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THE MATERIALS PROCESSING RESEARCH BASE
of the
MATERIALS PROCESSING CENTER

submitted by

MERTON C. FLEMINGS, DIRECTOR
MATERIALS PROCESSING CENTER
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139

submitted to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
400 MARYLAND AVENUE S.W.
WASHINGTON, D.C. 20548

ANNUAL REPORT FOR FY 1981

PREPARED UNDER GRANT NO. NSG 7645

(NASA-CR-169096) THE MATERIALS PROCESSING RESEARCH BASE OF THE MATERIALS PROCESSING CENTER Annual Report for FY 1981 (Massachusetts Inst. of Tech.) 295 p HC A13/MF A01 CSCL 11G G3/23

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Massachusetts Institute of Technology
Materials Processing Center
Cambridge, Massachusetts 02139
Tel. (617) 253-3233

June 28, 1982

Dr. Louis Testardi, Manager
Materials Processing in Space Office
NASA Headquarters, EN-1
600 Independence Avenue
Washington, D.C. 20546

Dear Lou,

Enclosed is the Fiscal Year 1981 Annual Report of the Materials Processing Center to the National Aeronautics and Space Administration for Grant No. NSG-7645 which is entitled "The Materials Processing Research Base of the Materials Processing Center." Three (3) copies are enclosed and two (2) copies have also been sent to the NASA Scientific and Technical Information Facility.

The Annual Report is presented in four (4) sections beginning with a description of the Materials Processing Center and summary of structure, goals, and current activities. Section II reports on the initiation of the Materials Processing Center/Industry Collegium, which now has more than thirty (30) industry members. Section III reports on the specific research activities within the thrust areas of nucleation and rapid solidification, fluid flow in crystallization processes, and adaptive materials processing which are supported by NASA Grant NSG-7645. Section IV outlines the overall materials processing activities at Massachusetts Institute of Technology, many of which benefit either directly or indirectly from the NASA supported activities, and vice versa.

The Materials Processing Center continues to enjoy much success and has a current total research volume in excess of $3 million per year. Substantial progress has been made in broadening the scope of interaction with industry with the formation of the above mentioned Collegium. This Collegium not only provides a forum for direct interaction with industry, but will also provide fellowships, seed funds for research projects, etc. Our success to date is directly attributable to the founding and continuing support of NASA, for which we are very grateful. We look forward to continued collaboration with NASA.

Sincerely yours,

Merton C. Flemings

Professor Merton C. Flemings, Director
Room 8-407

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encls.

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MATERIALS PROCESSING CENTER

School of Engineering

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Cambridge, Massachusetts 02139

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I. INTRODUCTION AND SUMMARY

THE MATERIALS PROCESSING CENTER

This is the second annual report of the Materials Processing Center, describing activities during calendar year 1981. Our activities grew greatly during this second full year of the Center's existence. Total funding of the Center grew to an annual rate of $3.5 Million, and we are particularly pleased that of this total, approximately $800,000 is funding by industry.

A generous gift from Toyota Motor Company to MIT established the endowed Toyota Professorship of Materials Processing, which has been awarded to the Center Director, Professor M. C. Flemings. The Associate Director of the Center, Professor H. K. Bowen, has been awarded the endowed Ford Professorship of Engineering. In addition, Norton Company has provided funds for three years to permit hiring an Assistant Professor of Materials Processing, and a search for this new faculty member is underway.

A major step of the Center has been to institute the Materials Processing Center/Industry Collegium, which is described in detail in a separate section of this report. The central aim of this Collegium is to provide a mechanism for improved interaction of MPC faculty, staff, and students with industry. This Collegium is now underway and is operating in close cooperation with MIT's Industrial Liaison Program.

The central thrust of activities of the Materials Processing Center remains the transition or "action" stages of the well-known "Materials Cycle" (see Fig. 1). These comprise extraction, processing into bulk materials, processing into engineering materials, fabrication, recycling, and disposal.

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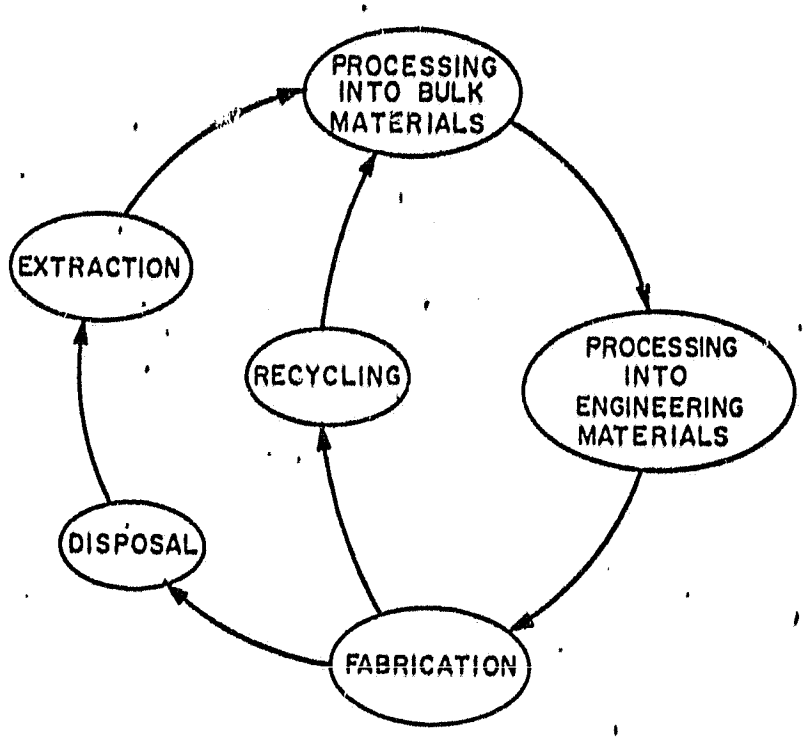

Figure 1: Materials Processing steps, as transition stages in the Materials Cycle. (Taken from the "Materials Cycle" of the Cosmat Report, Materials and Man's Needs)

We continue to view Materials Processing as the engineering field that seeks to control structure, shape, and properties of materials, and to do so in a cost effective way with acceptable social costs. It lies at the heart of the broader field of Materials Science and Engineering, linking basic science to societal need and experience (see Fig. 2).

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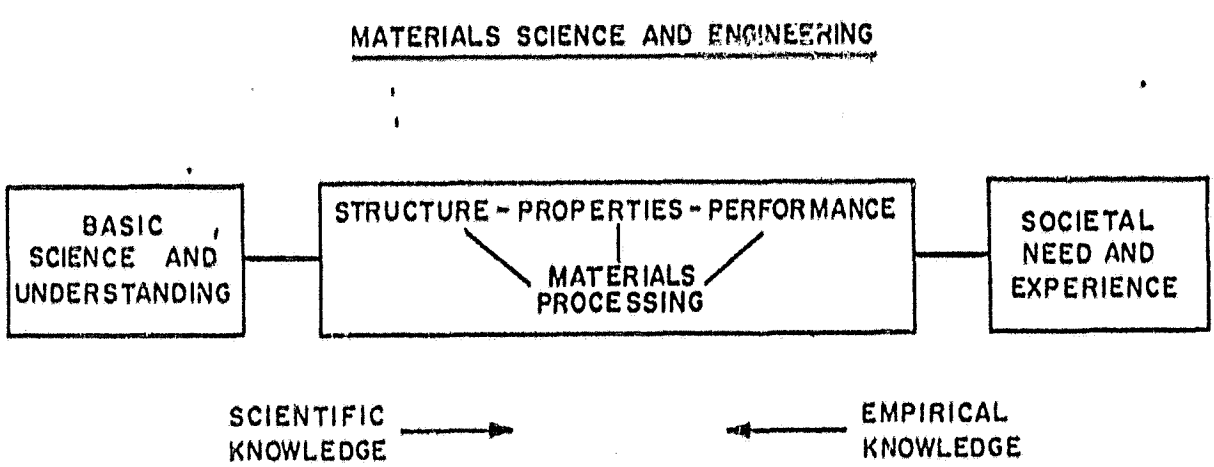

Figure 2: Materials Processing as part of Materials Science and Engineering

CURRENT CENTER ACTIVITIES

The Materials Processing Center is organized to enable it to conduct, or facilitate conduction of, three specific types of research programs: (1) discipline oriented research problems of the type ordinarily conducted by an individual faculty or staff member, and his associates and students, (2) technologically related problems that are so broad in scope that they require effective focused cooperation of a team of faculty or staff members, and (3) development of processing "science" or a "materials processing base" that cuts across traditional disciplinary and materials boundaries.

The current annual operating budget for the Center is $3.5 million dollars, of which approximately 0 comprises the central "nucleus" of a broad based grant from the National Aeronautics and Space Administration. Table I lists the programs of the Center. These cover a wide range of activities that fall within four central thrust areas of the Center -- areas which the Center views as being at the

heart of its research charter. These are:

- Process innovation and development of new materials through processing.
- Mathematical and experimental modeling of processes
- Computer aided processing.
- Economic issues relating to materials processing.

The research programs of the Center, listed in Table I involve 19 faculty members, 58 graduate students, 21 and staff members. Industrial interaction is a keystone of the Center and a number of programs within the Center involve such interaction. Approximately $800,000 of the Center's funding is provided by industry.

INDUSTRIAL ADVISORY BOARD AND THE CENTER INAUGURATION

Our Industrial Advisory Board, comprised of industrial leaders in materials related industries, continues to be essential in its role of advising the Center. The members of this Board and their affiliates are listed in Table II. The Board held its second meeting on March 5, 1981 and submitted a report of its conclusions and recommendations to the Dean of Engineering. An annual meeting is planned.

TABLE I

Materials Processing Center
Massachusetts Institute of Technology
Research Projects

Title	Funding Agency	Principal Investigator
Adaptive Materials Processing; Computer Aided Materials Processing; Basic Processing Thrust Development	NASA	Flemings
Rapid Cooling Effects in Polymers	NASA	McGarry
Polymer Melt Processing Operations	NASA	Roylance
High Quench Rate Processing	NASA	Grant
Studies of Metals Electroprocessing	NASA	Sadoway
Fluid Flow in Crystal Growth	NASA	Brown
Adaptive Control of Welding	NASA	Eagar
Fluid Flow in Crystallization Processing	NASA	Witt
Rapid Solidification of Microcrystalline Alloys	NASA	Yurek
Automation of the Laser Induced Gas Phase Powder Synthesis Process	NASA	Haggerty
The Oxidation Behavior of Rapidly Solidified Microcrystalline Alloys	NASA	Yurek

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TABLE I (cont'd)

Title	Funding Agency	Principal Investigator
Soft Ferromagnetic Alloys	NASA	Allen
A Basic Study of the Role of Convection in Grain Refining	NASA	Flemings, Szekely
Heat Flow Control and Segregation in Directional Solididification	NASA	Witt
Mathematical and Physical Modeling of the Electroslag Remelting Process	NSF	Szekely
Hitachi Grant to Ceramics Processing Laboratory for Fellowships, Equipment	Hitachi	Bowen
High Purity Manganese by Fused Chloride Electrolysis	NSF	Sadoway
Processing Ceramic Magnets	Delco	Bowen
Howmet Turbine	Howmet	Grant
Processing of Zinc Oxide	Intern'l Lead Zinc	Bowen
Rapid Solidification Processing of Magnesium Alloys	AMMRC	Flemings
Transport Phenomena in Improved Electrochemical Cell Designs for the Production of Magnesium	DOE	Sadoway
The Oxidation Behavior of Fine Grained Rapidly Solidified Iron-Base Alloys	Bethlehem	Yurek

TABLE I (cont'd)

Title	Funding Agency	Principal Investigator
Materials Processing Center/Industry Collegium	Industrial	Flemings
Advanced Aluminum-Lithium Base Alloys Produced by Rapid Solidification from the Melt	ARO	Grant
Undercooling and Rapid Solidification of Fe & Ni Base Alloys	ARO	Flemings
Fusion Welding Research	ONR	Eagar
Deformation Induced Structural Changes in Semi-Solid Materials	ARO	Flemings
Strengthening by Fractional Melting	AMMRC	Flemings
A Study of the Relationship between the Microstructure and Chemical Stability of Rapidly Quenched Iron Base Alloys	Bethlehem Steel	Latanision, Vander Sande
Resistance Welding of Lead Alloys	Gould Automotive	Eagar
Control of Segregation and Defect Formation During Large Diameter Crystal Pull of Si	DARPA	Witt
Electroslag Castings	NSF	Flemings
Heat Source - Materials Interactions during Fusion Welding	ONR	Eagar

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TABLE I (cont'd)

Title	Funding Agency	Principal Investigator
Physics and Chemistry of Ceramic Powder Processing	DOE	Bowen
Tektronix Grant to Ceramics Processing Laboratory for Fellowships, Equipment	Tektronix	Bowen
Surface Quality of Steel Ingots and Slabs	AISI	Flemings
Processing Ceramic Capacitors	5 Company Consortium	Bowen
Synthesis and Processing of Ceramic Powders	Standard Oil	Bowen
Metastable Microcrystalline and Glassy Alloys	ARO	Grant, Latanision, Johnson

TABLE II

Advisory Board for Materials Processing Center, M.I.T.

Dr. Turner Alfrey, Jr.*
Research Scientist
Dow Chemical Central Research

Dr. Donald J. Blickwede
Vice President & Director
of Research
Bethlehem Steel Corporation

Dr. Kenneth J. Brondyke
Director
Alcoa Laboratories
Aluminum Company of America

Dr. Harris M. Burte
Chief of Metal & Ceramics Div.
Wright Patterson Air Force Base

Dr. John R. Carruthers
Laboratory Project Manager
Solid State Laboratory
Hewlett Packard Labs

Dr. Paul A. Fleury
Director, Materials Research Lab.
Bell Laboratories

Dr. Rodney E. Hanneman
Vice President, Corporate Research
& Development
Reynolds Metals Division

Mr. Frank B. Herlihy
Vice President, Group Executive
- Hydraulics
Abex Corporation

Mr. Winston R. Hindle, Jr.
Vice President, Corporate
Operations
Digital Equipment Corporation

Mr. John R. Hutchins, III
Vice President & Director
of Research & Development
Corning Glass Works

Dr. Anthony D. Kurtz
President
Kulite Semiconductor
Products Inc.

Dr. Horace N. Lander
Senior Vice President,
Research & Development
AMAX Molybdenum Division

Dr. George Mayer
Director, Metallurgy
& Materials
Science Division
Army Research Office

Dr. Robert Mehrabian
Chief, Metallurgy Division
National Bureau of Standards
U.S. Department of Commerce

Mr. John H. Morison
Chairman of the Board
Hitchiner Manufacturing
Company, Inc.

*We regret the passing of a highly valued member of our Advisory Board, Dr. Turner Alfrey, Jr.

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Dr. Richard K. Pitler
Sr. Vice President-Technical
Director
Research Center
Allegheny Ludlum Steel
Corporation

Mr. Richard F. Polich
Chairman
Tallix Incorporated

Mr. James F. Rechin
Vice President
Turbine Components Division
Equipment Group
TRW Incorporated

Dr. George S. Reichenbach
Vice President, Bonded
Abrasives
Norton Company

Dr. Edward I. Salkovitz
Director, Research Programs
Office of Naval Research

Dr. Maurice E. Shank
Director, Engineering Tech.
Commercial Products Division
Pratt & Whitney Aircraft
Group
United Technologies
Corporation

Mr. Charles H. Smith, Jr.
Chairman of the Board
SIFCO Industries,
Incorporated

Dr. M.A. Steinberg
Director of Technology
Applications
Lockheed Aircraft Corporation

Dr. Louis Testardi
Manager, Materials
Processing in Space Office
NASA Headquarters

Mr. Thomas R. Wiltse
General Manager, Central Foundry
General Motors Corporation

Dr. Edward S. Wright
Director
AMMRC

II. THE INDUSTRIAL COLLEGIUM

INTRODUCTION

The Materials Processing Center/Industry Collegium was officially begun on November 1, 1981 after extensive discussions with MPC Advisory Board Members, faculty and staff of the Center, and the MIT Administration. The central aim of this Collegium is to foster mutually productive relationships between industry and Center faculty, staff, and students. Response of industry has been strongly positive and we have now ahead of us much to do to make the Collegium as effective as it can be.

A full description of the Collegium and its plan of operation has been prepared in the form of a brochure given to those companies interested in joining. That brochure is reprinted here in its entirety and comprises the remainder of this Chapter of the report.

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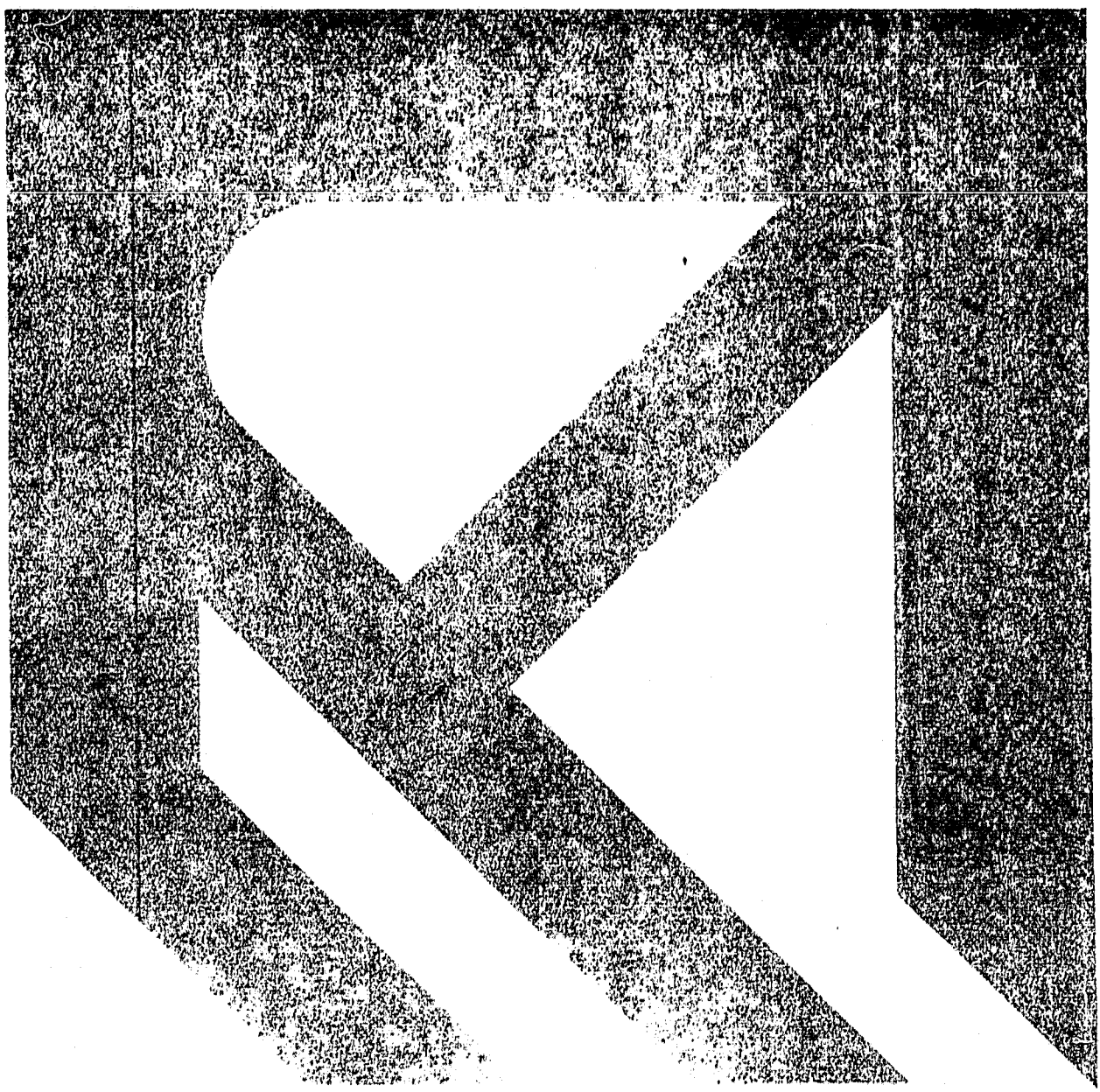
An Invitation to join
the Materials Processing Center/Industry Collegium
at the Massachusetts Institute of Technology



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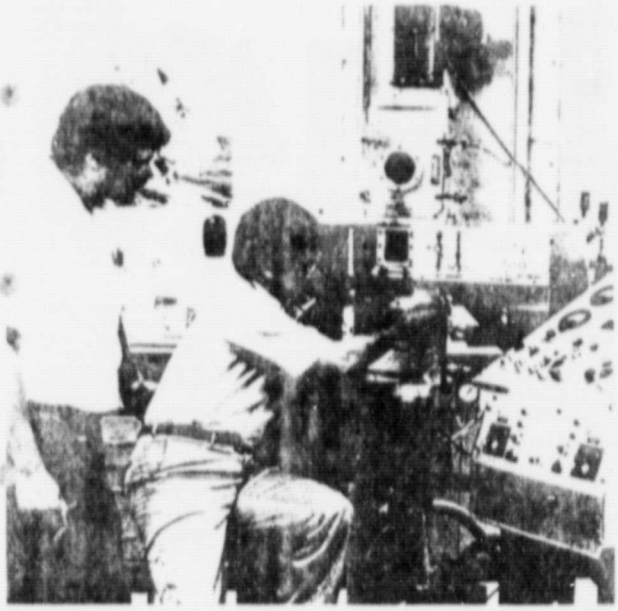

