencies above ~ 3 THz (i.e., $\lambda \leq 100 \ \mu$ m) in junctions with resistance 10 Ω or less.

MECHANISTIC LIMITATIONS ON THE SPEED OF RESPONSE OF ELECTROCHROMIC OPTICAL DEVICES

R. A. Huggins

ABSTRACT

Non-volatile electrochromic devices for both analog and digital information storage and display by means of electrically controlled changes in optical reflectance or absorption are being investigated in several laboratories. Broad absorption bands in the infrared may also lead to various other types of applications.

A general description of electrochromic systems is presented, along with the principles of their operation, and the range of operating characteristics of present systems.

The physical mechanisms involved in the operation of these systems are reviewed, and the limitations upon the speed of response under several sets of limiting conditions calculated.

Requirements for the active materials in electrochromic systems and the possibilities for the development of all solid systems are reviewed.

FUNDAMENTAL LIMITATIONS ON PERFORMANCE OF PYROELECTRIC VIDICON DETECTORS

M. Tinkham and A. Yariv

ABSTRACT

Even if one were given a pyroelectric material with arbitrarily large pyroelectric coefficient and a noiseless readout system, the sensitivity of a pyroelectric vidicon system would be limited by thermodynamic fluctuations. In this paper we first treat this ideal limit, then consider the degree to which practical systems approach it, and finally analyze the potential for improvements. From our analysis we conclude that:

1. The best present pyroelectric vidicons already have sensitivities that are close to the limit set by thermodynamic fluctuations in their retinas. Thus there is probably only limited scope for improved performance by further reduction of amplifier and electron beam noise, although an improved pyroelectric material might reduce the stringency of the amplifier requirements.

2. The only direct route toward better performance is by lowering both the thermal conductance and heat capacity of the retina, essentially by making it thinner. If fabrication can be managed, it appears in principle possible to operate

-66-

with a retina as thin as \sim 1.4µm, with a \sim 25-fold increase in signal and \sim 5-fold increase in fluctuation noise relative to a 30µm retina. A 5-fold reduction in minimum detectable temperature difference would result if such a thin retina could be used. The increased responsivity would actually make amplifier requirements less stringent than in present devices.

3. Reticulation of the retina can increase spatial resolution at the expense of temporal resolution, but only a proportionate reduction of both heat capacity and thermal conductance can improve sensitivity without change of response time.

4. If much thinner retinas can be developed, it will be important to devise improved readout schemes which involve less energy deposition in the retina, in order that the full potential benefit of reducing the thermal conductance of the retina can be realized.

-67-

CLOSURE ANALYSIS IN FATIGUE CRACK GROWTH B. Budiansky, J. W. Hutchinson, J. R. Rice

ABSTRACT

Experimental studies have indicated that the purely mechanical phenomenon of crack closure may be a significant factor in fatigue crack growth. Plastically stretched asperities left behind an advancing crack tip may cause the crack to close up prior to attainment of the minimum load. During the portion of the load cycle in which the crack tip is closed, it is essentially immune to changing load. A model including crack closure under steady cyclic loading has been formulated where the load, as measured by the stress intensity factor K, varies between K_{max} and K_{min}. The model is an extension of the Dugdale model and incorporates a residual stretch δ_{R} behind the crack tip as shown in Fig. 1. First contact of the surfaces occurs a distance S_c behind the tip at a value ΔK_{c} below K_{max} . The dependence of these quantities on $\delta_{\mathbf{R}}$, together with that of the reversed plastic zone size at first contact ω_{c} ', are shown in Fig. 2. Here ω_{max} and δ_{max} denote the plastic zone size and crack tip opening displacement at K max.

The residual stretch $\delta_{\rm R}$ is determined uniquely by the requirement for internal consistency that its magnitude be such

-68-








-70-

that the surfaces immediately behind the tip are closed at K_{min} with stresses which do not exceed yield in the contact region.

Preliminary estimates have been obtained for some quantities of interest for the case $K_{min} = 0$. We find

$$\delta_{\rm R}/\delta_{\rm max} = 0.86$$
 , $\omega'/\omega_{\rm max} = 0.093$

where the value of ω' pertains to $K = K_{\min}$ and is less than one half of the corresponding value found when closure is ignored. From Fig. 2 it can be noted that first contact occurs for $\Delta K_{\rm C}/K_{\rm max} \approx 0.50$ with an associated reversed plastic zone $\omega_{\rm C}'/\omega_{\rm max} \approx 0.07$. Relatively little further reversed plastic deformation takes place after first contact. Thus the effective variation of the stress intensity factor experienced by the material undergoing reversed straining at the tip if $\Delta K_{\rm eff}$ $\simeq 0.50 \ K_{\rm max}$ for $K_{\rm min} = 0$, in accord with Elber's experimental findings.