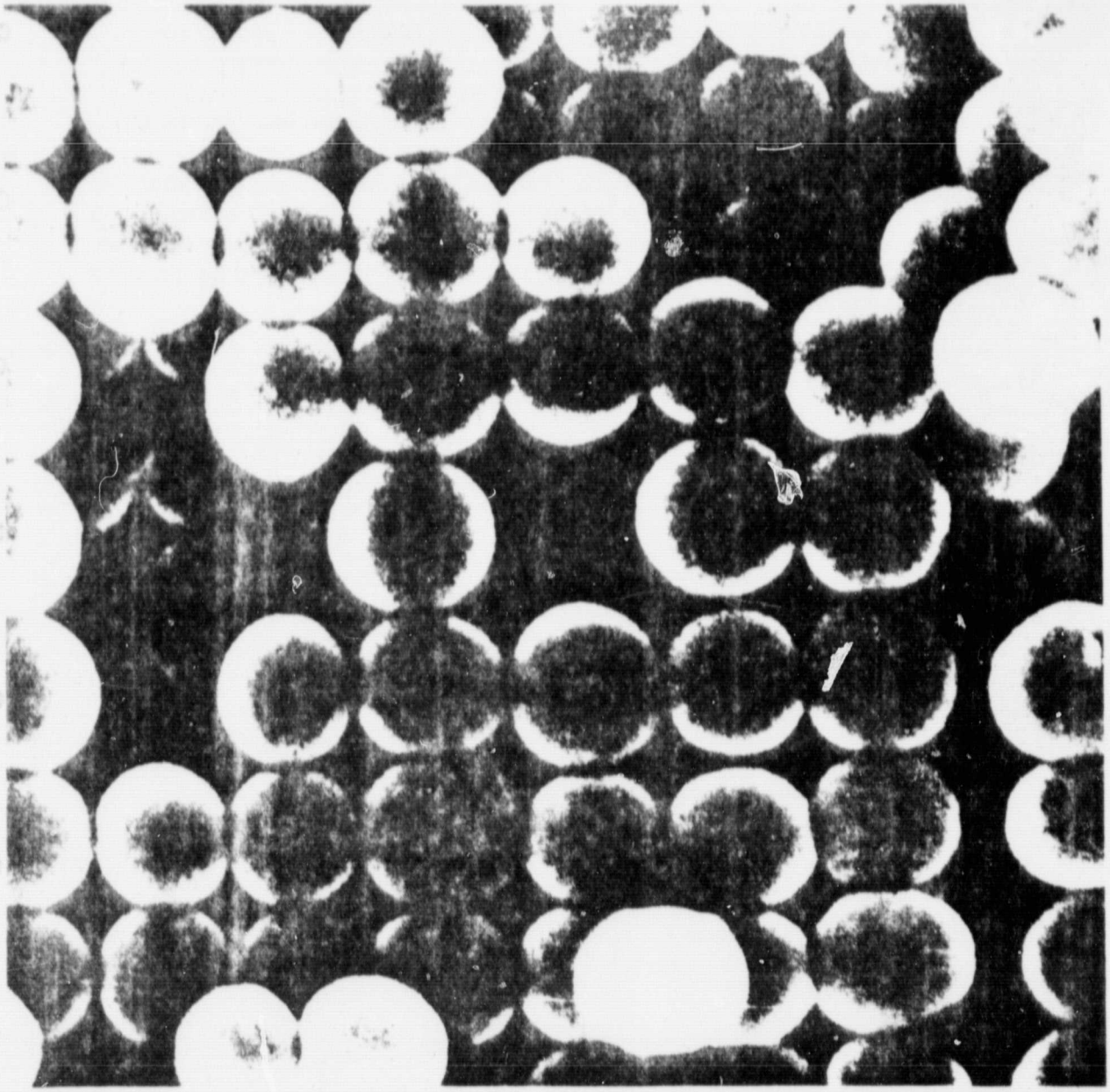

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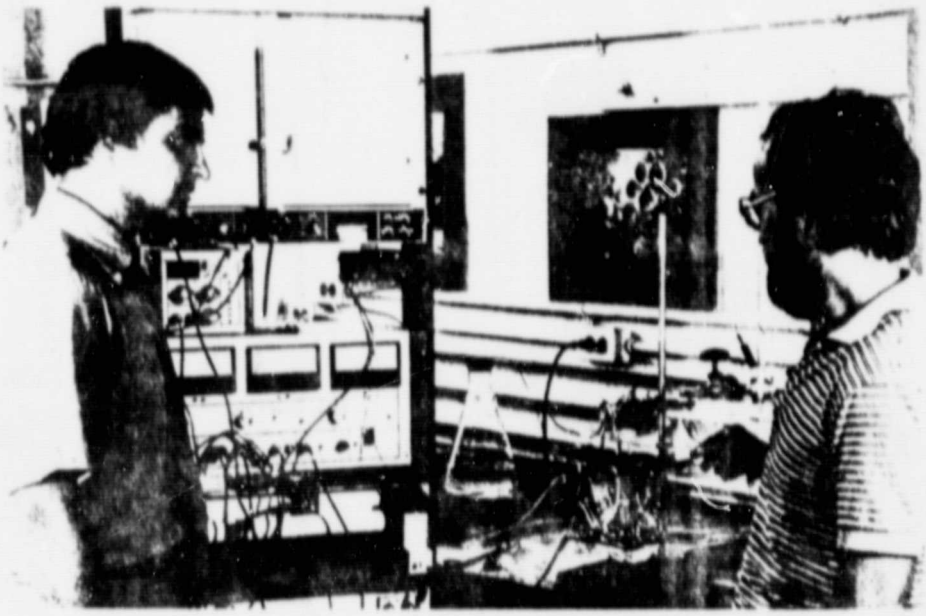
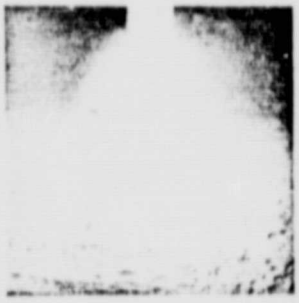
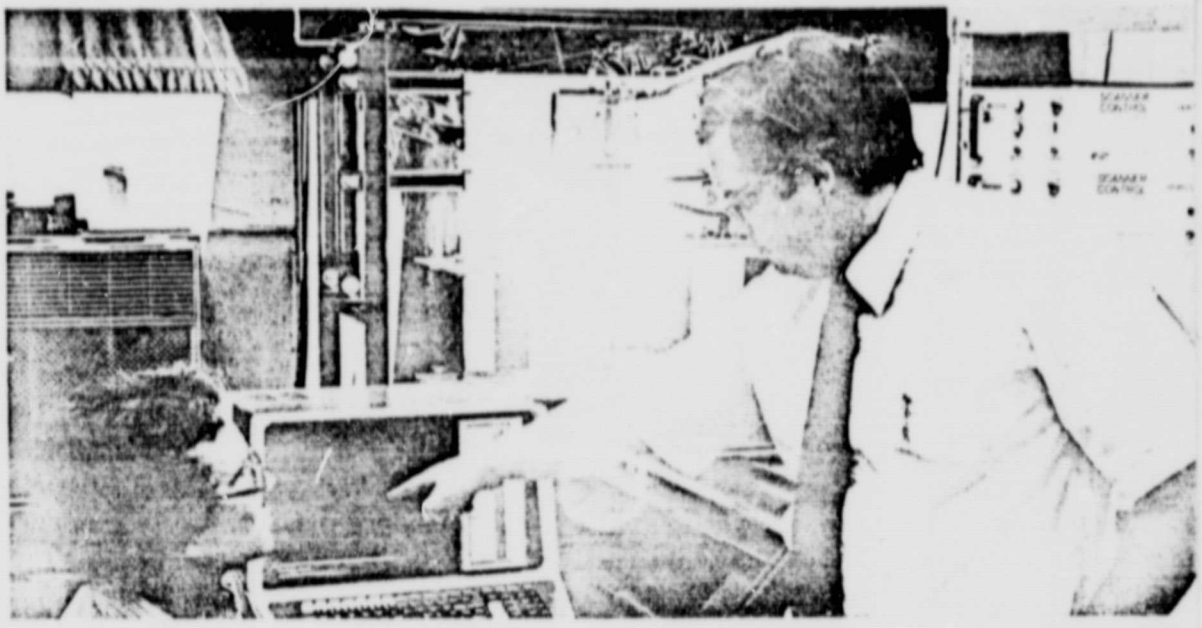
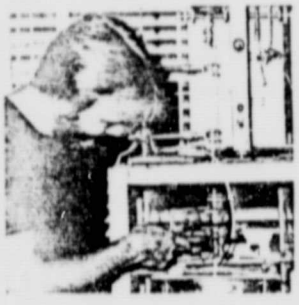


The Materials Processing Center/Industry Collegium is a partnership established to promote innovative research and development programs, information exchange, and personnel exchange. Its aim is to assist industry to profit from MIT research in materials processing, and for MIT to benefit through improved industrial interaction.

Through special publications, seminars, workshops, and personnel exchanges, the Collegium provides a forum for faculty, staff, students, and industrial representatives to exchange ideas, develop innovative research topics, and carry out cooperative or sponsored research and development programs oriented towards specific goals.







The Materials Processing Center was established in the School of Engineering at MIT in 1979. The Center aims to work in concert with industry and government on broad technological problems relating to materials production and forming—including aspects of those problems which relate to economic or societal costs and benefits. Some current central activities of the materials processing center are the following:

- Electronic Materials Processing Research
- Welding and Joining
- Powder Processing/Rapid Solidification
- Materials Systems
- Ceramic Processing and Engineering Research
- Electroprocessing
- Polymer Processing
- Mathematical and Physical Modeling
- Corrosion Research
- Mechanical Properties and Metal Forming
- Composites and Non-Destructive Evaluation
- Solidification Processing
- Computer Aided Processing
- Chemical Metallurgy

The foregoing activities of the Center involve over 20 faculty members, 50 research staff, and 140 graduate students.

An important part of the Materials Processing Center is this Collegium by which companies like yours can stay abreast of new technology in the Materials Processing area, influence the course of processing research at MIT, meet faculty involved in processing, and follow the professional development of undergraduate and graduate students. Close contact between industrial representatives and students is expected to be a particularly fruitful aspect of Center activities.

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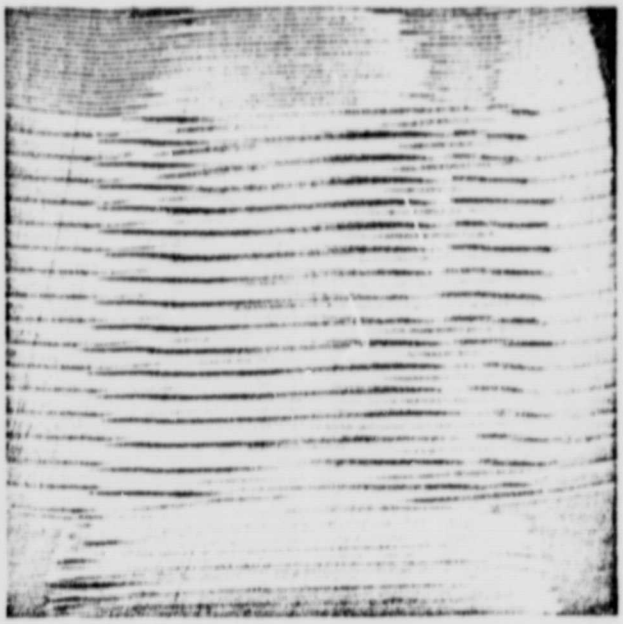

The Center plays a special role in acting as host and intermediary between MIT researchers and members of your company. Short visits for research discussions are readily arranged and the Center also encourages and facilitates personnel exchanges of all types including:

- Student cooperative work/study programs
- Faculty summer work periods in industry
- Visiting scientist appointments at MIT by industrial colleagues on extended leave
- Shorter visits for special purposes by industrial colleagues.

In addition, to keep members abreast of current research opportunities, the Materials Processing Center makes available periodically abstracts of current materials processing research, and provides a comprehensive annual summary of materials processing research at MIT.

Collegium members receive Opportunity Briefs not less than twice a year. Each Opportunity Brief outlines an area of ongoing research in Materials Processing at MIT which has long or short range business potential.

Following the publication of an Opportunity Brief, interested Collegium members attend a Workshop where they meet directly with faculty and students whose work has been summarized in the Brief. With participation from industry, university, and government agencies, Workshops allow for a fuller exploration of the research and its potential applications. In addition, Workshops give members an opportunity to suggest directions for future research and to lay the groundwork for future participation in research programs. Some examples of planned Workshops include:

- Materials Cost and Availability: 1980–2000
- Mathematical and Physical Modeling of Materials Processes
- High Energy Source Processing of Materials
- Innovations in Welding and Joining
- Rapid Solidification Processing
- Strategies for Systems Management of Materials Resources

We cordially invite your company to become a member of the Materials Processing Center/Industry Collegium. The Collegium membership fee is $10,000 per year. Special arrangements are possible for companies which are also members of the MIT Industrial Liaison Program, or are otherwise supporting programs related to the Materials Processing Center.

To join the Collegium, or for more information, please write or call:

Materials Processing Center
Room 4-415
Massachusetts Institute of Technology
Cambridge, Ma. 02139

Professor Merton C. Flemings, Director, (617)253-3233
Professor H. Kent Bowen, Associate Director, (617)253-6892
Dr. George B. Kenney, Assistant Director, (617)253-3244

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III. MATERIALS PROCESSING RESEARCH BASE

Research activities conducted under the Materials Processing Research Base during this second year are in three areas: (A) nucleation and rapid solidification, (B) fluid flow in crystallization processes, and (C) adaptive materials processing. The individual programs are listed below, and detailed research summaries follow.

A. NUCLEATION AND RAPID SOLIDIFICATION

1. S. M. Allen, "Processing of Sendust-Type Soft Ferromagnetic Alloys."
2. M. C. Flemings and J. Szekely, "Convection in Grain Refining."
3. N. J. Grant, "The Structure and Properties of Rapidly Solidified High Alloy Aluminum Materials."
4. F. J. McGarry, "Rapid Solidification of Polymers."
5. G. J. Yurek, "Development of Rapidly Solidified Oxidation Resistant Alloys."
6. J. S. Haggerty, "Laser Materials Processing Facility."

B. FLUID FLOW IN CRYSTALLIZATION PROCESSES

1. R. A. Brown, "Fluid Flow in Crystal Growth: Analysis of the Floating Zone Process."
2. D. Roylance, "Numerical Modeling and Optimization for Polymer Melt Processing Operations."
3. D. R. Sadoway, "Studies of Materials Electroprocessing in Molten Salts."
4. A. F. Witt, "Heat Flow Control and Segregation in Directional Solidification."

C. ADAPTIVE MATERIALS PROCESSING

1. T. W. Eagar, "Adaptive Control of Welding Processes."

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A. NUCLEATION AND RAPID SOLIDIFICATION

PROJECT A1: PROCESSING OF SENDUST-TYPE SOFT FERROMAGNETIC ALLOYS

Principal Investigator: Prof. S. M. Allen
Personnel: Mr. E. P. Kvam

RESEARCH ABSTRACT

The specific processing techniques which will optimize the magnetic properties of an Fe-Si-Al-Ni Sendust-type alloy are under investigation. The alloy being studied has magnetic properties comparable to Permalloys but with far less nickel content and hence less cost. Our objective is to develop a thorough understanding of the ways in which solidification processing, deformation processing, and heat treatment can be best utilized to produce material in suitable shapes, with excellent magnetic characteristics.

RESEARCH SUMMARY

I. INTRODUCTION

The *Sendust* composition, Fe-9.6 w/o Si-5.4 w/o Al, has long been recognized as an alloy with exceptional characteristics as a soft ferromagnetic material. These are: High permeability, low coercivity, high electrical resistance, and reasonably good saturation magnetization. These excellent properties result primarily from the fact that the composition has near-zero magnetostriction as well as near-zero magnetic anisotropy. Unfortunately, the material is also very brittle and applications in the past have been limited mainly to cast shapes and to forms made from compressed powder.

Two recent studies give promising results with respect to processing-related improvements for these alloys. The first is a report by Tsuya et al. [IEEE Trans. on Magnetics, 15, 1149 (1979)] of the use of a melt-spinning rapid-solidification technique to produce *Senduat* alloy ribbons of fine grain size. As cast, these ribbons were ductile enough to be rolled to 25% of their original thickness. After annealing treatments to optimize magnetic properties, however, the material was embrittled. The second study, by Yamamoto and Utsushikawa [Trans. Japan Inst. Metals, 19, 3261 (1978)], focussed on alloy modification through 3 w/o additions of nickel to an Fe-6 w/o Si-4 w/o Aℓ alloy. The resulting material was called *Super Senduat* because many of its magnetic properties were superior to those of the ternary *Senduat* alloy. Although the mechanical properties of the alloy were not studied, there is reason to expect that it will have better ductility than *Senduat*. Nickel additions to soft ferromagnets are generally believed to contribute to both magenetic and mechanical softness. Also, *Super Senduat* has approximately one-third less aluminum and silicon, each of which embrittles iron.

II. RESEARCH IN PROGRESS

Senduat alloy buttons have been prepared by vacuum arc melting. These ingots are then remelted and cast onto the inside of a rapidly rotating drum to produce thin ribbons approximately 2 mm wide. The microstructure of the as-cast ribbons is being studied to determine grain size, grain shape distribution through the ribbon, and crystal structure. Ductility of the as-cast ribbon material is also being characterized.

The magnetic behavior of the ribbon material is under investigation. Initially, we are studying the influence of

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annealing treatments on coercivity. As cast, the ribbons have a coercive force of approximately 2 Oersteds. Annealing at 900°C, followed by slow cooling, reduces the coercive force to approximately 0.7 Oersteds. Further reductions in coercive force should be possible through thermal treatments, and these are being pursued. At these low coercivities, the surface condition of the ribbons may also be important. As cast, the ribbons are rough on the broad face away from the quenching wheel. Deformation of the as-cast ribbons by rolling will be tried as a method to smooth the surfaces.

Phase transformations in *Super Sendust* are being studied via transmission electron microscopy analysis of samples annealed over a range of temperatures. An order-disorder transition has been located at about 675°C. The high temperature phase has the B2(CsCl) structure, while the low temperature structure is DO_3 (Fe_3Si or Fe_3Al) which is reported to be the desired structure for the best magnetic properties in the ternary *Sendust* alloy. The primary defects in these phases are antiphase boundaries (APBs). If antiphase domains are fine enough, APBs may interfere with magnetic domain wall motion. Our transmission electron microscopy results enable us to estimate antiphase domain coarsening kinetics at different temperatures, and this information should prove useful in optimizing annealing schedules for reducing coercive force.

In summary, our aim is to use a rapid-solidification processing technique to produce microcrystalline *Super Sendust* alloy ribbons. Such material, as cast, has a useful shape and because of its small grain size and homogeneity, should have reasonably good ductility. Without additional processing, however, it has relatively poor magnetic properties. A combination of deformation processing and thermal annealing treatments is being designed to optimize magnetic properties.

N82 27383

PROJECT A2: CONVECTION IN GRAIN REFINING

Co-Principal Investigators: Prof. M. C. Flemings
Prof. J. Szekely

Personnel: Dr. R. Abbaschian
Dr. C. W. Chang
Dr. M. Choudhary
Dr. N. El-Kaddah
Dr. J. McKelliget
Dr. Y. Shiohara
Dr. G. Oreper
Mr. G. M. Chu
Mr. D. MacIsaac

RESEARCH SUMMARY

The scientific aim of this program is to obtain a better understanding of the relationship between fluid flow phenomena, nucleation, and grain refinement in solidifying metals both in the presence and in the absence of a gravitational field. One ultimate technical aim is to determine ways to achieve significant grain size reductions in hard-to-process melts; another is to understand the effects of undercooling on structure in solidification processes, including rapid solidification processing; a third is to better understand how to control this undercooling to improve structures of solidified melts. The project has been divided into two subtasks. The actual grain refining and supercooling experiments are being carried out by Professor M. C. Flemings' group, together with thermal modeling of the solidification process, while the main thrust of the work of Professor J. Szekely's group has been to study the heat and fluid flow phenomena in the levitated metal droplets.

The main accomplishments in the heat flow, fluid flow, modelling area are:

1. A computational capability has been developed to determine the electromagnetic force field, the fluid flow field and the temperature field in induction stirred systems, including contained cylindrical melts and levitated spherical melts.
2. Calculations were carried out for a variety of conditions, including heat and fluid flow in a metal held in an inductively stirred cylindrical crucible and levitation melted specimens both on the ground and in a zero gravity environment.
3. Calculations have shown that the fluid flow field is markedly different for ground base and for zero gravity conditions. The theoretical predictions for the velocity fields and the temperature fields were found to be in good agreement with experimental measurements reported in the literature. Experimental measurements are being conducted to study the velocity fields in a low melting alloy system using hot wire anemometry. This is a pioneering undertaking which shows considerable promise in testing the model predictions.
4. The techniques developed for solving MHD type problems in molten metal and glass systems and the results generated are thought to have made an important contribution to this overall field.

The more important and significant results of the undercooling and structures research are:

1. Nickel base alloy samples of approximately 1 g have been successfully levitated in inert atmospheres and undercooled by amounts up to 270°C, and a wide range of grain sizes and solidification structures obtained, depending on amount of undercooling and cooling rate.
2. Two important innovative techniques have been developed to obtain much larger amounts of undercooling in high

temperature (iron, nickel, and cobalt base) alloys. In one of these, the metal is melted and then "emulsified" (stirred into fine droplets) in a molten oxide or salt. In the seond, small pre-alloyed metal droplets are interspersed at room temperature with finely crushed oxide or salt. The admixture is then melted.

3. Extremely large undercoolings have been obtained in the above two methods because of the fine particle size and cleansing action of the slag. For example, in 316 stainless steel, undercoolings up to 480°C have been obtained. This is approximately 300°C greater than any undercooling that has been previously recorded for any iron base alloy, and we do not think we have yet reached the maximum number. At the higher undercoolings, metstable BCC steel is obtained in place of the equilibrium FCC structure. These results are of fundamental importance in understanding structures produced by "Rapid Solidification Processing." They also point the way directly to new engineering processes for producing controlled solidification structures. The results have special implications for space processing as discussed below.

4. Emphasis of the experimental work at the present time is on increasing the amounts of undercooling obtainable, and therefore the types of structures obtainable through (a) use of alternate emulsification media, (b) increasing rate of heat extraction, and (c) process variations. One factor that limits applicability of the process in earth processing is the need, at 1 g, to have the slag viscosity high enough to prevent settling and coalescence of the metal particles.

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1. THE MATHEMATICAL AND PHYSICAL MODELLING OF FLUID FLOW IN CONTAINED AND IN CONTAINERLESS MELTS

In containerless processing applications the metallic specimens are positioned with the aid of an electromagnetic force field. In ground based applications of this positioning technique (viz levitation melting) the force field has to be very strong, while in space processing applications a much weaker force field should be sufficient.

In both these cases the applied force field will generate an electromagnetically driven flow, the quantitative assessment of which is thought to be crucial for both the interpretation of measurements and for the rational design of in-flight experiments.

This work has the following components:

(i) Calculation of the electromagnetic force field,

(ii) Computation of the fluid flow fields resulting from these electromagnetic force fields,

(iii) The verification of the calculations through experimental measurements,

(iv) Interfacing of these results with the grain refining studies.

(i) Calculation of the Electromagnetic Force Field

The calculation of the electromagnetic force field was performed by using the concept of the mutual inductances. This work was undertaken by the Space Science Center of the General Electric Corporation, who delivered a flexible computer program to us[1]. This program or some modification thereof was being utilized to compute the electromagnetic

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force field for spherical specimens processed in a containerless mode and for cylindrical melts held in crucibles.

(ii) Computation of the Fluid Flow Field

A formulation has been developed to represent turbulent, recirculating flow as driven by the combination of buoyancy and electromagnetic forces in levitated specimens and also in molten metals held in cylindrical containers. These latter calculations were performed because extensive measurements have become available concerning such systems, against which the predictions may be tested.

The general vectorial form of the governing equations is given as:

$$\nabla \cdot u = 0 \tag{1}$$

equation of continuity

$$- \nabla \cdot \rho \underline{u}\underline{u} - \nabla p - \nabla \tau^{(t)} + \rho F_b \tag{2}$$

where $\nabla \cdot \tau$ is the turbulent stress tensor and F_b is the body force field, which in general will include both the buoyancy and the electromagnetic forces.

The thermal energy balance equation takes the following form:

$$\underline{U} \nabla T = \nabla k \nabla T \tag{3}$$

where k_e is the effective thermal conductivity.

The system of equations (1-3) was solved numerically, utilizing the k - ε model to represent the components of the turbulent stress tensor.

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In essence three sets of calculations have been performed:

(a) The heat and fluid flow field was modelled in a levitation melted specimen under ground based conditions.

(b) Calculations were carried out modelling heat flow and fluid flow in an electromagnetically positioned metal sphere under zero gravity conditions, and finally,

(c) Calculations were carried out to represent the behavior of a molten mercury pool which was agitated by a current passed through induction coils surrounding the melt.

Some calculated results are given in the following and some additional computed results will be given subsequently in conjunction with measured data.

Figs. 1 and 2 show the computed lift force, acting on a 1 g levitated metal droplet, under ground based conditions, for coil currents of 200A and 300A respectively[2,3]. Also shown by the horizontal line is the weight of the levitated specimen. It is seen that the lift force would not be adequate to levitate for a coil current of 200A, but would be sufficient for a coil current of 300A. This finding agrees with experimental measurements. Fig. 3 shows the computed velocity field and the computed temperature field for a 1 g levitated specimen, under ground based conditions. It is seen that the linear fluid velocity is quite high, of the order of 0.2 - 0.3 m/s and that the temperature in the sphere is not completely uniform [4,5]. These predicted linear melt velocities were again found to be in good qualitative agreement with observations. Figs. 4 and 5 show the computed velocity and the temperature fields and the computed turbulence characteristics for a levitation melted Beryllium sphere, under zero gravity conditions. The input parameters for the

modelling calculations correspond to those used experimentally in the SPAR 1 runs. It is noted that the fluid flow field differs quite appreciably from that computed for the ground based conditions, exhibiting four rather than two circulating loops. The theoretically predicted temperature appears to be in good agreement with that measured in the experiments.

(iii) Verification of the Predictions, by a Comparison with Experiments

In this regard, three sets of experimental measurements have to be considered:

(a) Mass transfer in a levitation melted sphere,

(b) Experimental measurements in an induction stirred vessel, and

(c) Experimental measurements in a molten metal pool agitated by the direct passage of a current between two electrodes.

The former two refer to experiments conducted elsewhere, while the latter group involves experimentation in our laboratory.

Mass Transfer in a Levitation Melted Sphere

Experimental measurements were conducted on the rate at which a levitation melted iron sphere picks up carbon, when contacted with a CO_2/CO mixture. The overall rate of this process depends on both the rate of mass transfer in the gas

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phase and on the fluid flow and circulation in the metal sphere. Fig. 6 shows a comparison between the experimental measurements and the theoretical predictions. It is seen that the agreement is quite good, providing direct confirmation of the appropriateness of the mathematical model.

Fluid Flow in an Induction Stirred Vessel[7]

These experiments were conducted in the Engineering Department at Cambridge University, by Dr. Hunt and Mr. D. Moore, who kindly provided us with their data.

Fig. 7 shows a sketch of the experimental arrangement, which indicates a vessel holding molten mercury, which is being agitated by induction coils. Fig. 8 shows the computed radial body force field, while the corresponding axial component is shown in Fig. 9. The experimentally measured velocity field is shown in Fig. 10, while the corresponding theoretically predicted values are given in Fig. 11. The very good agreement is readily apparent. Fig. 12 shows a more detailed comparison of the theoretically predicted (broken lines) and the experimentally measured velocity field, again giving very reasonable agreement considering the fact that the theoretical predictions were based on first principles. Finally, Fig. 13 shows a comparison between the experimentally measured and the theoretically predicted values of the turbulence intensity, again giving very good agreement.

Experimental Verification of the Model in this Laboratory

In order to provide a direct experimental verification of the predicted electromagnetically driven flow fields

obtained in this laboratory under controlled conditions, an apparatus has been constructed in which molten Woods Metal is being agitated by the passage of a current between two submerged electrodes, as sketched in Fig. 14. The resultant velocity field will be measured by using a hot film anemometer, the output of which will be analyzed by a microcomputer. The apparatus has been constructed and the preliminary results are being obtained at present.

(iv) Interfacing the Modelling Work with the Grain Refining Experiments.

The results of the mathematical modelling efforts do provide a sound basis for helping with the interpretation of the grain refining experiments, conducted by Professor Flemings' group. Work has been initiated in this area, particularly by modelling the solidification of supercooled melts.

The work done to date may thus be summarized by stating that major advances have been made regarding the modelling of turbulent electromagnetically driven recirculating flows in both spherical and cylindrical geometries. A capability has been developed to predict the velocity fields in electromagnetically agitated melts, in both the spherical and the cylindrical geometry.

The model has been verified by a direct comparison with experimental measurements conducted in other laboratories, for ground based conditions and work is in progress to perform additional experiments in this laboratory with this objective. Predictions have also been made regarding the heat and fluid flow in a zero gravity environment, corresponding to one of the previous space experiments. The predicted temperature fields were in good agreement with the

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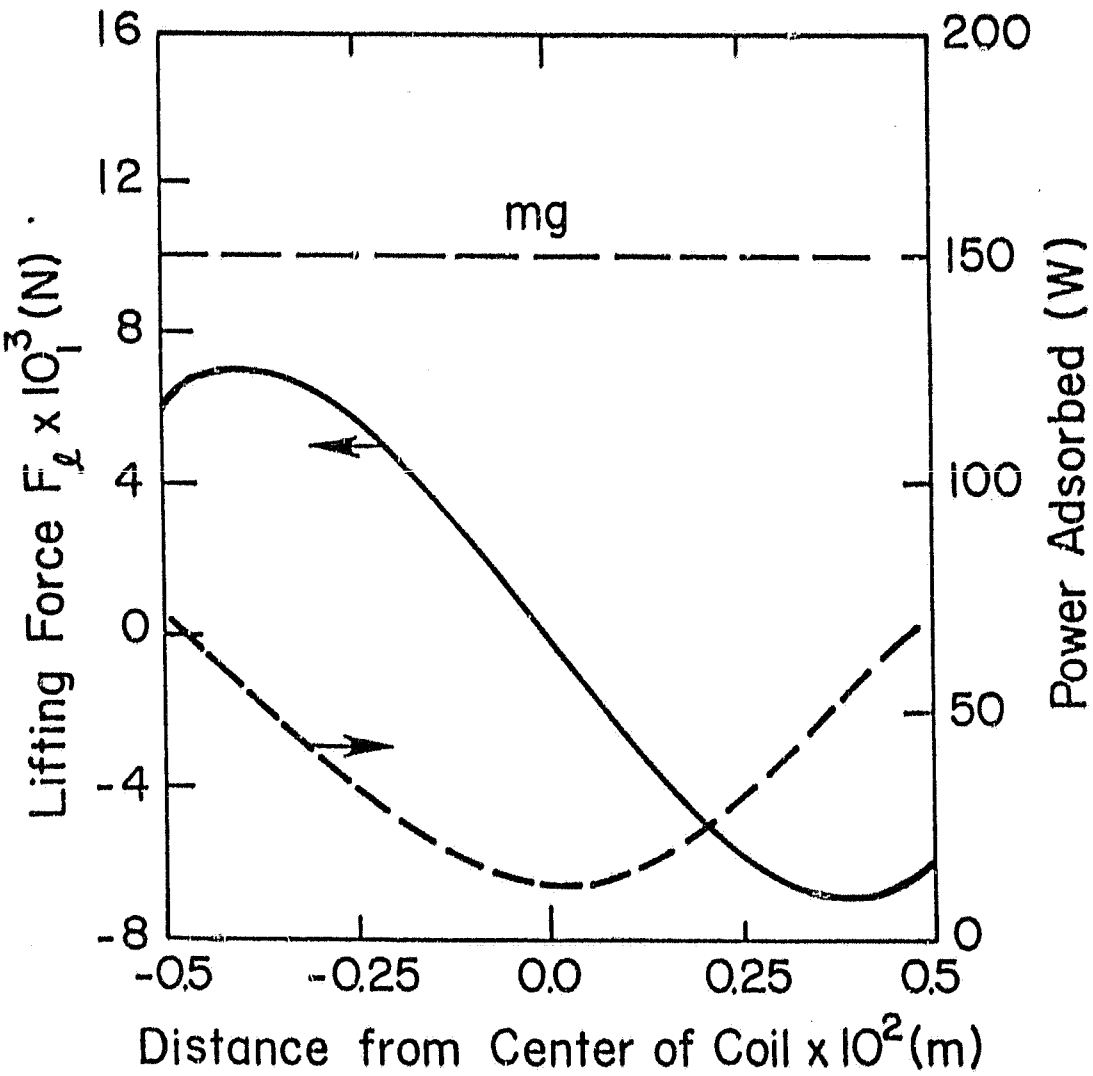

Figure 1: The computed lift force acting on a 1 g iron droplet for a coil current of 200 A.

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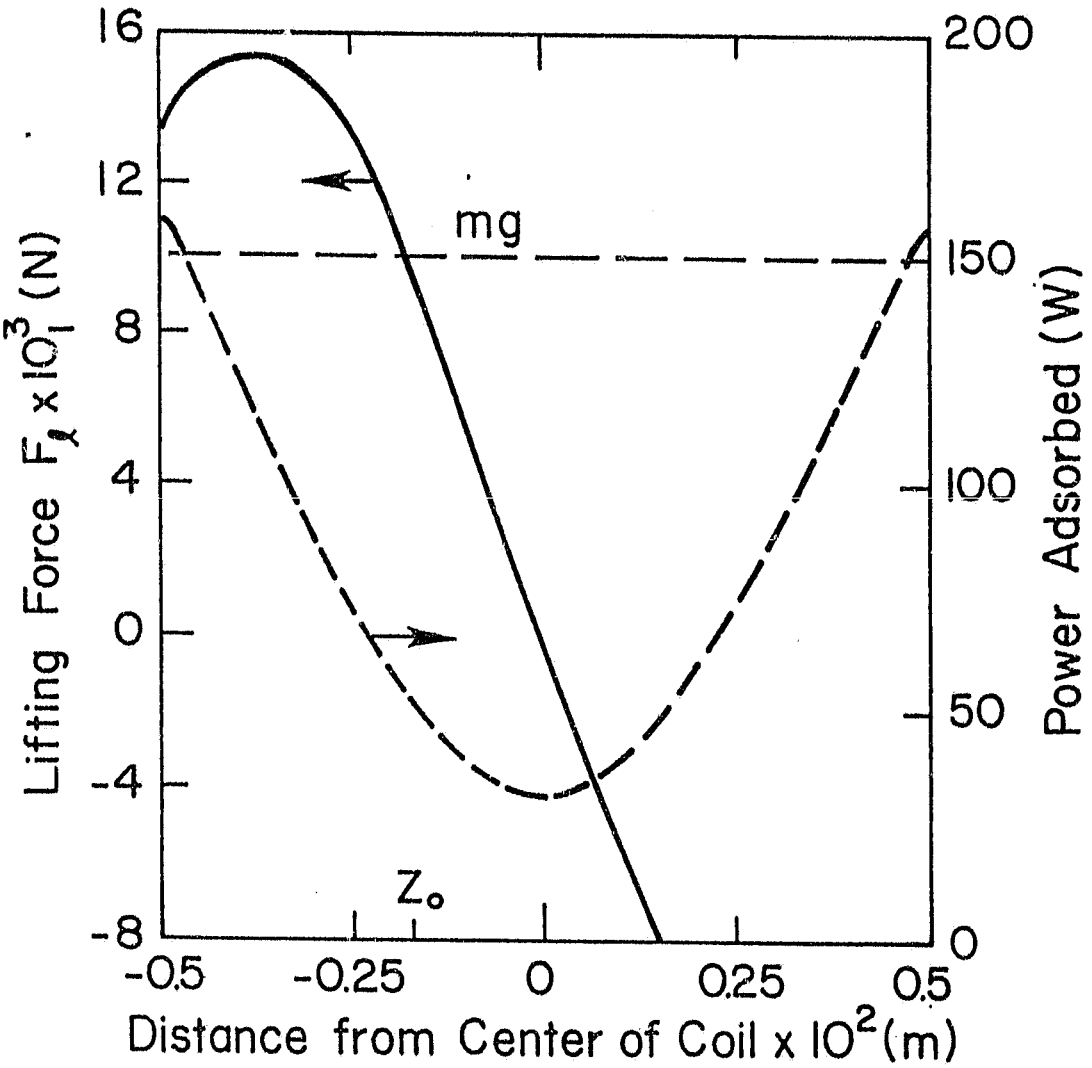

Figure 2: The computed lift force acting on a 1 g iron droplet for a coil current of 300 A.

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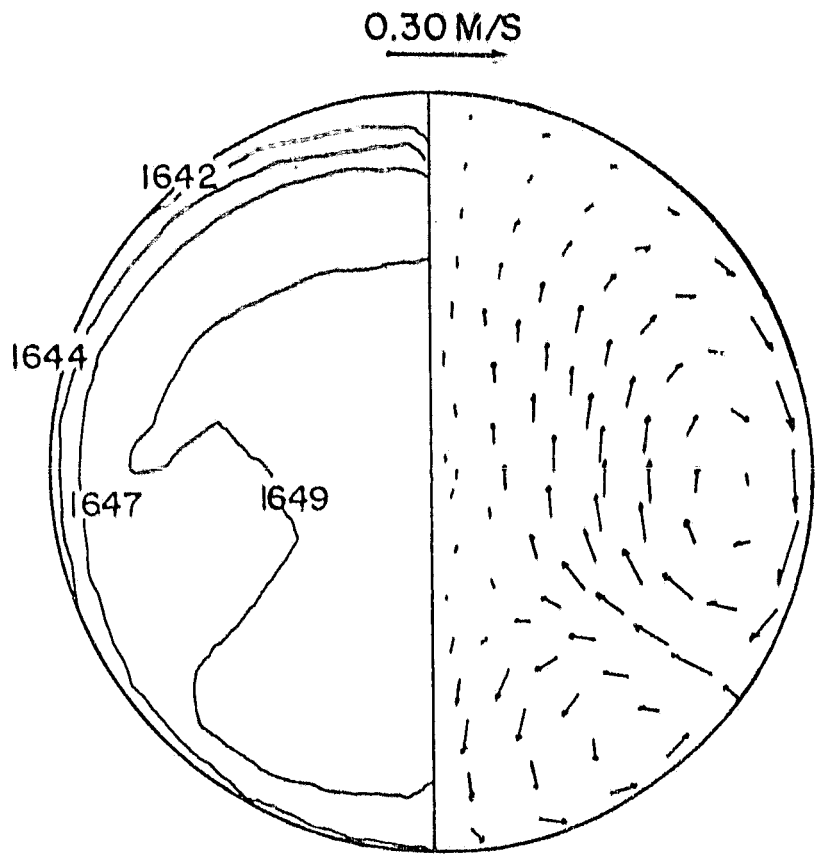

Figure 3: The computed temperature field and the computed velocity field for a levitated iron droplet.

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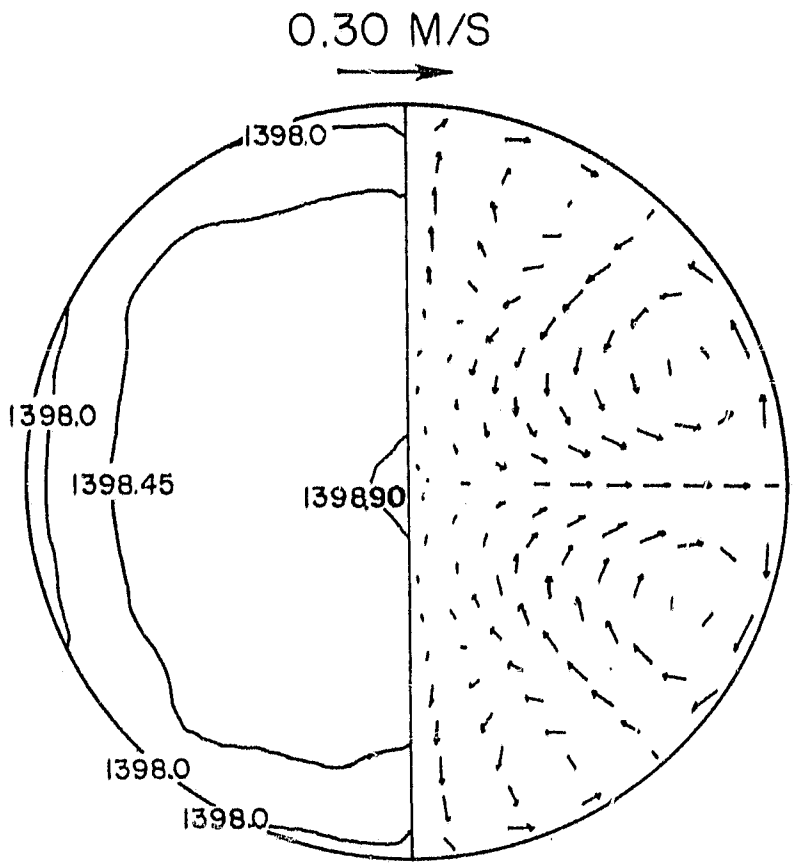

Figure 4: The computed velocity field and temperature field for a Beryllium sphere which is induction heated under zero gravity conditions.