We intend to sharpen the definition of ΔK_{eff} and then explore the effect of load ratio, K_{min}/K_{max} . Extensions to variable amplitude loadings will also be considered.

DYNAMIC ELASTIC CRACK TIP STRESSES AND DISPLACEMENTS FOR FRACTURE CRITERIA

F. A. McClintock

ABSTRACT

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 increases from 10% through a factor of 2 at speeds of 1/3 to 2/3 of 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.

-72-

COMPUTATIONAL NEEDS FOR PREDICTING PLANE STRAIN FRACTURE

F. A. McClintock

ABSTRACT

Numerical solutions in plane strain plasticity are needed to help predict fracture from small, relatively plastic or creep-fatigue types of test specimens; to predict possible improvements in alloy microstructure; and to test semiempirical fracture criteria. Plane strain is chosen to allow modeling of most of the physical mechanisms of fracture and the effects of triaxiality, because at least some analytical solutions are available, because of the feasibility but high cost of numerical solutions, and because the methods for plane strain can be easily extended to plane stress, but not necessarily conversely.

An outline is presented to help gather information for planning, coordinating, and interpreting such numerical solutions for problems involving fracture under monotonic or repeated loads.

-73-

FATIGUE CRACK GROWTH

P. C. Paris

ABSTRACT

A review is given of fatigue crack growth, with particular reference to the role of crack closure as a basis for understanding load ratio and overload effects in fatigue.

ON THE RATIO OF TENSILE STRENGTH TO MODULUS OF RUPTURE OF CERAMICS

D. C. Drucker

ABSTRACT

A direct tensile test of a brittle material, such as a ceramic, requires great care in alignment of load and specimen. Stress concentrations due to fillets and end attachments are very troublesome. It is far more convenient to perform a bend test which offers just a few easily solved problems of support and load point constraint. If the material everywhere is linear elastic to failure the modulus of rupture, Mc/I, is the tensile strength of the material in the outer region of maximum stress. A tensile specimen of the same dimensions as the beam would be expected to fail at a somewhat lower stress because the number of flaws of a given size in its surface or volume is so much greater than in the small region of high tensile stress in the beam.

The major point to be made here is not to highlight this well-known statistical effect which currently is taken into account. Rather it is to bring out equally well-known effects that nowadays tend to be ignored although they cause the modulus of rupture to be an appreciable overestimate of tensile strength. These include creep, plastic deformation, stable cracking and

-75-

and crack growth prior to final fracture. Plasticity or highly nonlinear creep leads to the well-known factor approaching 1.5, found for sintered tungsten carbide, even when so localized at the boundaries of the ceramic particles or grains as to give an apparently linear load-deflection curve to fracture. Extensive stable cracking or much larger creep rates in tension than compression shifts the neutral axis and can give ratios of modulus of rupture to tensile strength as high as 2 or 3 in extreme cases.

HIGH STRENGTH OPTICAL FIBER

R. L. Coble

ABSTRACT

For the programs underway, emphasis has been placed on glass fibers and claddings; support of the development of crystalline fiber is warranted because:

1) Crystalline Al_2O_3 fiber (1 to 125 mils diameter) has been grown continuously at rates up to 200"/hr (at a net cost that is regarded as competitive with other high modulus reinforcement);

 The intrinsic attenuation is lower for crystalline fiber;

3) The susceptibility of Al_2O_3 to strength degradation due to handling or to static fatigue due to water vapor corrosion is much lower than for silicate based glasses (the average strength achieved in uncoated Al_2O_3 fiber after handling was +900 Ksi in a humid atmosphere).

An analysis of cost projections with equipment designed for production (rather than laboratory operation) is needed, and an investigation of purification effects on increased growth rates and reduced attenuation losses is warranted because positive results can be expected for both if this program is pursued. Growth of crystals other than Al_2O_3 which are more amenable to the development of graded indices of refraction should also be supported (e.g. MgAl₂O₄).

-77-

HIGH STRENGTH OPTICAL FIBER A. G. Evans, F. A. McClintock, R. L. Coble

ABSTRACT

The high strength optical fiber development programs have in common a lack of agreement between the strength tests on short fiber and the strength exhibited in long lengths; the strengths in short lengths being greater than that found in desired service lengths. It is not now known whether this discrepancy arises from: 1) inadequate assessment of the low stress probabilities of failure because of small sample sizes; or 2) a second flaw population not related to the sources of those which govern the small sample strengths; or 3) aging effects; or 4) further damage sources in proof testing, handling, cable fabrication, or early service testing. Of this group, positive approaches toward answers can be made to several of the problem areas, while the possible entry of unrecognized variables precludes definitive analysis of the remainder.