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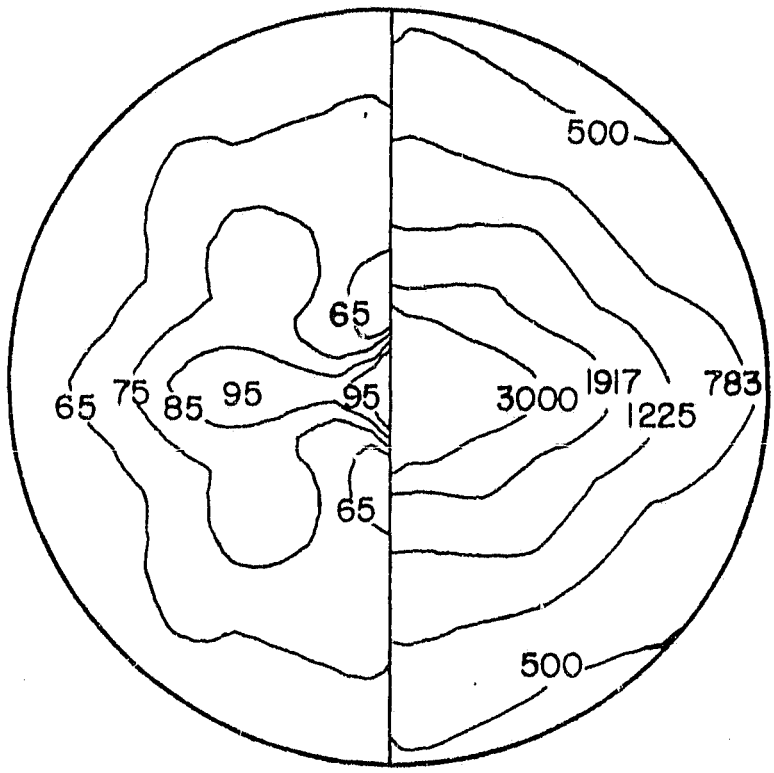

Figure 5: The computed turbulent kinetic energy (r.h.s.) and the computed ratio: effective viscosity/ molecular viscosity for a Beryllium sphere under zero gravity conditions.

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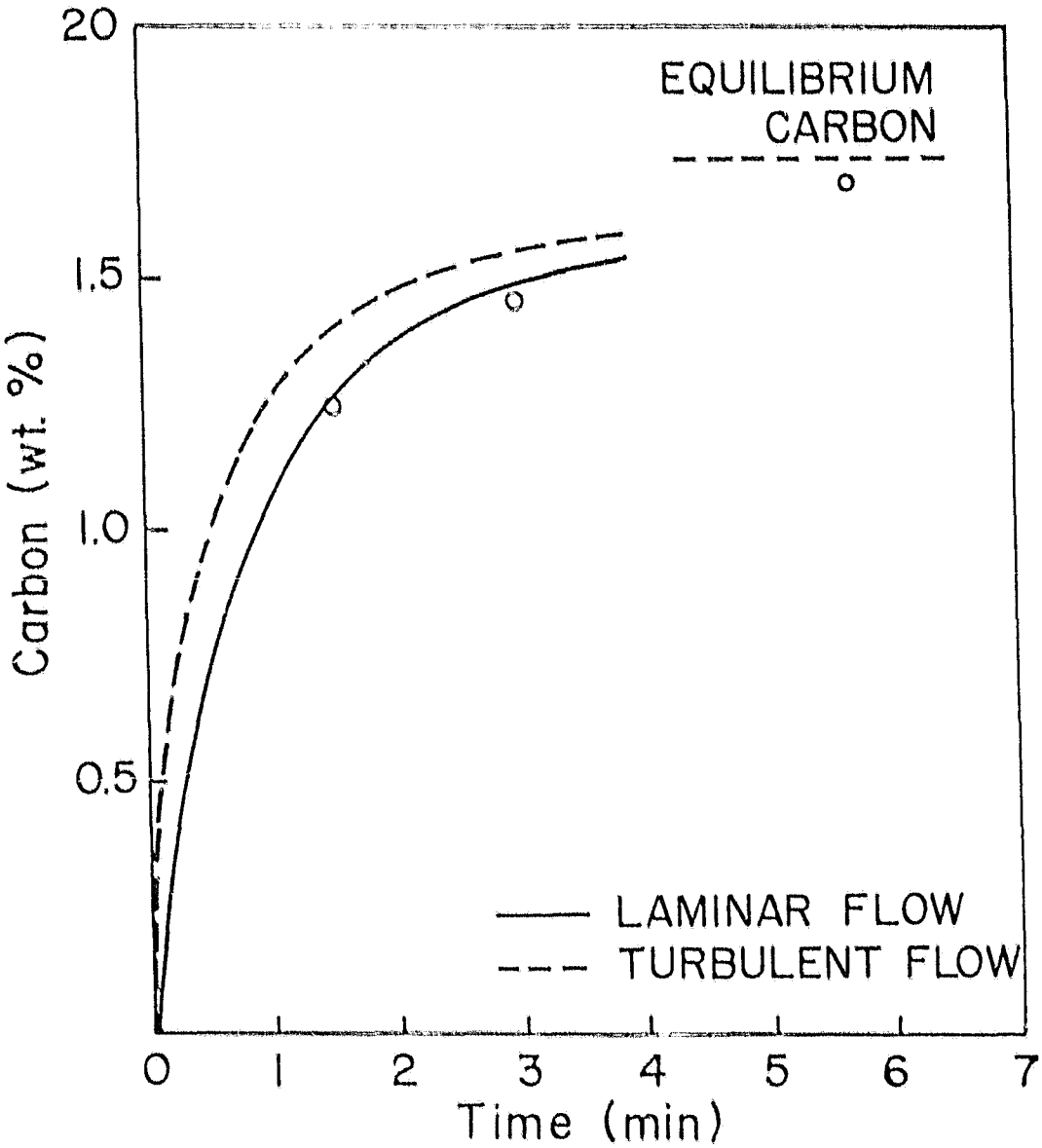

Figure 6: Comparison of the experimentally measured and the theoretically predicted carburization curves for a levitated iron droplet.

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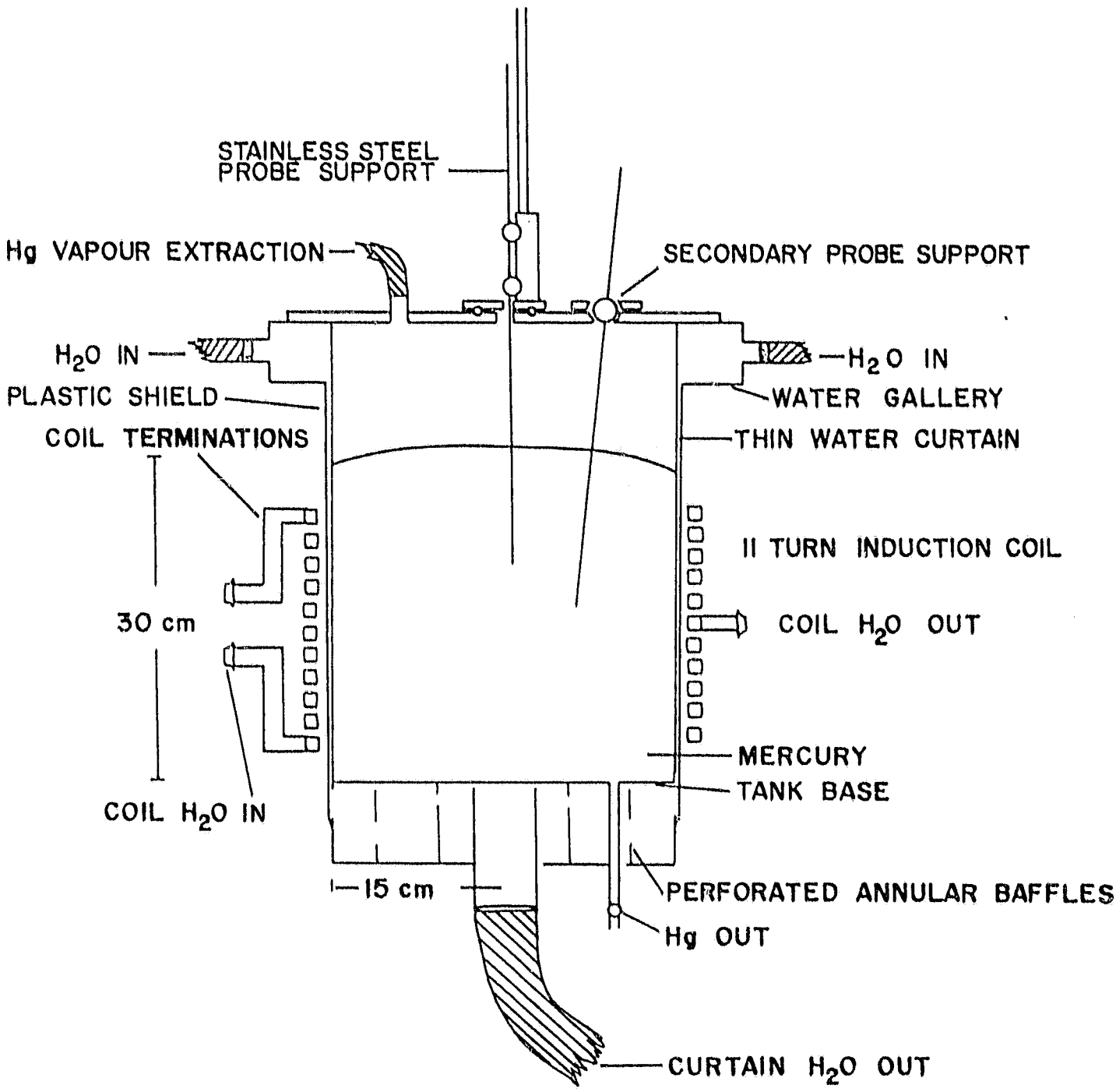

Figure 7: Sketch of the experimental arrangements for measuring the velocity fields in an induction stirred mercury pool under ground based conditions.

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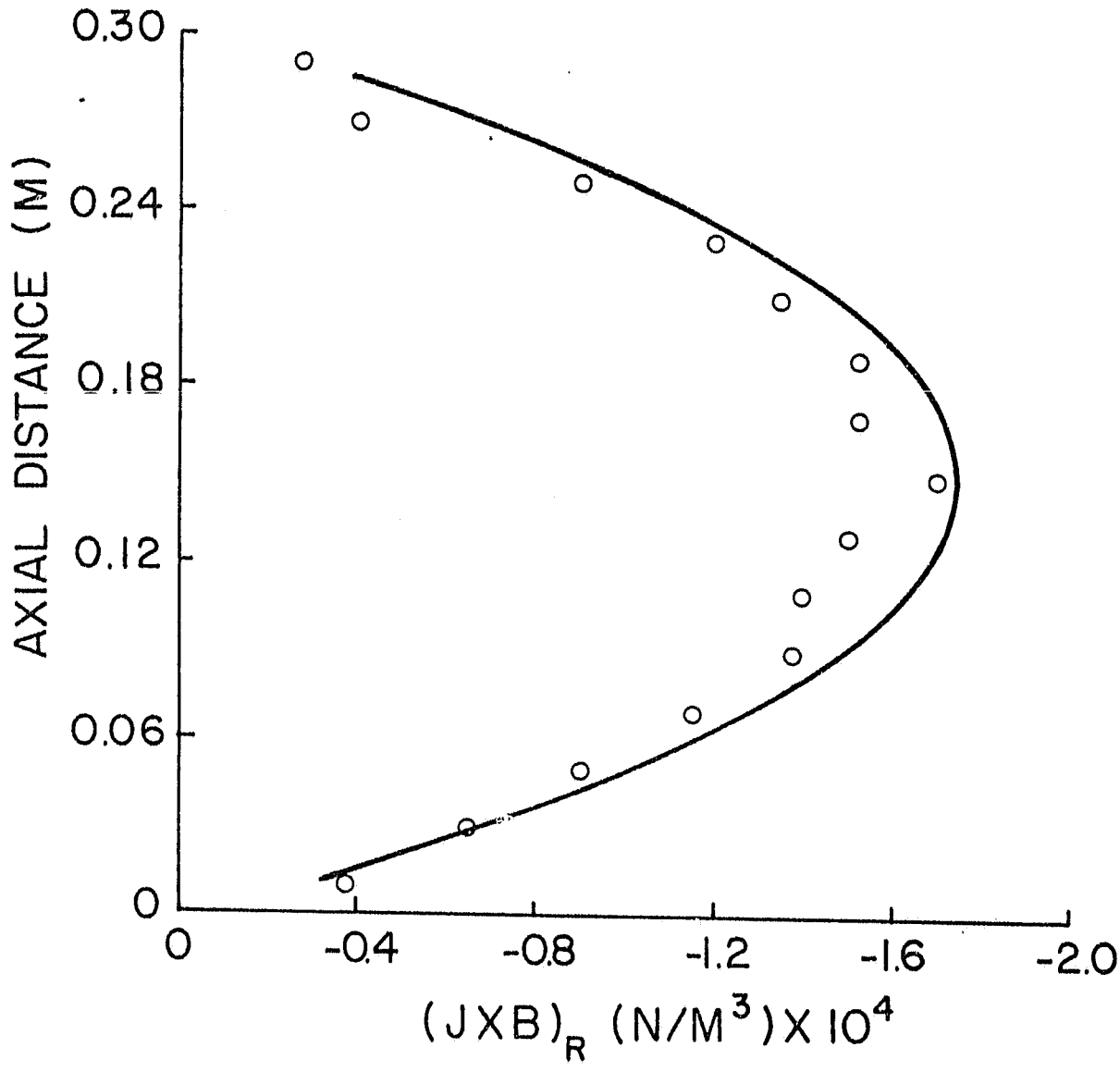

Figure 8: Comparison of the experimentally measured (discrete data points) and the theoretically predicted radial body force field for the mercury system.

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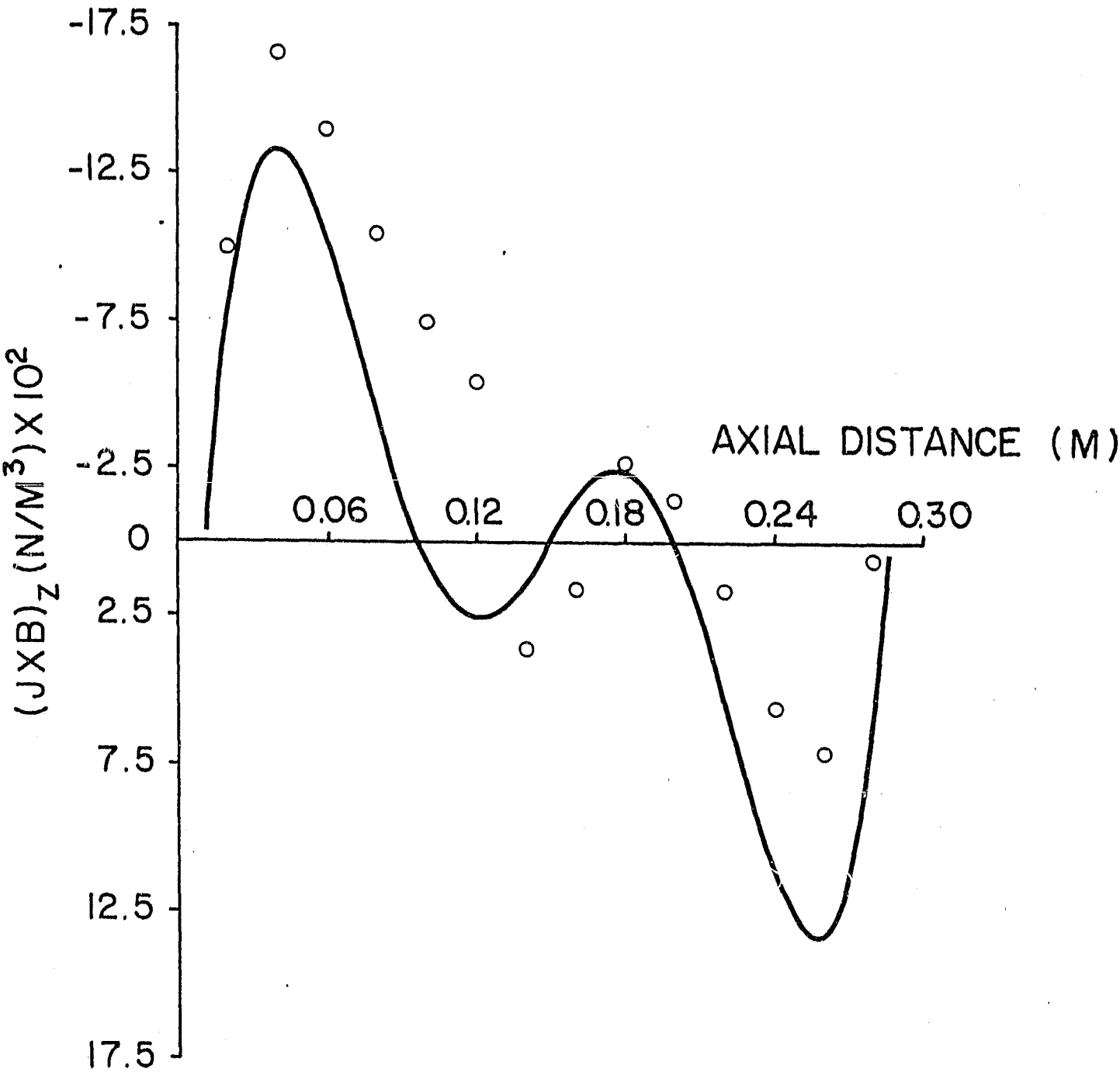

Figure 9: Comparison of the experimentally measured and the theoretically predicted axial body force field for the mercury systems.

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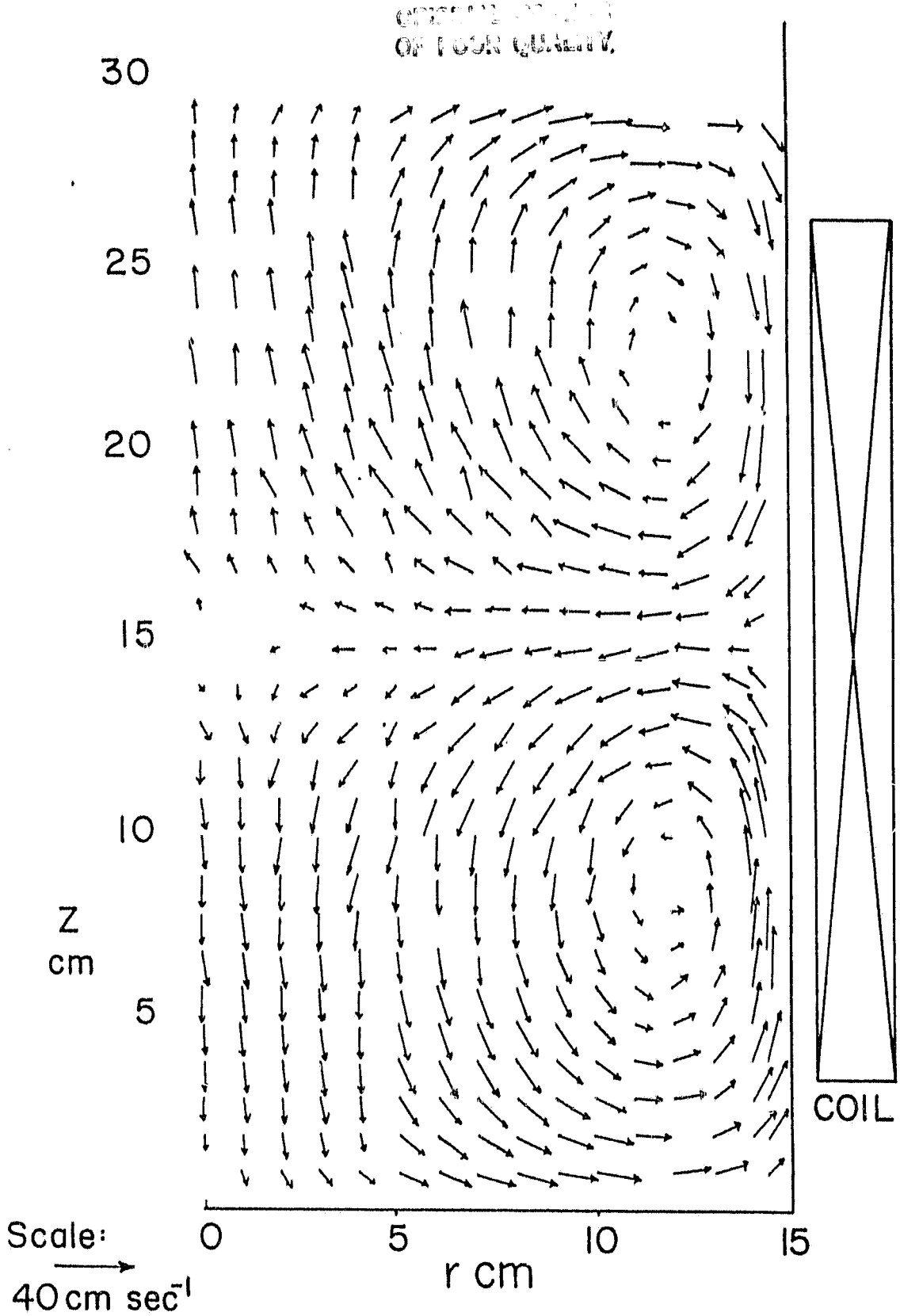

Figure 10: The experimentally measured velocity field in the ground based mercury system.

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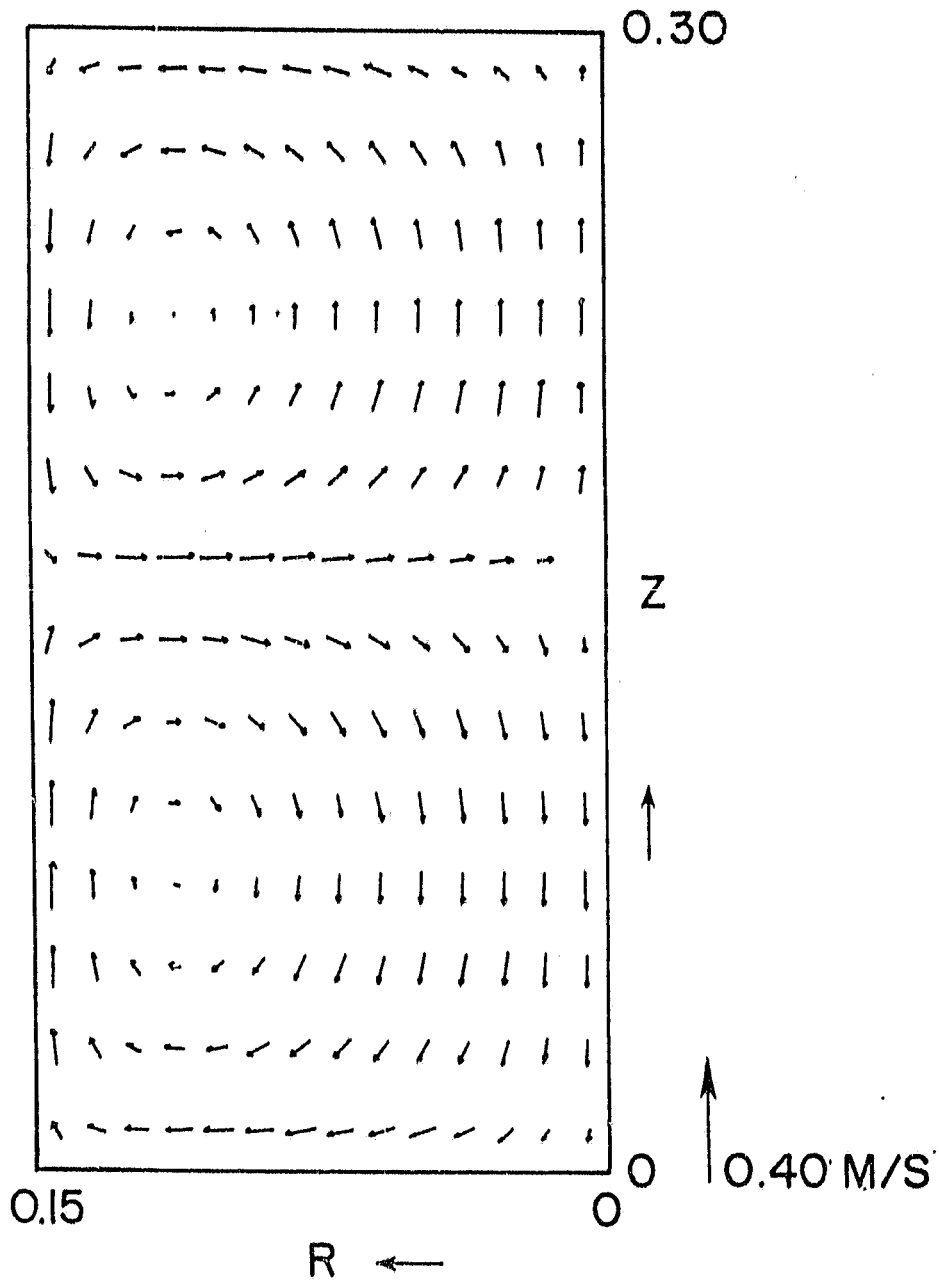

Figure 11: The theoretically predicted velocity field in the mercury system.

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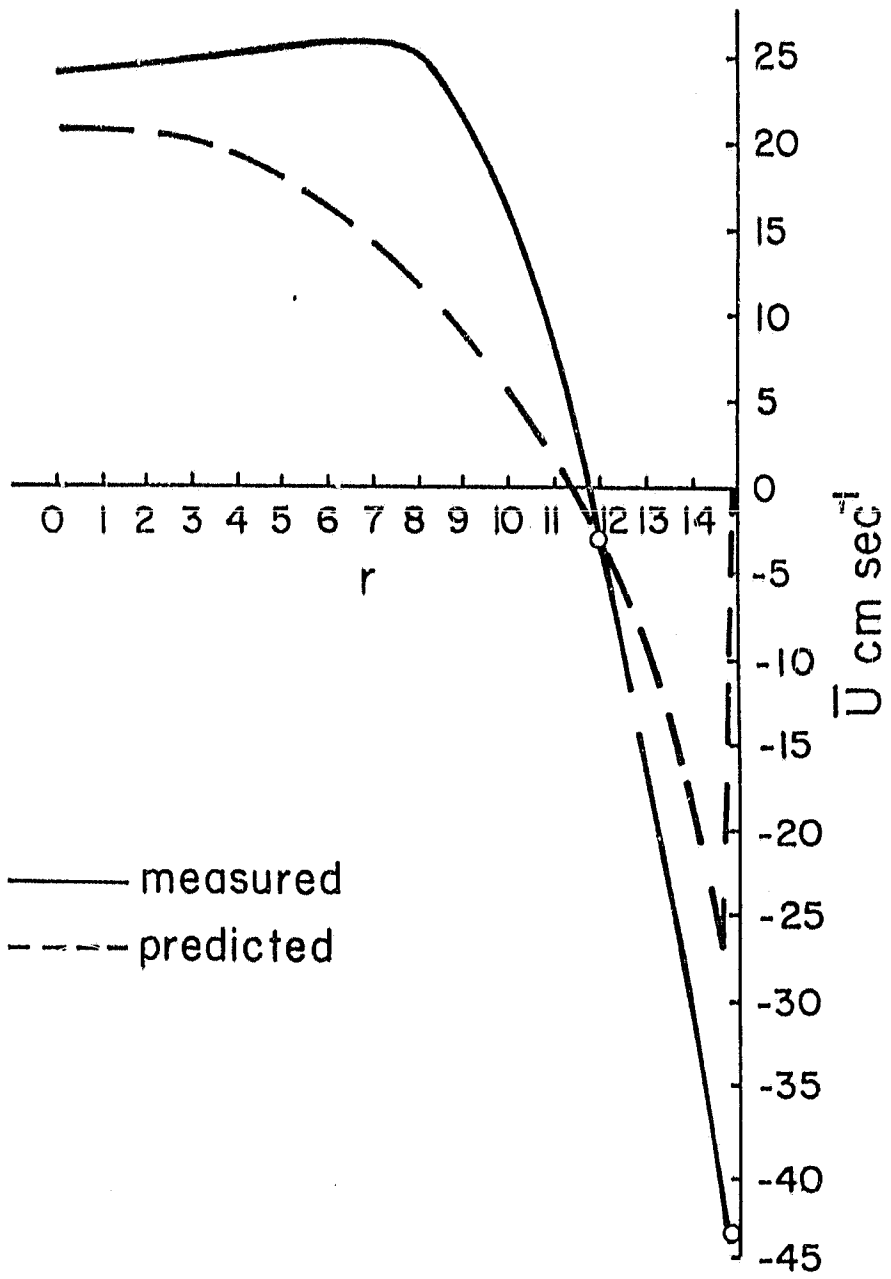

Figure 12: Comparison of the experimentally measured and the theoretically predicted axial velocity component at one practical vertical position within the mercury system.

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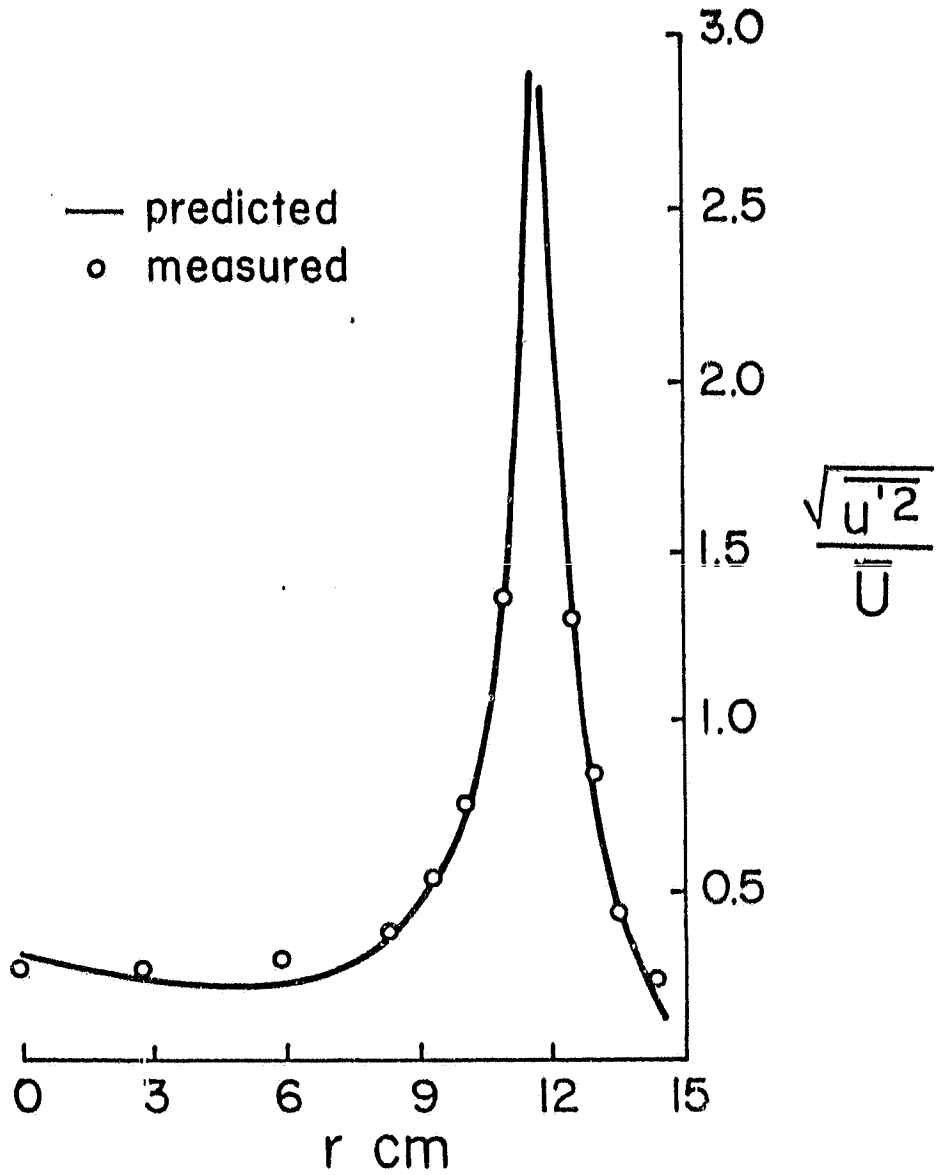

Figure 13: Comparison of the experimentally measured and the theoretically predicted turbulence intensity in the mercury system.

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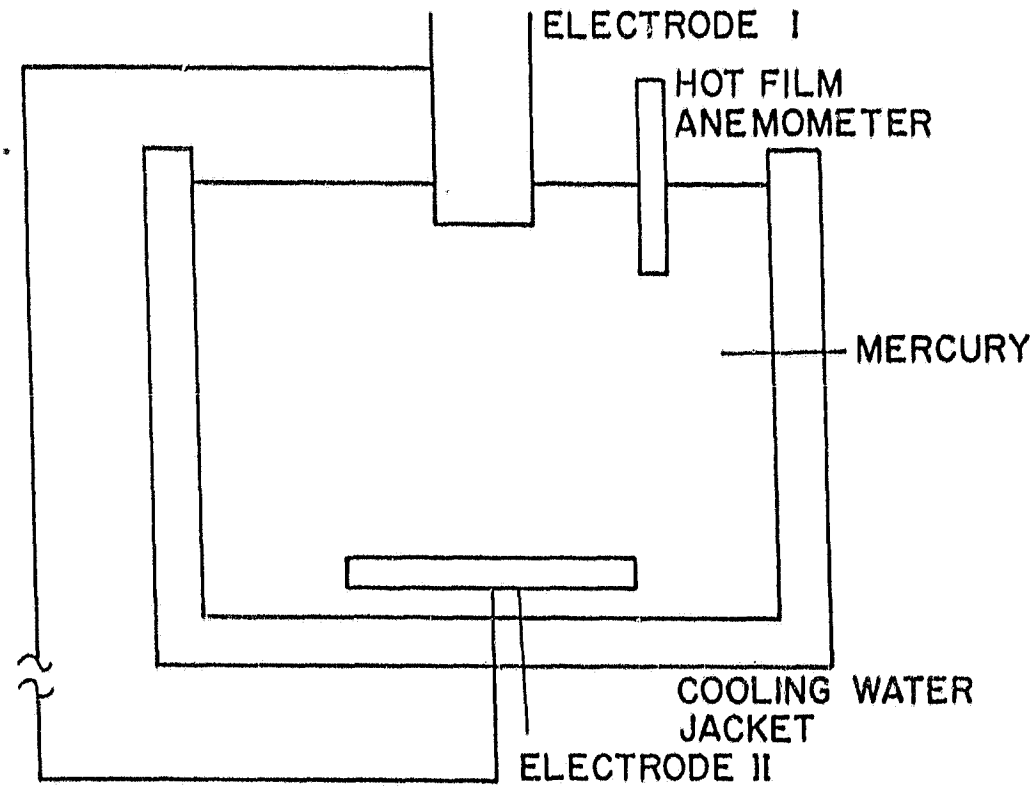

Figure 14: Schematic sketch of the apparatus designed for measuring the electromagnetically driven velocity field in the Woods Metal system.

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measurements. Work is currently in progress in order to relate these findings to the grain refining experiments and to the planning of an experimental program to be conducted in a zero gravity environment.

References

1. R.T. Frost and C. W. Chang, Symposium on Materials Processing Research in Reduced Gravity Environment of Space, Nov. 16-19, Boston, 1981.
2. N. El-Kaddah and J. Szekely, Symposium on Materials Processing Research in Reduced Gravity Environment of Space, Nov. 16-19, Boston, 1981.
3. N. El-Kaddah and J. Szekely, to be published in Met. Trans. B.
4. D.G.C. Robertson and E.A. Jenkins, Heterogeneous Kinetics at Elevated Temperature, p. 393, Plenum Press (1970).
5. N. El-Kaddah and D.G.C. Robertson, Met. Trans. B., (1978), 9B, 191.
6. N. El-Kaddah and J. Szekely, J. Appl. Physics, submitted for publication.
7. N. El-Kaddah and J. Szekely, J. Fluid Mechanics, submitted for publication.

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2. EXPERIMENTAL PROGRAM ON NUCLEATION AND STRUCTURE IN UNDERCOOLED MELTS

INTRODUCTION

The central focus of this work has been on undercooling and structural refinements in droplets of molten metal levitated

in an induction field and/or by dispersion in a fluid carrier. Initial work, summarized in the last annual report and in a technical paper[1] was on metal base alloys. More recent work has been on nickel base and lower melting point alloys levitated in molten carrier fluids[2,3]. Major thrusts of current work are: (1) dispersion of molten alloy droplets in a high temperature fluid following the procedures developed by Perepezko and co-workers for lower melting point alloys, (2) obtaining a similar dispersion by room temperature mechanical mixing of particles of the metal and solidified liquid carrier, and (3) solidification of single relatively large droplets in a transparent fluid carrier, enabling high-speed temperature measurement of the recalescence and subsequent cooling behavior.

During the last year, it has become evident that work on undercooling of metal has broad practical implications, both for space and terrestrial processing, and particularly in the important technological area of rapid solidification processing.

As the solidification rate of a metal alloy is increased progressively from those rates encountered in conventional casting processees, the structure (dendrite arm spacing) is first observed to become finer, then supersaturation of the primary phase may be observed, metastable phases may be encountered, and ultimately the alloy may solidify as a metallic "glass." In all of these instances, substantial undercooling must exist in the liquid in front of the growing solid front, and in many instances, much of the undercooling may be developed in the liquid before any solidification begins. For example, the relatively homogeneous structures, sometimes termed "microcystalline," found in atomized ultra-fine liquid droplets probably result from undercooling in the droplet before.[4-8] The metastable BCC phase in atomized Fe-Ni alloys, and stainless steels,[7,8] certainly results from undercooling before nucleation.

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Thus, the question of melt undercooling before nucleation and its influence on solidification behavior and solidification structure is fundamentally important with direct practical implications. And, as has been pointed out by Perepezko[9], this undercooling can be studied not only in usual "rapid solidification processes" but also, and more directly, in any of several processes designed to produce significant undercoolings at relatively low cooling rates or, more exactly, at relatively low rates of heat extraction to the surroundings. Examples of such processes are undercooling of bulk samples and undercooling of dispersed droplets. Of course, even though the rate of heat extraction to the surroundings in these processes may be very slow, solidification rate immediately after nucleation is not. In the case of small dispersed droplets, the cooling rate after recalescence may also be quite rapid because of the temperature difference between the recalesced droplets and the surrounding fluid.

3. EXPERIMENTAL AND ASSOCIATED ANALYTICAL WORK

Experimental work has been on a low melting alloy, Sn-25% Pb, and on high temperature alloys, Ni-Sn and IN-100.

Tin-25% Lead Alloy

The apparatus used for the low melting point alloy is shown in Fig. 1; it is modelled after the apparatus of Perepezko and co-workers[9,10-13]. Droplet dispersions are produced in the apparatus by emulsifying a mixture of the liquid alloy and an organic carrier fluid (Polyphenylether), at a high speed (3800 rpm). The atmosphere in the furnace is argon. The temperature is kept at 25°C above the melting point during shearing, which continues for 40 minutes, producing

fine droplets dispersed in the oil. The emulsified samples are then transferred to sealed aluminum pans for analysis in a differential thermal analyzer (DTA) or a differential scanning calorimeter (DSC). The emulsified samples are later ultrasonically cleaned for observation of cross-sectional microstructures by scanning electron microscopy (SEM).

Our current work comprises primarily study of metal structures as a function of solidification variables (undercooling, cooling rate). Working with droplets in the size range 2 to 30 microns, we can readily obtain undercoolings up to about 85°C and find the measured undercooling is a function of the cooling rate in the differential scanning calorimeter, Fig. 2. Fig. 3 is a typical example of structures obtained. The dark areas are tin-rich and light areas lead-rich.

Sn-25% Pb is a two-phase alloy at equilibrium - it would have approximately 71 wt% tin-rich phase and 29 wt% lead-rich phase after equilibrium solidification. Note in Fig. 3 that these phases are distributed differently in two distinctly different two-phase regions. There is a small circular Pb-rich region (hereafter termed V_1) that is clearly lead rich because of the large volume fraction of the light colored phase. There is also a larger Sn-rich region, V_2, which has predominantly the darker tin rich phase. The volume fraction of V_1 decreases with increasing cooling rate before nucleation (and therefore with increasing undercooling, Figs. 4 - 6). Structure fineness also increases with increasing undercooling; i.e., spacing of B particles in the α matrix decreases, Fig. 4. Data in these figures are for droplets in the size range of 10-15 μm.

In this work we have not found, nor have we been searching for, metastable phases such as those found by Perepezko and

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co-workers. Our central aim has been to study the effects of undercooling and process variables on structure fineness, solute redistribution and, where present, supersaturation. Towards this end, we have begun preliminary study of the heat flow during solidification of these droplets, and of several models of solidification behavior, as discussed below.