 State-of-the-art statistical analysis techniques and test techniques to generate the Weibull parameters are straightforward for determination of whether the short versus long length samples' flaw populations are single/bimodal.

2. Fracture of the longer lengths takes place at low

-78-

stress levels such that the specimen does not disintegrate. Both ends of the samples at each break should be collected for fractography; examination of the fracture surfaces to trace to the origin and inspection for inclusions, pores, surface particles, or surface irregularities, and beam probe analysis of the fracture surfaces and origins should reveal whether extraneous matter is responsible for the problem.

3. Aging effects only arise with flaws present, imposed tensile stresses, and a corrosive environment. In this case, the generally unspecified histories of sample handling, storage and cable winding from past data can not be unravelled. However, procedures for these operations can be designed to ameliorate the conditions such as to reduce strength degradation in aging.

4. Other possible damage sources are not specified except for those which might arise in proof testing: stick-slip on the capstans used in continuous testing, and damage due to flaw growth during unloading. Both could be eliminated by 1) making the capstan surface very compliant (tangentially) and 2), proof testing in liquid nitrogen, respectively.

-79-

STRUCTURAL RELIABILITY OF OPTICAL FIBERS A. G. Evans and F. A. McClintock

ABSTRACT

When optical fibers are fabricated in very large lengths (~l km), a significant proportion of failures are commonly encountered at relatively low stress levels. It is important that these failures either be statistically predictable or be eliminated by proof testing.

Methods for characterizing strength distributions in optical fibers from tensile tests on relatively short fiber lengths are described; and the use of such distributions for predicting failure on long lengths of fiber, subjected to axial strains and localized bending moments, is discussed. Also, the role of strength distributions as the isolation of defect origins is indicated.

The proof testing of optical fibers to truncate the strength distribution at an appropriate strength level is an attractive possibility. However, proof testing in environments that cause significant slow crack growth does not necessarily produce the desired truncation. The key relationships between the proof test cycle and the resultant strength distribution are thus described, to provide a rationale for devising effec-

-30-

tive proof cycles. Alternatively, proof testing might be conducted at temperatures, \leq -100°C, where slow crack growth does not occur. Heat transfer through coated optical fibers has been evaluated to demonstrate the feasibility of proof testing at such temperatures. ULTRASONIC FLAW DETECTION IN CERAMIC TURBINE COMPONENTS G. S. Kino and A. G. Evans

ABSTRACT

Several types of surface and internal defects can be created in the fabrication of complex ceramic components such as turbine rotors. Certain of these defects should be amenable to detection by ultrasonic waves. Hence, short and long term ultrasonic approaches that might be used to detect such defects in both the preform and sintered condition are discussed. For short term requirements, primary emphasis is placed on the detection of relatively large flaws using existing circuitry in conjunction with single transducers designed to induce either surface or bulk waves in the 2 to 20 MHz range. For longer term problems, the potential of multi-transducer B-scan and imaging systems for use at frequencies up to ~400 MHz are explored.

-82-

PROSPECTS FOR SUPERPLASTICITY IN CERAMICS A. G. Evans and R. L. Coble

ABSTRACT

The deformation characteristics of polycrystalline ceramics have been examined in order to determine the prospects for attaining superplasticity. The stress dependence of the deformation rate (m) for most ceramics appears to exhibit a useful range of temperature and stress wherein plastic stability $(m \ge 1)$ should be realized. However, the deformation of typical ceramic polycrystals (within this regime of stress and temperature) in the presence of a tensile stress is invariably accompanied by the formation of cracks or cavities. Three approaches have been identified that might limit this crack development; (a) the use of a multiphase system which forms a large proportion of viscous phase at the deformation temperature, (b) the application of hydrostatic compression in the forming process, (c) the design of microstructures that optimize the microstructural size, the coefficients of diffusion and the grain boundary viscosity. The latter approach, which is the most desirable in terms of both forming facility and material quality (creep and fracture resistance) after superplastic deformation has been examined in detail, leading to suggestions for microstructural design studies that might result in tensile superplasticity.

-83-

CERAMIC TURBINE PROGRAM

R. L. Coble

ABSTRACT

The Ford ceramic turbine demonstration program will fail unless defects generated in fabrication can be eliminated from all parts or a NDE or early proof test technique can be used to identify parts that are free from defects to be processed through sintering, hub-bonding, spin testing, and finally, engine testing. Improved grinding and cleaning procedures for the powder, and an emphasis on avoidance of contamination in processing are essential to eliminate inclusions larger than the particle size that is basic to the Si_3N_4 chemistry. Other fabrication flaws which originate from injection molding may be surveyed in the as-fabricated condition by suspension of the parts in a variable density liquid column or a temperature controlled liquid with a density that matches the as-fabricated parts. These should help to identify the presence of low density regions in the parts that evolve into large fabrication voids upon sintering. Alternatively, spin testing after burnout of the polymer used for injection molding could also be used to eliminate samples with undesirable fabrication voids from the population.

-84-

To assist in the identification of fabrication flaws, fractography should be applied to all samples previously broken (when possible) and also to other finished test samples or components after destructive testing. Binocular optical microscopy with a diffuse light source and scanning electron microscopy, coupled with beam-probe analysis of identifiable inclusions, should be used for tracing back to the sources of extraneous included matter. Otherwise, the shapes and sizes of holes, pores, or cavities and any change in the local grain size or pore distribution near the fracture source in comparison with the average (good?) matrix microstructure should be noted.

FRACTURE MECHANICS AND THE STATIC FATIGUE OF STRONG SILICA FIBERS

D. C. Drucker

ABSTRACT

An explanation is proposed to resolve a troublesome paradox reported by John Ritter. Fracture mechanics concepts provide a consistent correlation of the tensile strength of very strong silica fibers with their time to failure in static fatigue at lower stress. Similar consistency is found for conventional fracture mechanics specimens with purposefully introduced macrocracks. The embarrassing paradox arises when the data obtained from macrocracked specimens is applied to the fibers; the static fatigue lifetimes as predicted from their tensile strength are many orders of magnitude too long and the exponent -N of the stress dependence is -35 instead of -20.

The explanation offered here is that the very small surface microcracks or equivalent defects cause the effective stress intensity factor K_e at the surface of the fracture mechanics specimen to be appreciably higher than the K for the macrocrack itself. Rapid brittle fracture occurs under continually increasing load when K_e , not K, reaches the critical value of K_{Ic} . However, it is K and not K_e that controls the

-86-

slow advance of the macrocrack in the long static fatigue lifetimes regime. A hidden or ignored ratio of $K_e/K=2$ would appear as (2)^N in the expression for time to failure, and give the consequent enormous overestimate (or order 10^{10}) of static fatigue lifetime of the fiber based on its tensile strength. It also would account for the apparent increase in N, and so fully reconcile the static fatigue lifetime data from the strong fibers and the fracture mechanics specimens.

THERMAL STABILITY OF CFX IN FLUORINE

P. Kamarchik and J. L. Margrave

ABSTRACT

The thermal decomposition of CFX (carbon monofluoride of variable stoichiometry) has been studied over a range of temperatures in vacuum, in O_2 , in N_2 and in F_2 . Also, the products c decomposition have been collected and characterized by matrix-isolation spectroscopy. In vacuum or in N_2 the decomposition proceeds extensively at 500-600°C to yield mainly C_2F_4 (gas) with smaller amounts of CF_4 (gas), C_2F_6 (gas) and C_3F_8 (gas). In the presence of O_2 , some COF_2 is also formed which dissociates to CO_2 and CF_4 .

In the presence of F_2 , solid CFX decomposes very slowly even at 800°C. It appears that F_2 at a level of only 1-2% is sufficient to suppress CFX decomposition. Thus, solid carbon or graphite objects with a CFX protective layer should be useful in the presence of elemental fluorine at temperatures of 01000°C.

-88-

REACTIONS OF Li ATOMS IN LOW TEMPERATURE MATRICES

C. Krishnan, P. Kamarchik, P. Meier, R. Hauge and J. L. Margrave

ABSTRACT

In matrices of Ar, N₂, O₂, etc., at low temperatures one can observe electron-transfer processes involving Li, Na, K, etc., as electron donors via IR, Raman and ESR spectroscopy. Thus, in the presence of CO one observes CO⁻, C₂O₂⁻, and C₂O₂⁼. This latter ion $(O-C=C-O)^{=}$ is of considerable potential as a starting material for organic syntheses.

With $\rm H_2O,~H_3N$ and various amines, one observes partial charge transfer and reactions like

Li + H H $\rightarrow 0$ ---H H $\rightarrow 0$ + Li $\rightarrow 0$ + H

With C_2H_4 , C_2H_2 and various C_2H_3X species there is partial charge transfer and, in some cases, halogen abstraction to form LiX and a hydrocarbon radical.

ESCA STUDIES OF FLUORINATED PVC AND CFX G. Parks and J. L. Margrave

ABSTRACT

ESCA studies of CFX samples of various stoichiometries have failed to show any evidence for intercalated F or F_2 in the layered structure. Only -C-F and CF₂ types of fluorine were identified.

The reaction of F_2 with thin films of polyvinyl chloride has been monitored by ESCA. The hydrogens are successively replaced and after long fluorination, the polymer is converted to $\{C_2F_3Cl\}_{x}$; no chlorine is displaced.