Heat Flow in Solidification of Undercooled Droplets

There have been three studies made to date of heat flow behavior in solidification of undercooled droplets.[4,14,15] These studies have considered droplets that are undercooled and solidify in a gaseous medium (i.e., atomized droplets). All assume plane front solidification, and consider resistance to heat flow within the solid as well as at the droplet-gas interface. However, the Biot numbers achievable in practice in usual droplet atomization (Bi<<0.1) mean that heat flow can be considered Newtonian for purposes of calculating overall solidification times. Even in Newtonian cooling, significant thermal gradiants can occur on the solid droplet and so calculations of G, thermal gradient; G/R, thermal gradiant divided by growth rate, etc., require consideration of heat flow in the solid.[1]

$$\Delta H\, p_s\, V\, df_s = [p_s\, V\, f_s\, C_p^s + (1-f_s) p_L\, V C_p^L]\, dT + qA dt \qquad (1)$$

In our preliminary work on heat flow analysis in droplets emulsified in a liquid, we are using the basic methodology of Levi and Mehrabian[4], modified for the different surrounding medium and are beginning to explore application of these ideas to alloy (and dendritic) solidificatition. Our basic model is one in which droplets are emulsified in oil and cooled uniformly to their nucleation temperature, T_N. Upon nucleation, recalescence occurs creating a temperature difference between the droplet exterior and its

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surroundings so that heat flow occurs both outwards to the surroundings and inwards to the liquid core. We assume the liquid droplets are sufficiently far apart that their thermal fields do not overlap. Our work to date has been using a Newtonian model so the heat balance relating heat flow from the droplet to fraction solidified is:

$$\Delta H \rho_s V df_s = [\rho_s V f_s C_p^s + (1-f_s)\rho_L V C_p^L] dT + qAdt.$$

where: ΔH is the latent heat of fusion
V is the volume of metal droplet
f_s is fraction solid
ρ_s, and ρ_L are densities of solid and liquid
C_p and C_p are the specific heats of solid and liquid
q is the heat flux to the oil from a metal droplet
A is the surface area of a metal droplet
T is temperature and
t is time

Heat flow to the surrounding still liquid medium is given not by the convective heat flow correlation used when solidification occurs in a flowing gas but by the unsteady state form of the second law of heat conduction:

$$\frac{\partial T}{\partial \tau} = \alpha \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial R} \right) \qquad (2)$$

where α is thermal diffusivity of the surrounding medium and r is radius. In the example to be given, the solid is assumed to grow so the remaining liquid is spherical. In addition to the usual boundary conditions, the only other needed expression is a relation of growth velocity to melt undercooling. In addition to exploring kinetic coefficients of the types proposed by Turnbull[16], and Cahn and coworkers,[17,18] and employed by Levi and Mehrabian[4], we are examing the behavior of the growth front assuming the solid is growing dendritically with a narrow-liquid-solid

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range, and a dendrite tip velocity versus undercooling of the form

$$R = a\Delta T^n$$

where a and n are constants with $n \approx 2$. Relations of this form have been obtained by many investigators, and specifically by Schaeffer and Glicksman.[19]

Combined Solidification and Heat Flow Model

To relate the preceding thermal equations to solidification variables of an alloy requires some assumptions as to solidification behavior, and we are beginning to examine some different possibilities. One example of these is illustrated in Fig. 7. Here, solidification is assumed to be partitionless between T_N and T_o so solid composition is C_o. The "T_o" temperature is calculated from the equal molar free energies of the liquid and the solid using the regular solution approximation. The dependence of the temperature on the molar free energy is calculated from the Gibbs-Helmholtz relationship. Above T_o, the solid composition at the interface is the maximum thermodynamically possible solubility. This composition is calculated from the intersection of the molar free energy curve for the solid and the tangent line to the molar free energy curve for the liquid at the composition as described by Cahn.[17]

Combining mathematical description of this solidification model with the preceding heat flow analysis enables predicting details of heat flow behavior and some sample computer calculations for Sn-16 at% Pb (Sn-25 wt% Pb) are given in Fig. 8. The heat extraction during recalescence significantly affects thermal behavior and maximum recalescence. For example, a sample undercooled 60°C reaches a cooling rate of 105°C/sec just after its maximum recalescence tem-

perature, as it cools through the eutectic temperature of 183°C (at this time, it is still 0.5 liquid).

Solidification models such as this, to the extent they are proven valid, will ultimately permit prediction of effects of solidification variables on structure fineness, and will also permit prediction of amounts, compositions, and distributions of phases present, including any supersaturation. We are concentrating our efforts in this direction. Clearly, the problem is a complex one, and we intend to closely couple any computational work we do in this regard with experimental studies.

High Temperature Alloys

Our current experimental work on high temperature alloys is aimed at developing methods for undercooling droplets of iron and nickel base alloys. Three independent and related techniques are being employed. These are (1) emulsification of droplets in a high temperature liquid carrier (i.e., a technique similar to the technique of Perepezko and coworkers used for lower melting point alloys), (2) dispersion of fine droplets in a liquid carrier by intimate room temperature premixing of finely divided particles of the metal with particles of the solidified liquid carrier, and (3) undercooling of a single large metal droplet in a transparent slag to permit rapid temperature measurement of the recalescence and subsequent solidification. Exploratory work performed to date has been on Ni-Sn alloys and on the superalloy IN-100, but the techniques being developed are intended to be applicable to a broad range of iron and nickel base alloys.

Droplet Dispersal by Emulsification

The emulsification apparatus for high temperature alloys which has been constructed is shown schematically in Fig. 9.

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Crucible and stirrer are made of aluminum oxide and all runs are conducted under argon or nitrogen atmosphere. Rotation speeds of up to 2000 rpm are used and droplet sizes in the range of 2-10 μm are readily obtained by separation of the smaller size droplets from the broader distribution produced by emulsification. Slags of several glasses including Pyrex and B_2O_3 have been used with success, and experiments are also planned with salts.

A high temperature differential thermal analysis (DTA) unit has been acquired and installed and is being utilized to study these materials. The unit is a Perkin-Elmer DTA-1700 System which can be used at temperatures up to 1550°C. Fig. 10a shows a typical DTA curve obtained for droplet samples of Ni-34% Sn in the 2-10 μm range, which were emulsified in Pyrex. The curve shows undercooling of 219°C.

Fig. 10b shows an example of the structure obtained in the undercooled Ni-34% Sn dispersed in Pyrex. The electron micrograph is taken after DTA. Interphase spacing is the order of one micron, which is far finer than that of similarly undercooled bulk specimens.

Range of droplet diameters obtained after DTA is typically 2-100 μm. Current work in this part of the program is on obtaining more uniform and finer droplet dispersions through varying processing parameters including the liquid carrier, and on studying the undercoolings and structures obtained.

Droplet Dispersal by Powder Processing

Particles of IN-100, less than 20 μm in diameter, prepared by gas atomization have been mechanically dispered among fine particles of a solidified carrier fluid for analysis in the DTA. Heating of this powder mixture forms the metal droplet dispersion in a liquid carrier. Fig. 11 shows a DTA curve

for IN-100 droplets which indicates undercooling of 300°C. Examination of the droplets after DTA shows that some have combined to form larger droplets while others remained isolated. Examples of the microstructures in Fig. 11b show that the larger droplets (20 - 100 μm) are two-phase while the smaller droplets <10μm show no structure. This variation in microstructure is perhaps related to the two peaks on the DTA cooling curve which correspond to different degrees of undercooling. Similar single phase supersaturated microstructures have also been observed in undercooled gas atomized droplets, but usually only in much smaller particles.[3-8]

Large Droplet Undercooling

One limitation of working with the dispersed droplets described in the previous sections, is that it is not possible to measure the thermal behavior of individual droplets. That is, it is not possible to pin-point the precise undercooling of any given droplet nor is it possible to measure its thermal history during and after recalescence. Therefore, it is not experimentally possible to verify calculated curves such as those of Figure 8.

We have therefore initiated a series of experiments on undercooling of individual droplets of high melting point alloys, in the size range of about 5 mm. The experimental apparatus is shown in Fig. 12. As shown, a small droplet is placed inside a Pyrex or quartz tube and surrounded by crushed glass. The sample is then induction melted and the surrounding glass is also melted. Vigorous stirring of the droplet by the magnetic field in the presence of the glass slag results, pre-sumably, in absorption of nucleating agents, leading to very large degrees of undercooling even in the relatively large droplet. Most importantly, thermal behavior of the droplet surface during recales-cence can be

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directly observed. (This experiment can be similarly done by levitation melting without the surrounding glass.)

The apparatus used to measure the rapid recalescence and subsequent cooling involves a sensing device, a data acquisition and storage device, and a data manipulation device. The sensing device is a Capintec Ratioscope III, two-color pyrometer sensing head with a 135 mm close-up lens kit to observe the small sample. This device provides two sig-nals from silicon photodiodes filtered at different wavelengths which can then be ratioed and calibrated at the observed metal temperature.

The data acquisition and storage device is a Nicolet Explorer III Digital Oscilloscope which converts the analog output of the sensing head to digital bits of information which can more easily be converted into temperature values. The digital oscilloscope is interfaced to an HP-85 personal computer for data manipulation and interpretation.

This measurement system records the thermal information directly from the photodiode sensors into the digital oscilloscope. In this manner, the thermal and time data are not delayed or dampened by amplification systems, and thus the fast recalescent profile can be properly recorded. Factors which could limit the ability to obtain accurate thermal data at the high speeds involved are: (1) the response time of the silicon photodiode sensors (which is the order of microseconds), and (2) the recording time for the digital oscilloscope, which is capable of 0.5 microsecond per bit of information recording time. Initial experiments indicate that these response delays are inconsequential compared to the recalescent rise time of an undercooled sample (which, for samples of this size, is on the order of milliseconds as will be seen below).

In conducting thermal experiments, the metal sample is usually surrounded by a transparent viscous medium such as crushed Pyrex glass. The sample is placed in an induction melting coil within the viewing range of Capintec ROS-III two-color sensing head. The induction melter consists of a copper coil having two reversed turns which is coupled to a 400 KC, 10 KW high frequency generator. The sample is stoppered, evacuated and backfilled with argon to provide a clean environment around the sample.

The sample is heated into the molten state and allowed to cool and solidify. After several thermal cycles, the sample comes into intimate contact with the glass and achieves better undercooling. A thermal cycle is then run, and the two-color measurements of nucleation and recalescence are digitized and stored within the Nicolet digital oscilloscope. Conversion of the two-color measurements to temperature is being performed by a linear relationship of the two-color ratio. In current experiments we are checking the validity and reproducibility of this linear relationship using thermal artifacts including the solidus temperature and the B-B' solid-solid transformation (in the Ni-Sn alloy) for calibration.

One experimental thermal profile obtained to date is shown in Fig. 13. Recalescence time is approximately 30 milliseconds for these 5 mm diameter droplets. This curve is representative of early data acquired with newly obtained equipment and much experimental work is necessary to improve quality, prove reliability and usefulness, and determine the minimum size metal droplet on which the experiment can be successfully carried out. The aim of this research is to compare experimental curves such as Fig. 13 with calculated profiles such as those presented in Fig. 8, or with calculated profiles based on other solidification models such as a pure metal model comparable to that of Levi and Mehrabian.[4]

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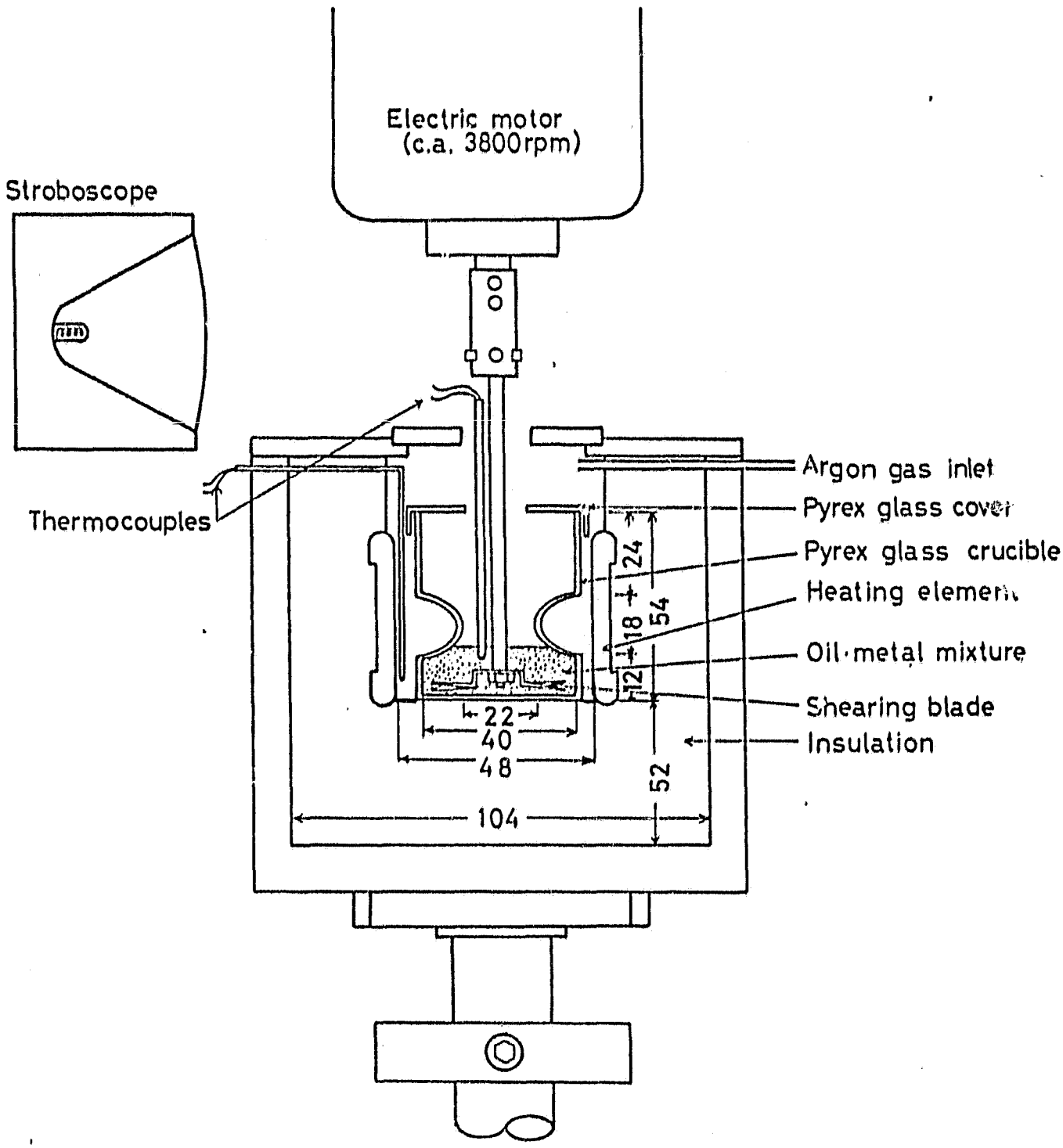

Figure 1: Schematic diagram of the experimental setup for emulsifying droplets of molten low melting point metal in oil.

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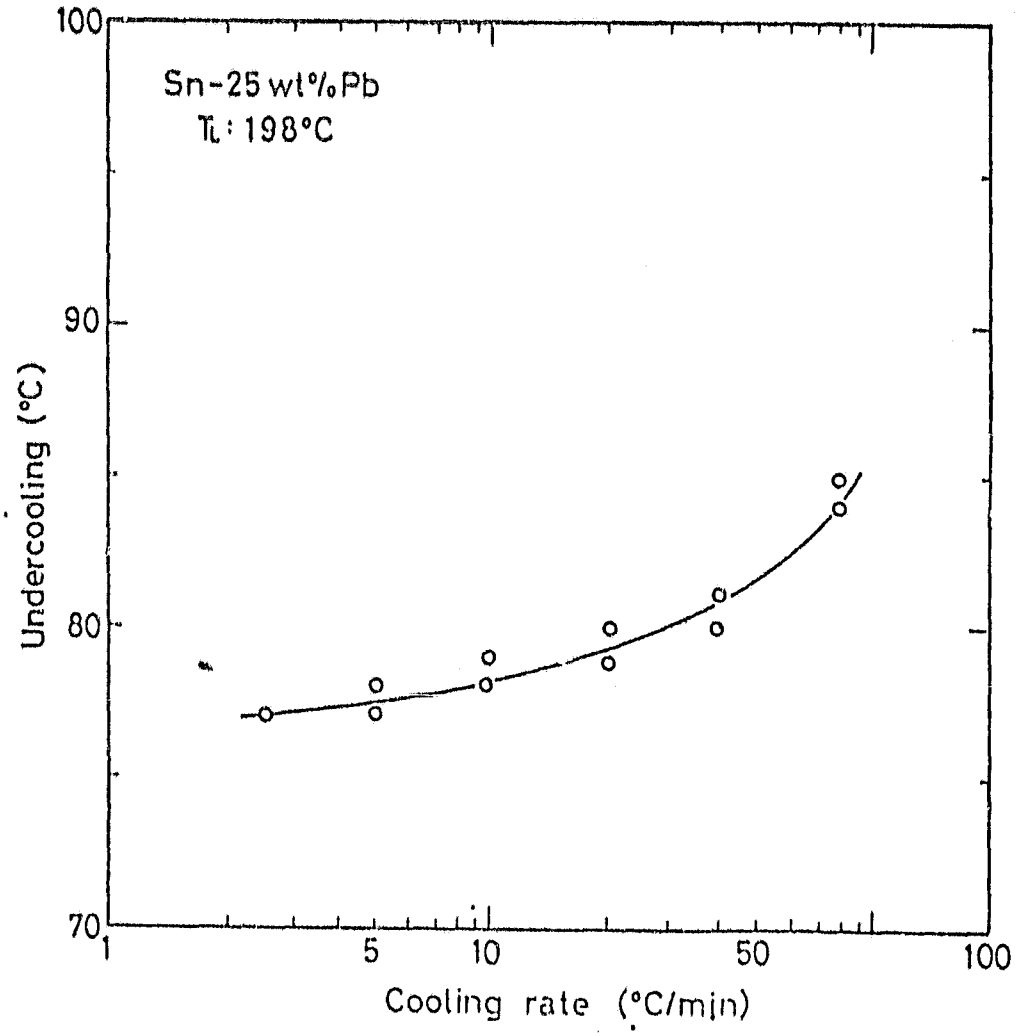

Figure 2: Effect of cooling rate in the differential scanning calorimeter on undercooling of Sn-25 wt% Pb droplets. (Data for 10-15μm diameter droplets.)

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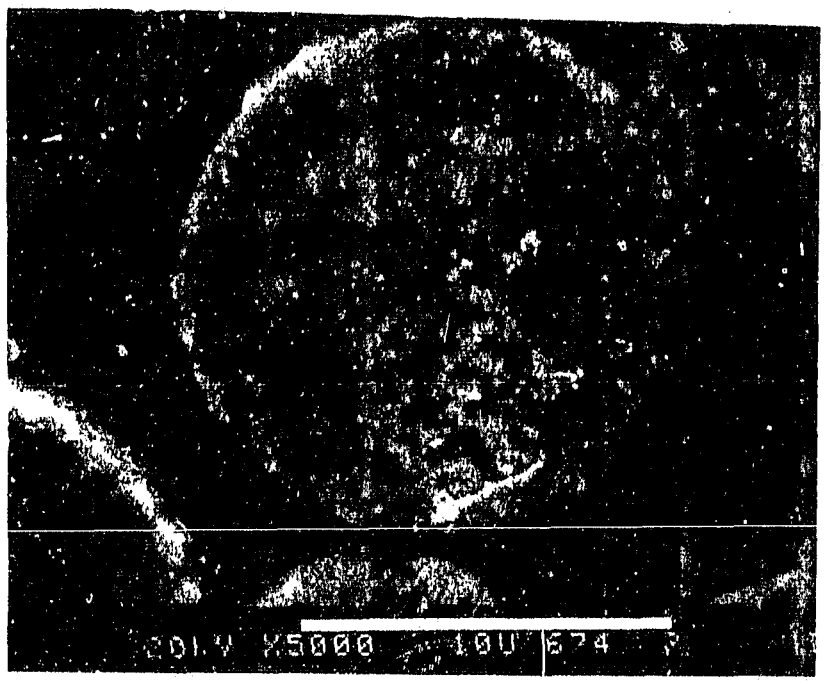

Figure 3: The cross sectional microstructure of a droplet of Sn-25 wt% Pb solidified with a DSC cooling rate of 10°C/min, and with 80°C of undercooling.