CHLOROFLUOROCARBON UPDATE, 1976

J. L. Margrave

ABSTRACT

In order to allow a reliable evaluation of the potential effects of chlorine-containing molecules being introduced by man into the atmosphere there have now been several sampling studies at various levels to establish the concentrations of CCl_4 , CCl_2F_2 , CCl_3F , HCl, etc., as quantitatively as possible.

There is still evidence for both a natural origin and a natural sink for CCl₄. Also, HCl and CCl₄ can result from high temperature reactions in fumaroles and volcanos. A new molecule, HCOCl, some ionic clusters and the ClO ion have been studied quantitatively. The importance of carbenes in the upper atmosphere is still unknown.

When the available data are inserted into the ozone layer model calculations, it is still not possible to make definitive statements about the relative effects of natural and anthropogenic chlorine on the ozone layer thickness. As a first iteration, it now appears that "natural" CCl₄ and the surprisingly high HCl concentrations in the stratosphere tend to reduce the threat to the ozone layer by anthropogenic chlorine. It is obvious that there is still a lot of unknown chemistry of the atmosphere to be elucidated.

-91-

SOLID SOURCES OF ELEMENTAL FLUORINE

I. THERMAL STABILITIES OF SOLID PERFLUORIDES AND SUPERFLUORIDES

J. L. Margrave

ABSTRACT

Various possible interactions of elemental fluorine with ionic or covalent fluorides to provide $\{F-F\}$ (perfluoride) or $\{F-F-F\}$ (superfluoride) character are considered from the viewpoints of thermodynamic cycle and bond energy arguments. Preliminary calculations suggest that ionic solids like $(K^+; F_2^-)$ or $(K^+; F_3^-)$ are likely to be stable enough to serve as practical sources of $F_2(gas)$ when heated moderately.

The perfluorination of electron-deficient molecules like BeF_2 , BF_3 , AlF_3 , etc., to yield perfluoro-species is energetically favorable. For example, the following molecules

- (a) $F_2Be = F_2BeF_2$
- (b) F₃B---F-F---BF₃
- (c) F₃Al---F-F---AlF₃

are thermodynamically stable and should decompose to yield F_2 (gas) at temperatures in the 500-1000°C range.

A perfluoro-bridge between two HF molecules is also energetically and structurally acceptable.

-92-

SOLID SOURCES OF ELEMENTAL FLUORINE II. THERMAL STABILITIES OF TERNARY FLUORIDES J. L. Margrave

ABSTRACT

The interaction of binary fluorides involving an alkali fluoride and the highest oxidation state fluoride of either Group V elements (P, As or Sb) or Group IV elements (Si, Ge, Sn or Pb) leads to two families of ternary compounds:

 MAF_6 where a = a Group V element and M = a univalent cation M_2BF_6 where B = a Group IV element and M = a univalent cation

the A and B elements have multiple oxidation states and reactions like

 $\begin{aligned} & \text{MAF}_6(\text{solid}) = \text{MAF}_4(\text{solid}) + \text{F}_2(\text{gas}) \\ & \text{M}_2\text{BF}_6(\text{solid}) = \text{M}_2\text{BF}_4(\text{solid}) + \text{F}_2(\text{gas}) \end{aligned}$

occur according to recent mass spectrometric studies.

Thermodynamic data to evaluate the equilibria quantitatively are only estimated but experimental data show that $KAsF_6$ and $KSbF_6$ do yield appreciable elemental fluorine when heated at 300-500°C. Also, M_2SnF_6 , M_3FeF_6 , etc., can be formed and should yield elemental fluorine when heated.

-93-

Solid materials like these should be practical field sources of fluorine for H_2/F_2 lasers and an optimum material can be selected on the basis of economic, chemical and engineering criteria.

VERY RAPID QUENCHING WITH THERMAL SPIKES G. H. Vineyard

ABSTRACT

When a heavily ionizing particle such as a fission fragment passes through matter, a process of rapid heating followed by rapid cooling occurs in the neighborhood of the track of the particle. In radiation damage this effect is called a thermal spike. It is suggested here that this process of very rapid cooling may be of interest as a means of studying the effects of ultra rapid quenching in alloy systems, and possibly even of processing material. The process is examined quantitatively. For a fission fragment in a metal of moderate atomic weight such as iron, temperature rises of more than 500°C are predicted to occur inside a cylinder 200Å in diameter and quench rates inside this cylinder are calculated to exceed 10¹² °C/sec.

-95-

NUCLEATION, UNDERCOOLING AND HOMOGENEOUS STRUCTURES IN RAPIDLY SOLIDIFIED POWDERS

J. P. Hirth

ABSTRACT

The possibility is considered that sufficient undercooling of powder particles can be achieved to result in a microstructure consisting of homogeneous microcrystallites. A relation is developed for the maximum achievable undercooling for comparison with the undercooling required for such homogeneous powder. Sample calculations for the case of mercury, where homogeneous nucleation data are available, show that it is possible to attain such undercoolings.

From a practical viewpoint, the results show that effort to achieve even greater rates of cooling would be worthwhile. Also, they indicate that in addition to cooling rate, attention should be directed to decreasing impurities and other heterogeneities which would tend to cause heterogeneous nucleation and prevent the attainment of the maximum possible undercooling.

-96-

CURVATURE EFFECTS IN THE THERMODYNAMICS OF MULTICOMPONENT SYSTEMS: POSSIBLE EFFECT ON DENDRITE SPACING IN RAPIDLY COOLED SMALL LIQUID METAL DROPS

H. Reiss

ABSTRACT

It is shown that the chemical potential of a component of a small drop, crystal, or crystal dendrite, contains a previously overlooked term if the drop of crystal is multicomponent. The new term involves the derivative of the surface tension with respect to the mole numbers of the component in question, and becomes negligible for drops or crystals of macroscopic dimensions. On the other hand, for small systems the equilibrium between the drop or crystal and the surrounding phase may be severely affected by the new term.

This can have important implications for the aging of a precipitate (Ostwald ripening) or for the fine grained dendrite structures found in rapidly cooled (10⁵deg/sec) small liquid metal drops. Such dendrite structures age by a process similar to Ostwald ripening.

A model system is introduced in connection with which illustrative calculations can be, and are, made to demonstrate the magnitude of the new effect.

-97-

RAPID-SOLIDIFICATION PROCESSING (RSP) OF THERMOELASTIC ALLOYS M. Cohen

ABSTRACT

In some alloy systems, the strain energy accompanying the displacements of martensitic transformations on cooling can be accommodated elastically in the alloy, and this becomes available to help drive the reverse transformation on heating. Except for some hysteresis, a thermoelastic balance is set up between the chemical driving force and the stored elastic energy. These thermoelastic systems exhibit rubberlike behavior on loading and unloading because the applied stress shifts the thermoelastic balance; in other words, the operation of martensitic shears on loading and the reverse transformation shears on unloading result in extraordinary stress-strain characteristics for metallic systems.

One of these alloys is Cu-14Al-3Ni, which is relatively inexpensive and could be commercially feasible, but it suffers from undue brittleness arising from grain boundary precipitates occurring on cooling of the parent phase to room temperature. This undesirable precipitation cannot be inhibited in bulk materials, even by the most rapid quenching, but may well be suppressed or rendered innocuous by RSP methods. If the pre-

-98-

cipitation happens to take place during the consolidation step, it is not likely to be intergranular and hence should not cause embrittlement. Another limitation of conventional Cu-Al-Ni alloys is that they are typically coarse grained and do not respond to grain refining treatments. In contrast, the RSP approach should lead to ultrafine grain sizes with beneficial effects on the mechanical properties, and thus provide a superior base for the thermoelastic behavior.

A KEY BOTTLENECK IN THE EXPLOITATION OF RAPID-SOLIDIFICATION PROCESSING (RSP)

M. Cohen

ABSTRACT

A case is made for the implementation of flexible, small scale RSP powder making facilities in order to extend and diversify research and development on many materials systems, particularly in the direction of structural control and structure/property relationships. The availability of such equipment, preferably adaptable to laboratory operation and not necessarily of a single design, is likely to do as much as anything else to expand the understanding and applicability of RSP materials. Moreover, the full benefit of RSP technology will inevitably require detailed studies of numerous parameters and their optimization, e.g., compositional variables, solidification rates, consolidation steps, and heat treatments. This type of development will likewise depend on ready access to small quantities of RSP powders.

Under these circumstances, it would be desirable for ARPA to elicit proposals for several types of small lot (1/4-10 lbs.) RSP powder making machines with designated versatility for a range of materials. These proposals could be aimed at either the design and construction of the equipment in question or at the operation of central facilities for supplying the necessary RSP materials on request.

-100-

COMMENTS ON ALTERNATIVE METHODS THAT MIGHT BE USED TO PREPARE SUPERHOMOGENEOUS-FINE PARTICLES OF METALS

R. A. Huggins

ABSTRACT

There is certainly greatly increased interest in the preparation of bulk materials by consolidation of fine particles. In some cases, fine particles provide superplasticity, and thus aid densification processes. In others, microstructural homogeniety can be greatly enhanced in a final product fabricated from particles with fine internal microstructures which resulted from rapid cooling of small particles from the melt.

This latter point is of special importance, and a great deal of effort is being expended on techniques for the production of fine metallic droplets and their rapid quenching in order to obviate the segregation processes that normally accompany solidification of multicomponent liquids.