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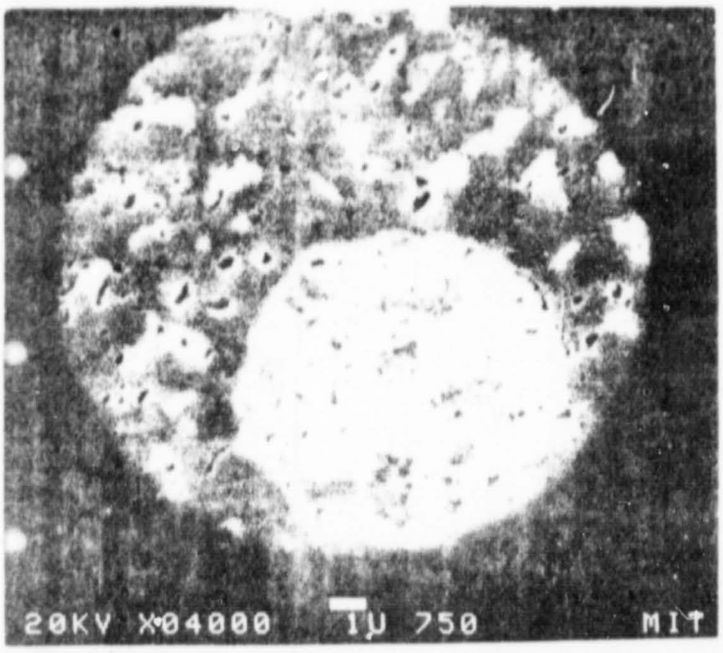

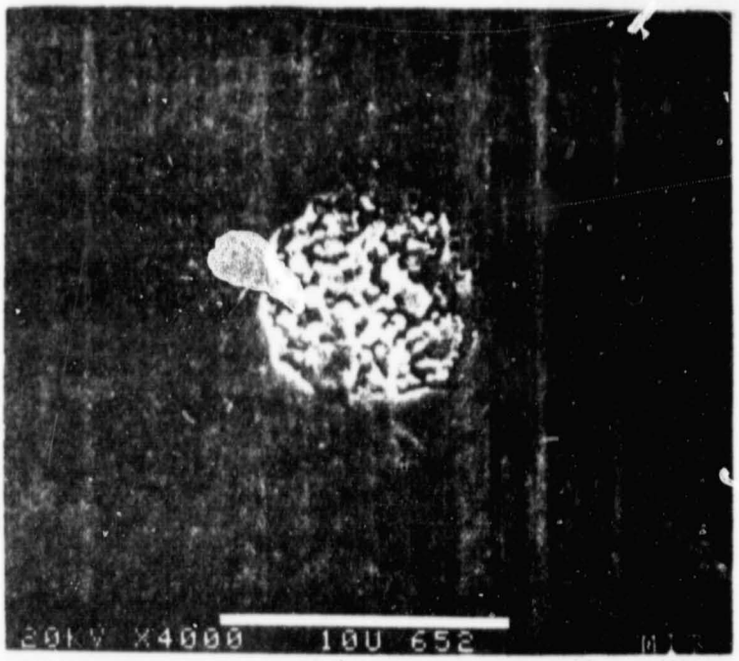

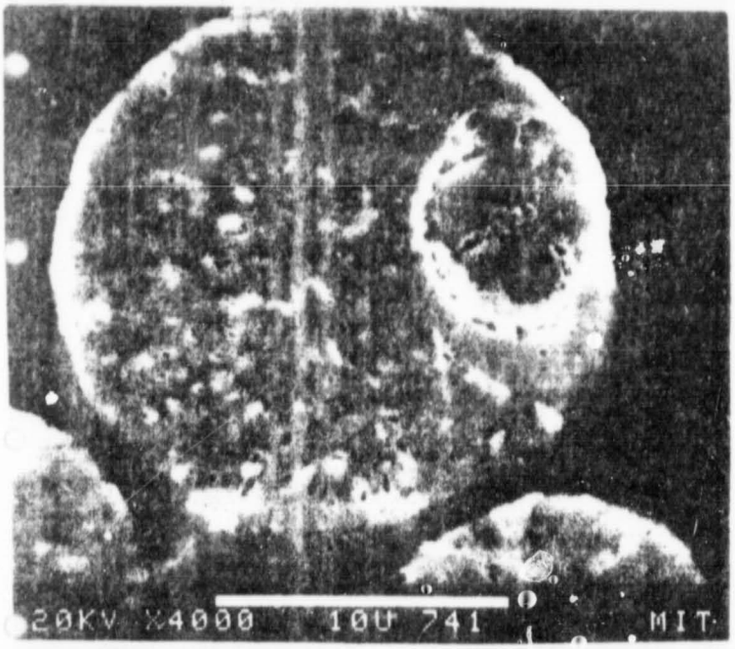

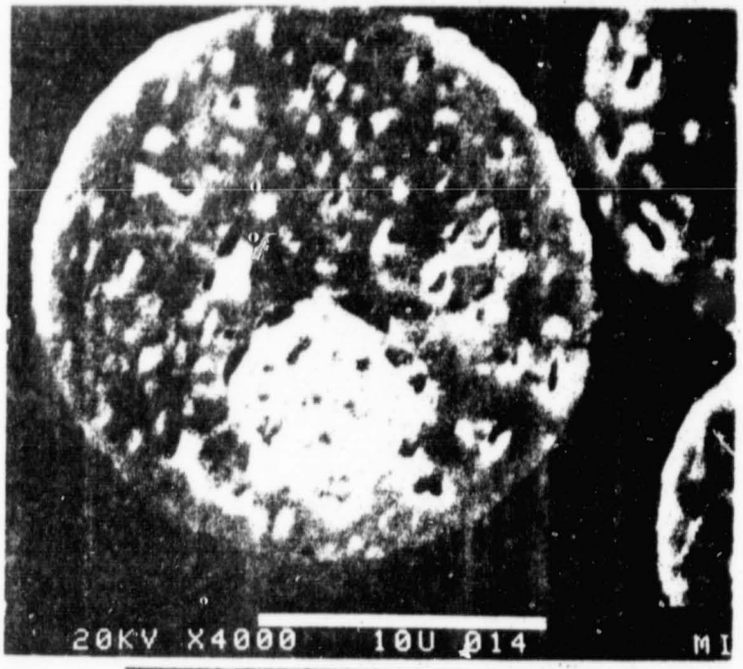

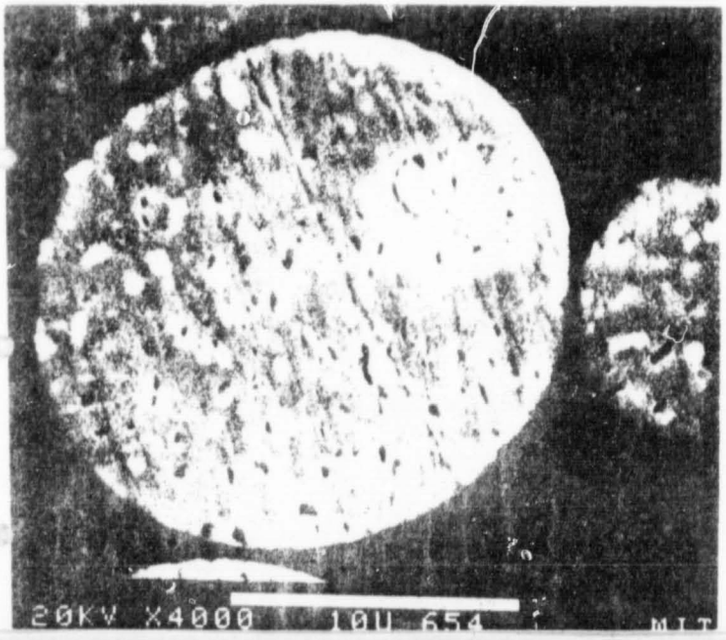

5°C/MIN	10°C/MIN
20°C/MIN	40°C/MIN
80°C/MIN	

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Figure 4: Microstructures of droplets of Sn-25 wt% Pb solidified with DSC cooling rates for 5-80°C/min.

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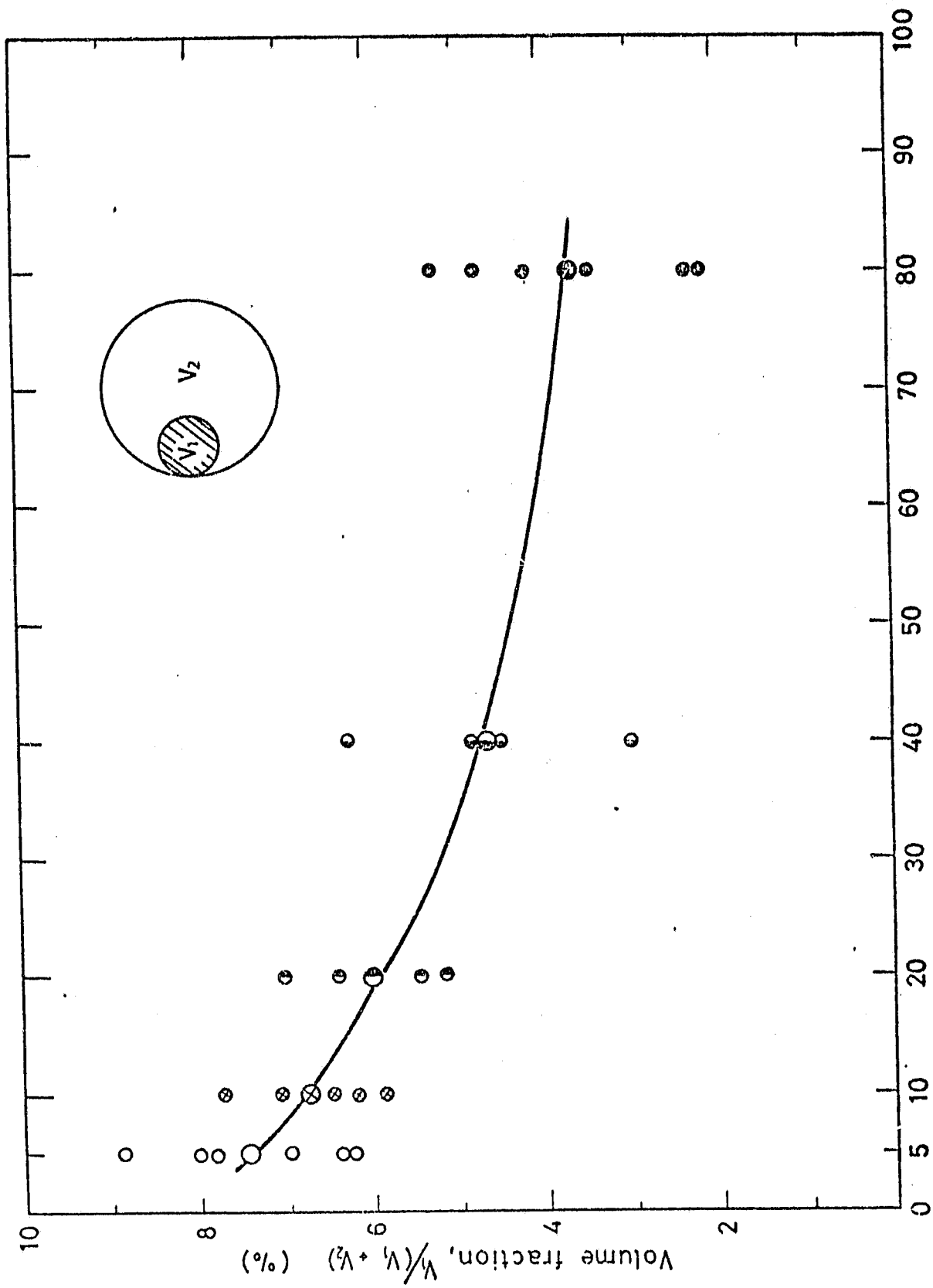

Figure 5: Volume fraction of the lead rich region, V_1, versus DSC cooling rate. Data for 10-15μm diameter droplets.

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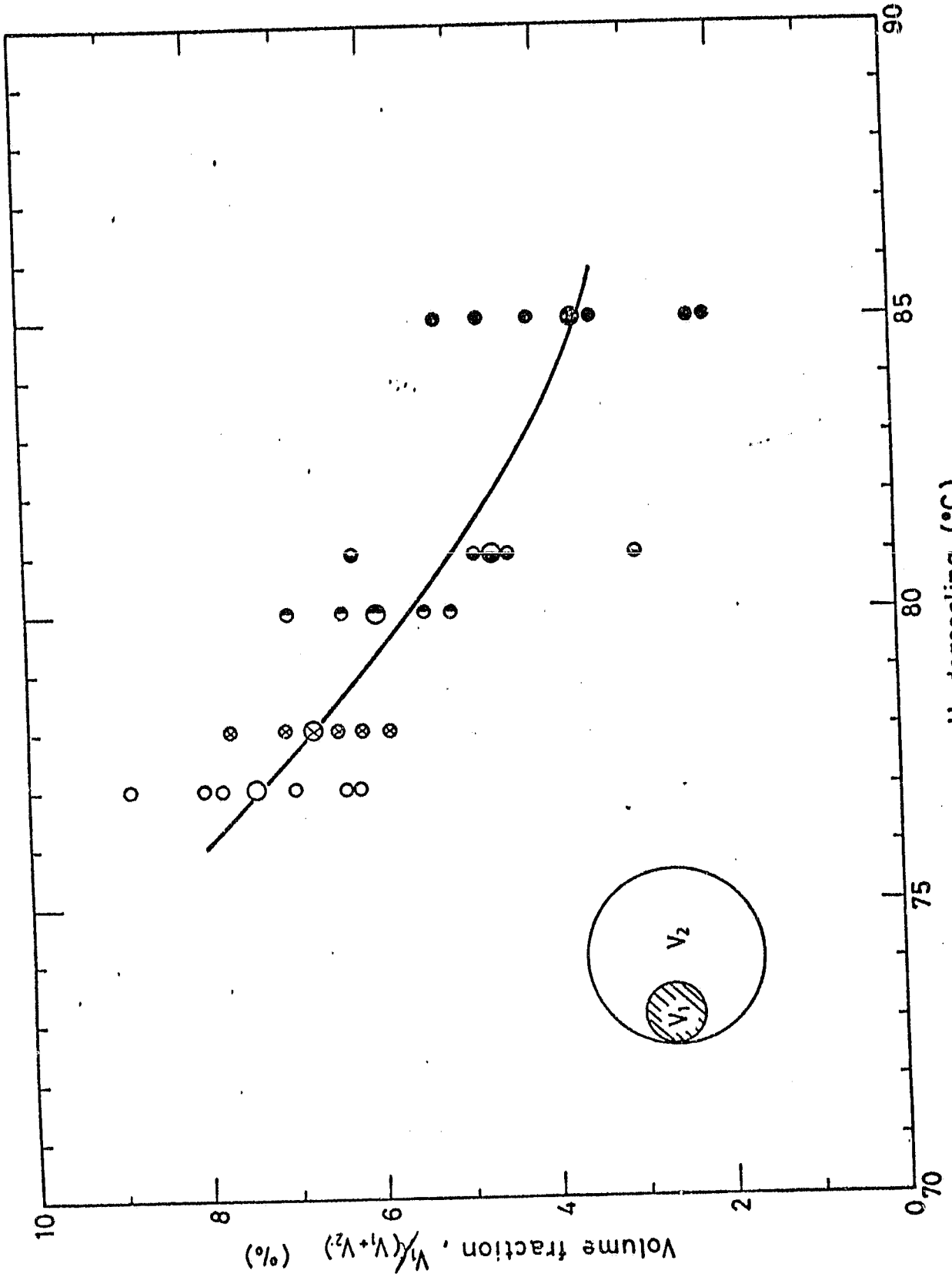

Figure 6: Volume fraction of lead rich region, V_1, versus undercooling. Data for 10-15μm diameter droplets.

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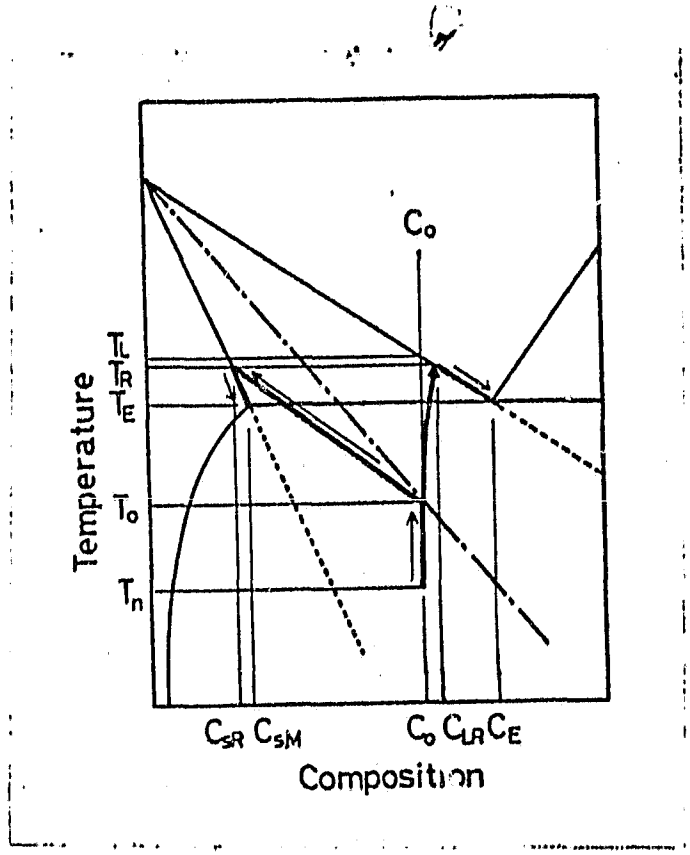

Figure 7: One possible solidification path for an alloy of composition C_o. Solidification is partitionless from T_n to T_o. Between T_o and T_R the solid that forms is of the maximum composition thermodynamically possible. Thereafter the solid forming is of the composition of the equilibrium solidus.

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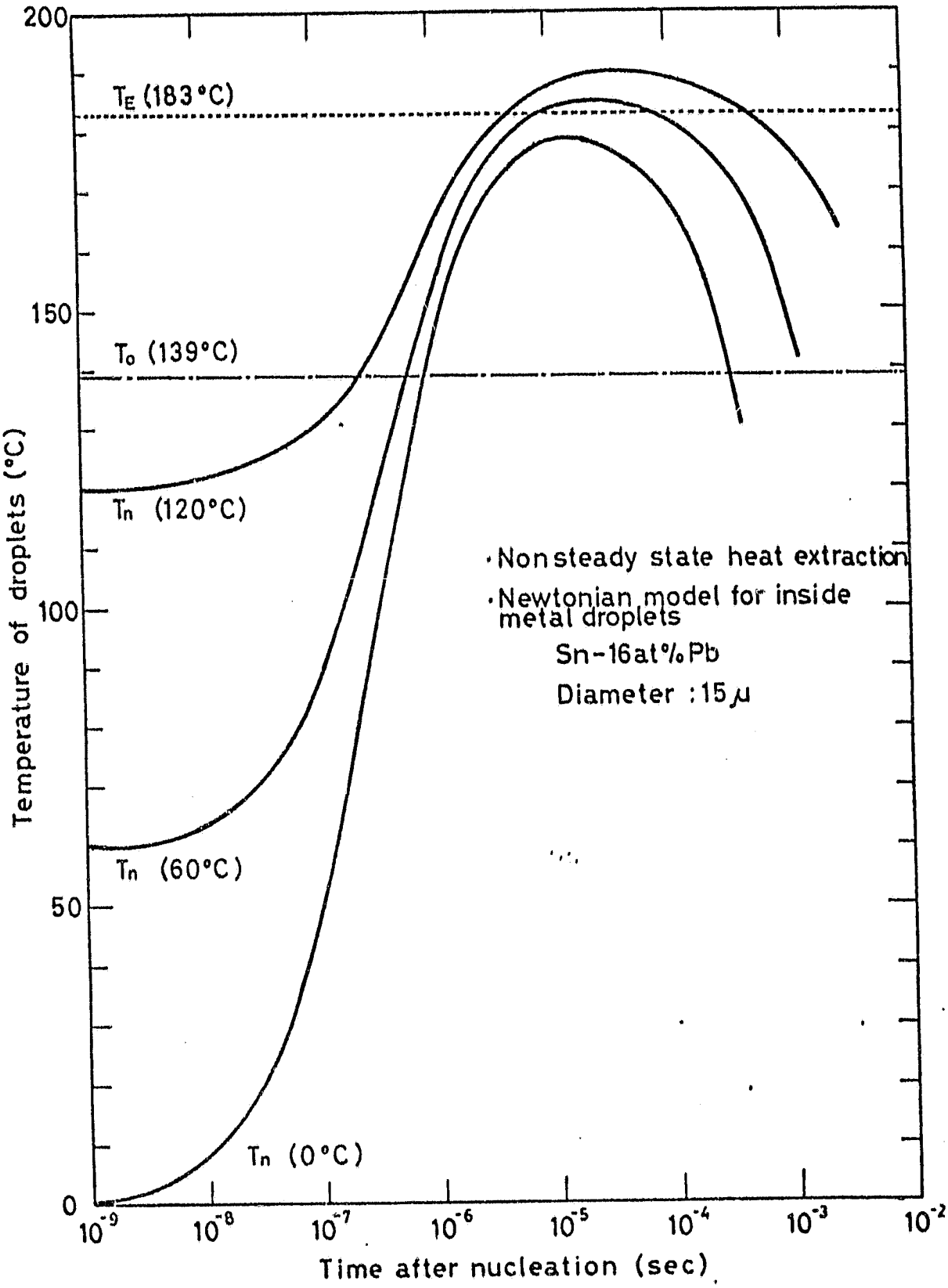

Figure 8: Calculated temperature profile for a Sn-25 wt% Pb (Sn-16 at% Pb) alloy nucleated at three different temperatures, T_n.