This memo points out other approaches that might be considered for the preparation of superhomogeneous metallic particles, based upon various relatively low temperature techniques for the production of solid particles from liquids containing metal cations of desired ratio which are mixed on a molecular scale. In some cases, these methods have been developed for applications in other areas, such as food processing and the preparation of certain high performance ceramics.

-101-

SMALL PARTICLE TECHNOLOGY

R. L. Coble

ABSTRACT

Vaporization of candidate super alloys should be used to produce homogeneous small crystallite sized powders for HIP processing in order to show what limits in property improvements can be achieved from the ultimate possible dispersion of the constituents in the starting powder.

THEORY OF DENDRITE SOLIDIFICATION DURING VERY RAPID COOLING

M. C. Flemings

ABSTRACT

A discussion is first given of heat flow in cooling and solidification of atomized liquid droplets. At high relative velocities between particle and gas, extremely rapid cooling and solidification rates are possible. At least to moderately high cooling rates (perhaps 10^{4} °C/sec or higher) solidification of alloy droplets can probably be described by simple classical expressions and the relation between dendrite arm spacing and cooling rate can be understood using concepts developed from solidification studies on samples cooled at 10^{2} °C/sec and lower.

At higher cooling rates the "classical" approach is probably not applicable and different types of structure and segregation behavior are expected.

-103-

PRESSURE IN A SPHERICAL CAVITY OR ON A SOLID SPHERE IS LIMITED BY INSTABILITY

D. C. Drucker

ABSTRACT

Hope has been expressed that truly enormous pressures can be contained in a spherical cavity or applied to a solid sphere through brute force or a clever variation of the autofrettage techniques used in gun barrels and high pressure devices. Certainly, no matter how high the pressure, mechanics solutions can be written down that satisfy the stress-strain relations for elastic and plastic material along with the equations of equilibrium and compatibility. For example, calculated maximum pressure p_a for a cavity of radius <u>a</u> in a fully plastic sphere of outer radius b is $2\sigma_y \ln(b/a)$ assuming a perfectly plastic material with yield strength σ_y . In principle, b and therefore p_a can increase without limit.

However, this result is misleading because the equilibrium configuration is unstable beyond a limiting pressure. The analogy is to a long column under axial compression. All the equations are satisfied by a solution which takes the column to be perfectly straight and under uniform compressive stress. Yet a long column will buckle well before the yield

-104-

strength is reached. Similarly, the radius <u>a</u> of the spherical cavity will increase indefinitely once a limiting pressure is reached. The equilibrium solution for higher pressures is unstable. A contained solid sphere under higher pressure would expand outward until the pressure dropped to the limiting value.

An easily found upper bound to a continually increasing pressure is

$$p_{a} = \frac{2}{3}\sigma_{y}\left[1 + \ln \frac{E}{(1+\nu)\sigma_{y}}\right]$$

which, when Poisson's ratio is 1/2, agrees with Hill's form for the pressure needed to expand a spherical hole in an infinite body

$$p_{a} = \frac{2}{3}\sigma_{y}\left[1 + \ln \frac{E}{3(1+\nu)\sigma_{y}}\right]$$

Work hardening increases the limiting pressure somewhat but the maximum pressure that can be contained in most materials is less than $5\sigma_v$.

The result for a cylindrical cavity is a somewhat smaller but comparable pressure. Of course, practical difficulties of any construction will reduce the maximum pressure appreciably below the theoretical limit.
A FLUID THERMAL SWITCH

H. Reiss

ABSTRACT

A phenomenon observed in a diffusion cloud chamber in which two states of apparently stable thermal conduction have been observed when the same temperature gradient is impressed across a thin layer of liquid and a thicker layer of gas in contact with it is analyzed conceptually. Although the system is heated from below, the gas remains mechanically stable while the liquid undergoes cellular convection. It is shown that such thermal "switching" is possible if the effective thermal conductivity of the liquid layer possesses a region of negative slope (with respect to temperature gradient impressed across the liquid). Furthermore, the two states of thermal conductivity will then be locally stable.

The switching is thought to be connected to a transition between one mode (excitation) of cellular convection and another. Switching in the cloud chamber is associated with fairly violent cooling (as in boiling) of the liquid layer.

TIGHT BINDING THEORY OF METALLIC ADHESION W. Kohn and R. Gomer

ABSTRACT

Metallic interfacial energies, e.g., grain boundary energies or adhesive energies between identical or different metals are of great importance in materials problems such as adhesion, wear, crack growth and strength of multiphase alloys. To our knowledge this problem has so far only been attacked in terms of the density-functional formalism which is suitable mainly for simple, i.e., non-transition metals. We have attempted to formulate the theory of interfacial energy between two (identical or different) metals in tight binding approximation for the case of simple cubic lattices without mismatch. For this purpose each infinite bulk phase and each phase including a surface are first treated using a Hartree Hamiltonian (i.e., neglecting exchange and correlation) and are then allowed to join. Particular attention is paid to self consistency which gives rise to dipole layers at the surface and at the interface. The latter dipole potential is essential for establishing a common Fermi level in the system.

This provides the groundwork for an explicit calculation of interfacial energy, by the method of moments of the density

-107-

of states. A model calculation for the case of two half-filled bands, limited to second moments, is carried out.

The parameters entering the theory consist of the diagonal and nearest neighbor off-diagonal matrix elements of the Hamiltonian. The terms relevant to the interface consist of a hopping integral coupling atoms of the two different metals and two modified diagonal shifts. For many applications the hopping integral will be the important parameter. It can be estimated from the corresponding integrals for the bulk metals and the overlaps of nearestneighbor wave functions within each metal (a) and (b) and between (a) and (b) atoms at the interface. It seems probable that it can be obtained from monolayer adsorption measurements.

It is expected that these calculations can be extended to fcc and bcc structures and that mismatch at the interface can also be taken into account.

EFFECT OF ELECTROLYTE ON DIPOLE LAYER POTENTIALS AT A LIQUID-SOLID OR LIQUID-AIR INTERFACE

R. Gomer and H. Reiss

ABSTRACT

Recent experiments in R. Gomer's laboratory measure absolute half cell emfs to within the uncertainty posed by the possible existence of a dipole layer at an H20-air interface which would cause the electrostatic potential in the interior of the H2O phase to differ from that at its free surface. Such a dipole layer has been postulated on the grounds that the total free energy of the H2O phase could be lowered by non-random orientations of H2O molecules near the surface. A knowledge of absolute half cell emfs is of importance to electrochemistry in general; it provides absolute Gibbs free energies of hydration for single ions and also allows some estimate of electric fields at electrode surfaces. It is therefore also very relevant to corrosion research. It is therefore of some interest to explore the existence of the putative potential near the water-air interface. Such a potential would tend to be screened out by mobile charge, i.e., by the presence of an electrolyte, and this screening should be a function of Debye length, L, i.e., of (electrolyte concentration) -2. Thus, a variation of experimental half cell emfs with total electrolyte concentration should give some

-109-

information on whether there is an appreciable potential difference between the free surface and the interior of liquid H_2O .

We have calculated the effect of an electrolyte on the layer potential, which amounts to solving the Poisson-Boltzmann equation for this case. The linearized equation could be solved analytically for the cases of a fixed dipole layer potential of dipole length λ and a potential decaying exponentially into the liquid of form $V_0(z) = V_0 e^{-z/\lambda}$. The results are similar, and for the second case take the extremely simple form

$$V(0)/V_{0} = a/(a+1)$$

where V(0) is the potential at the liquid surface after elecrolyte addition and $a = L/\lambda$.

The non-linear case was solved by computer by M. Mandel, working with H. Reiss at UCLA. The results are virtually identical with the linear solution up to $V_0g/kT \leq 10$, for small values of a, a ≤ 0.5 , but show more screening as V_0 and an increase.

These results indicate that a strong effect on the putative dipole layer potential at the air-H₂O interface should be observed when the electrolyte concentration is varied in the range 1-0.01 M <u>if</u> the dipole layer length $\lambda \ge 10$ Å, which must almost certainly be the case.

These results are also relevant to potential drops existing at solid electrode-liquid H_2^0 interfaces. However, it should be noted that a basic difference exists in the latter

-110-

case if the potential drop is an equilibrium potential difference, fixed by thermodynamics. In that case the presence of an electrolyte cannot screen out the potential, since the system will adjust itself to maintain the equilibrium value.

Finally, the possibility of a dipole layer arising from the electrolyte itself was investigated. This could come about if the change in solvation energy as ions approach the surface differs for cations and anions because of their different sizes. It turns out that this effect is negligible if the full dielectric constant of H_2O is maintained up to the surface. If K is reduced from 80 to 4, a potential of 80 meV for c = 0.1M could result, but would decrease very rapidly with decreasing electrolyte concentration.

A MECHANISM FOR LIQUID PHASE EPITAXIAL GROWTH OF NONEQUILIBRIUM COMPOSITIONS PRODUCING A COHERENT INTERFACE

J. P. Hirth and G. B. Stringfellow

ABSTRACT

A model is presented for growth by so-called pulling, wherein an epitaxial deposit grows coherently but with a composition different from that which would be in bulk equilibrium with the liquid phase from which growth occurs. The breakdown of coherent growth occurs when a dislocation nucleates at a ledge at the growing solid-liquid interface. An expression for the critical condition for breakdown is presented.