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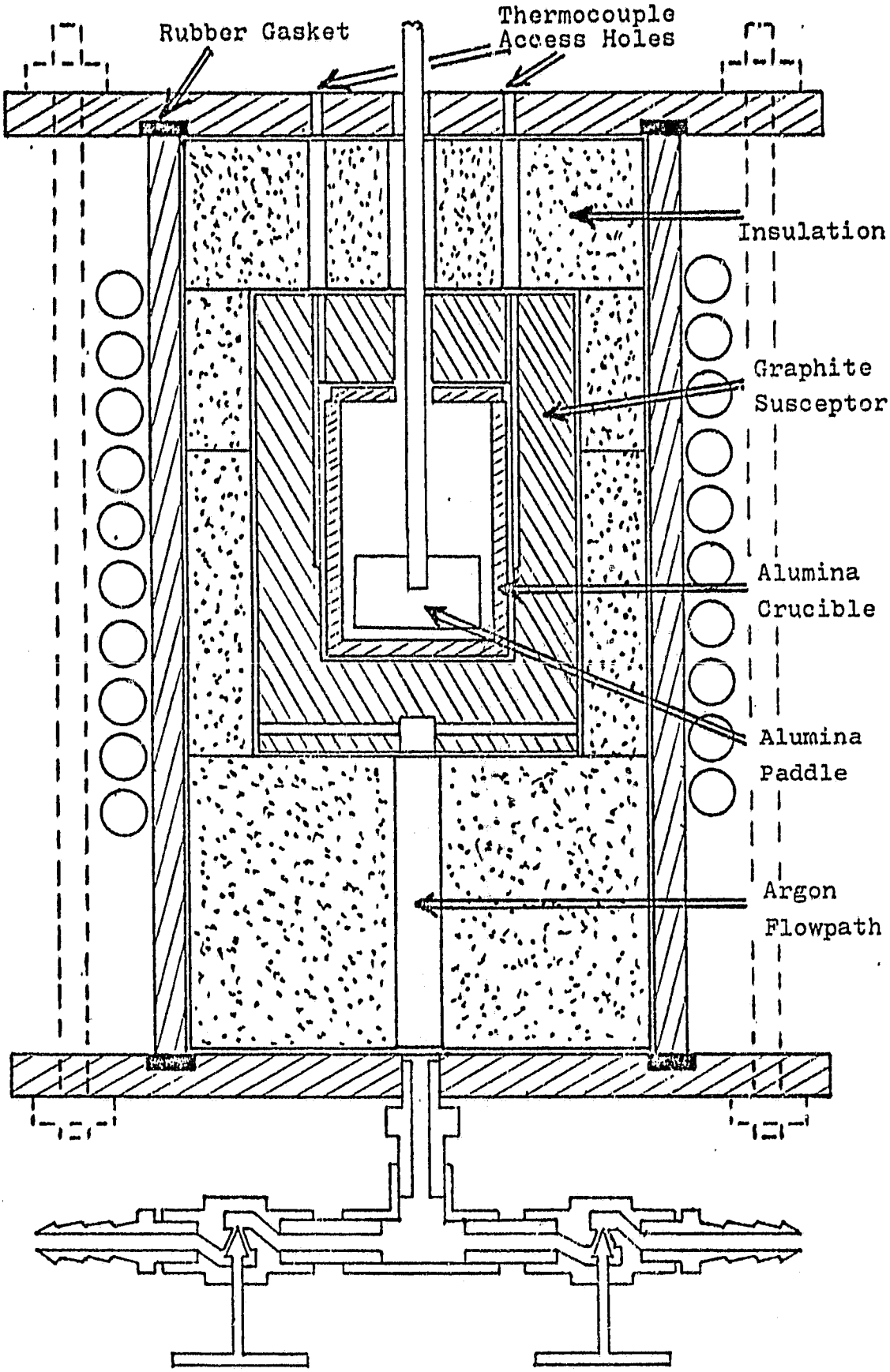

Figure 9: Schematic diagram of apparatus from emulsifying high melting point alloys.

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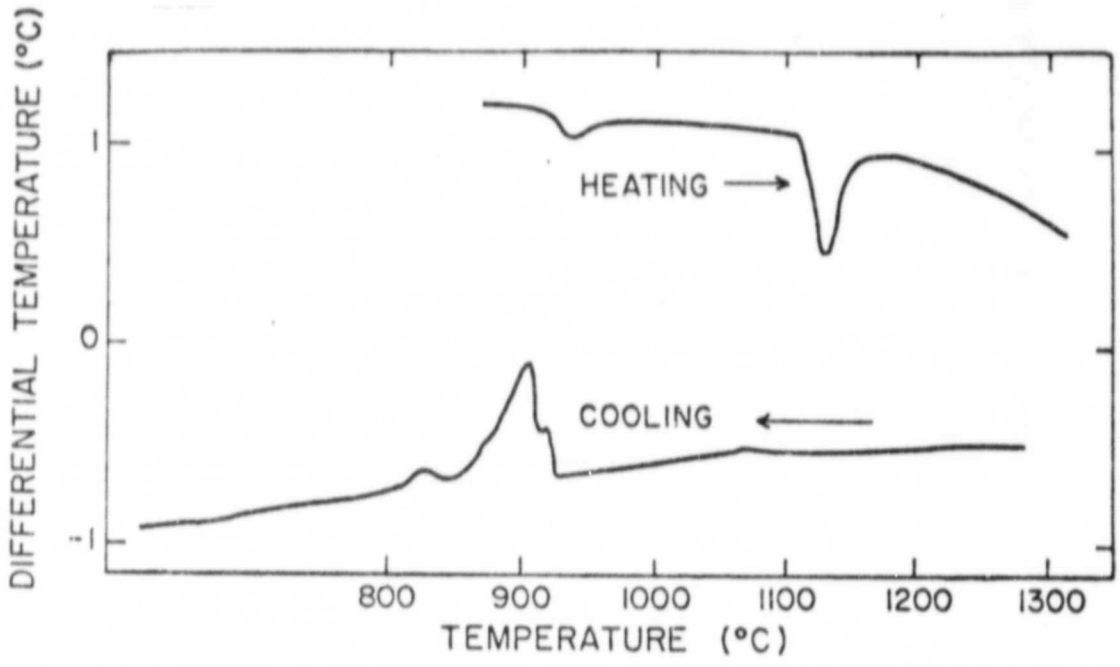
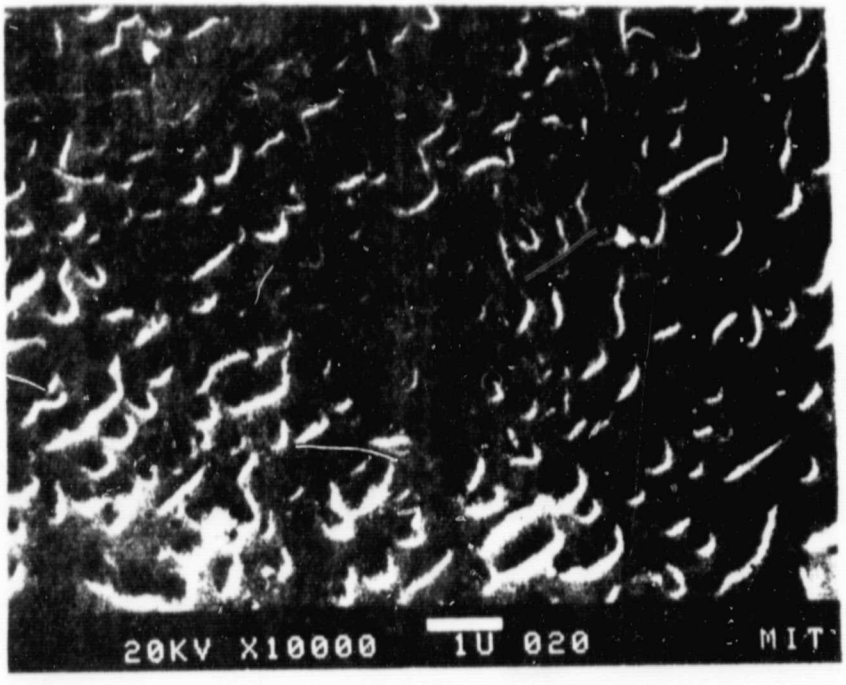


(a)



(b)

Figure 10: Differential thermal analysis (DTA) and microstructure of Ni-34% Sn emulsified in Pyrex. DTA curve shows sample undercooled 219°C. Second peak is solid state transformation.

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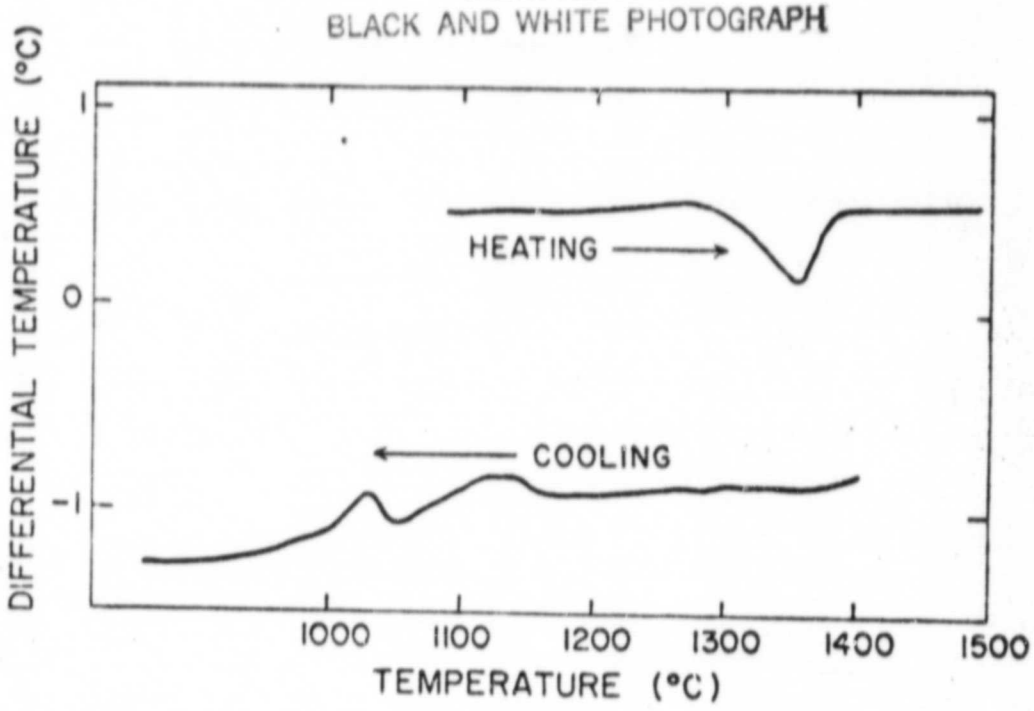
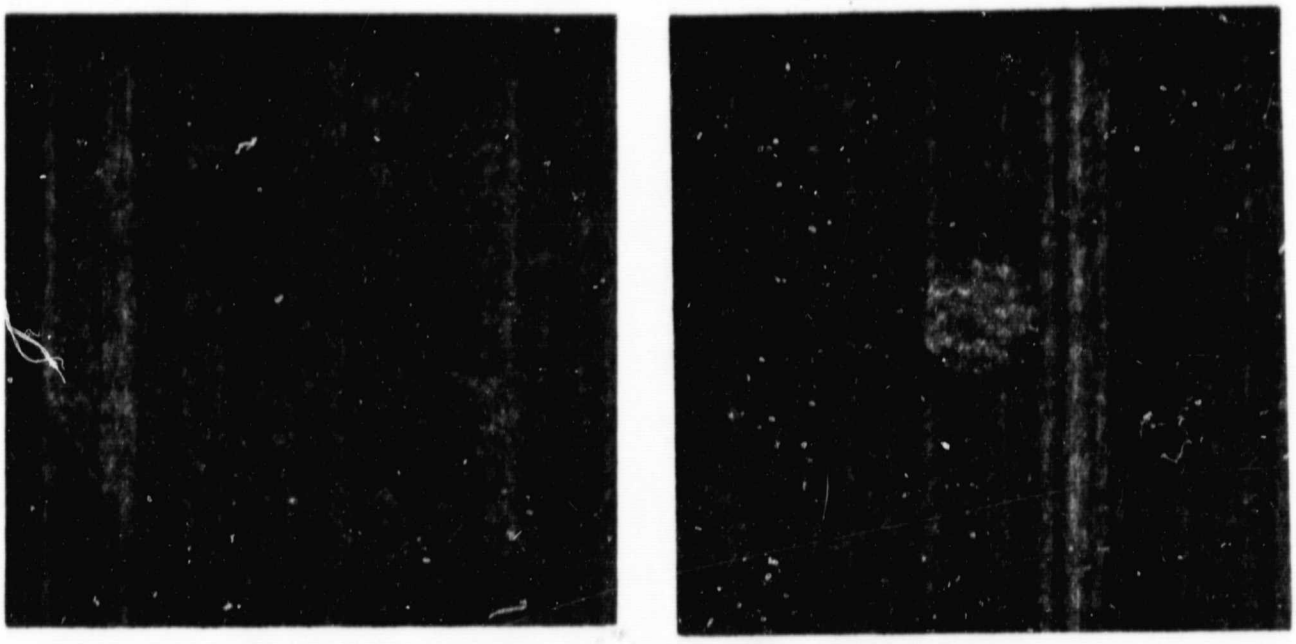


(a)



(b)

Figure 11: Differential thermal analysis (DTA) and microstructure of IN-100 alloy mechanically dispersed in Pyrex. DTA shows two peaks corresponding to undercoolings of 190°C and 300°C respectively. Photomicrographs (at 1000X) show the larger droplets have a two phase structure while smaller droplets are apparently single phase.

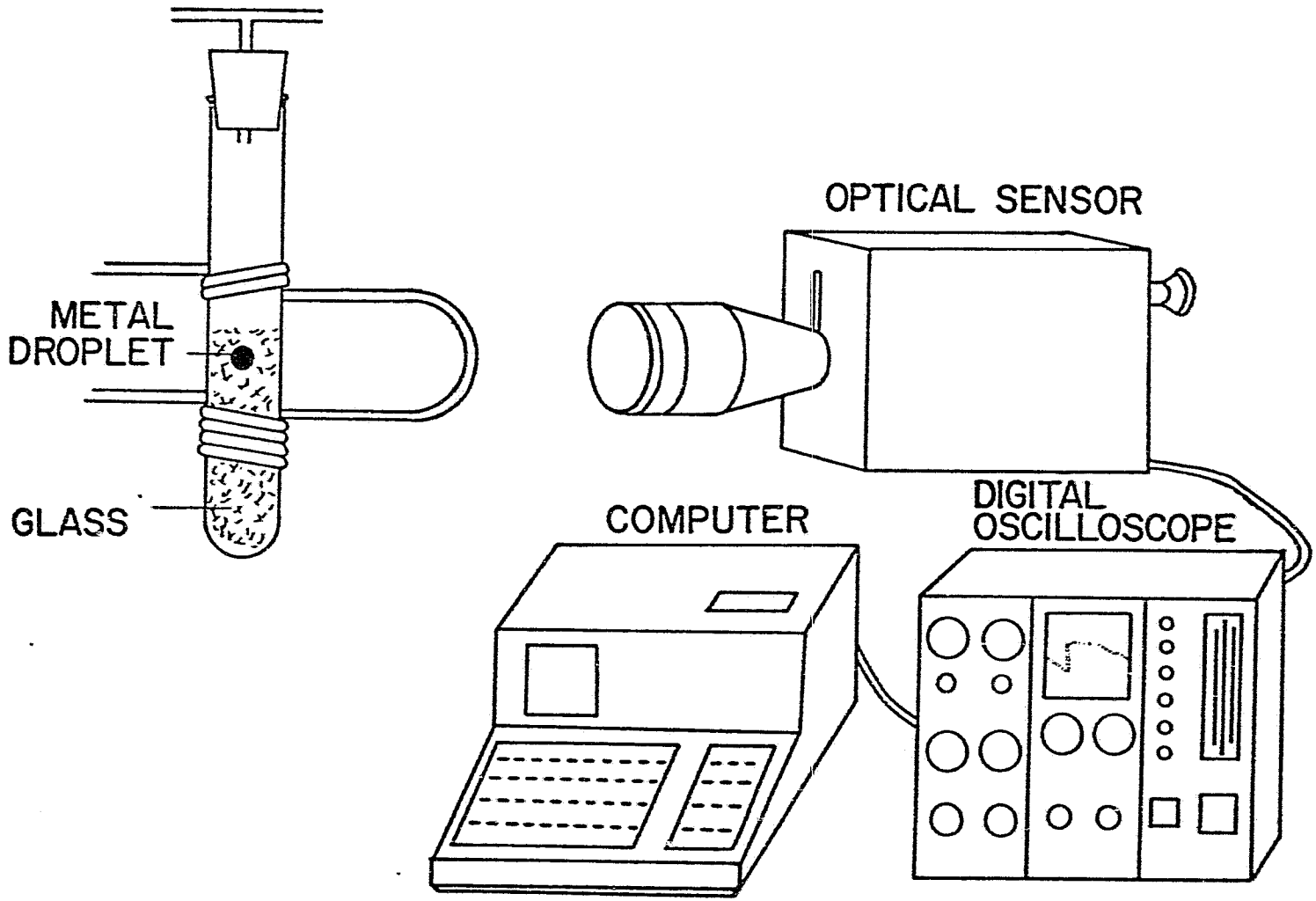


Figure 12: Schematic diagram of large droplet solidification apparatus, showing metal sample induction melted in glass, an optical sensor, a digital oscilloscope and a computer.

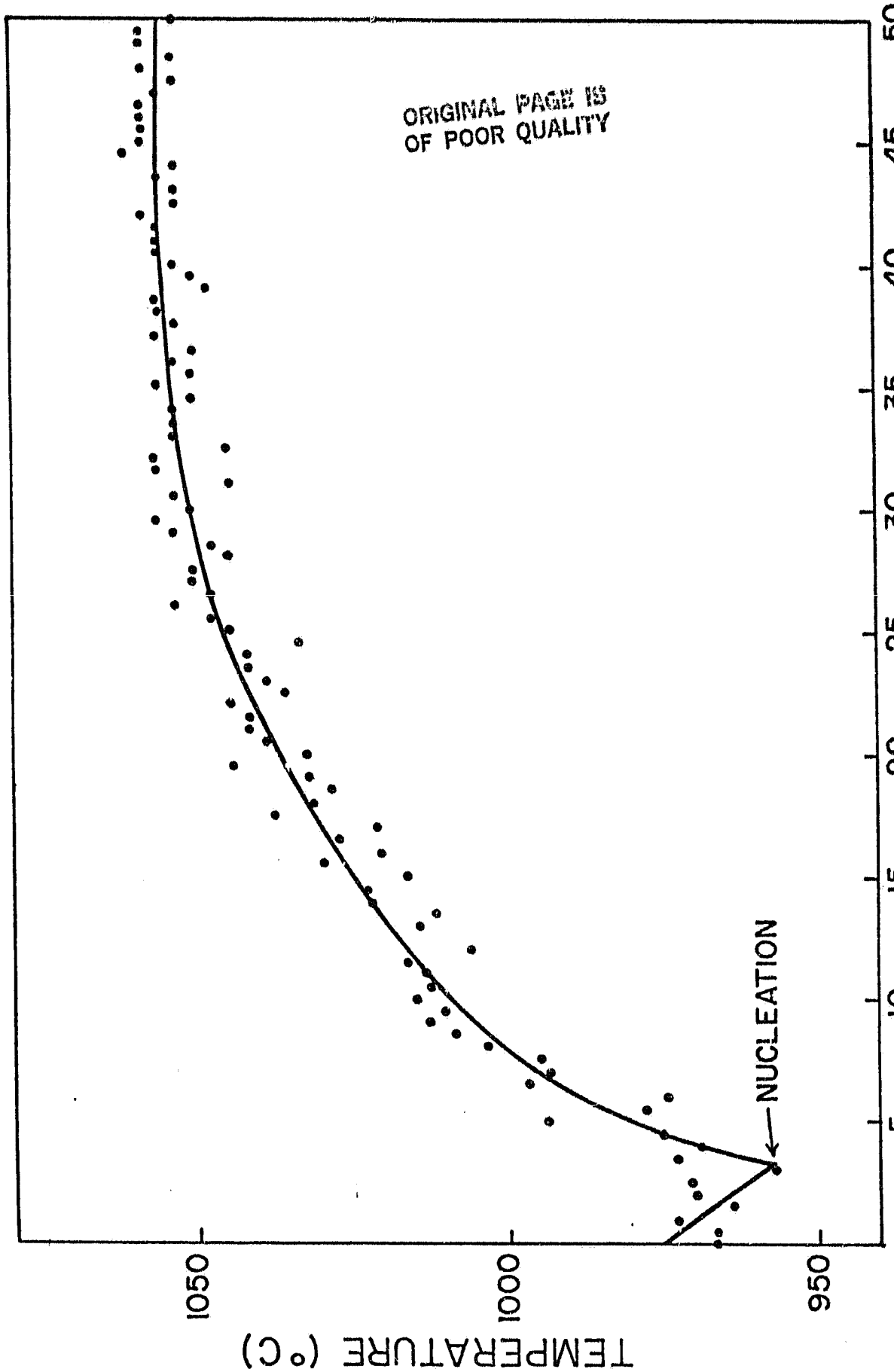


Figure 13: Thermal profile of the surface of a recalescing 5 mm droplet of Ni-32.5% Sn.

REFERENCES

1. R. Abbaschian and M.C. Flemings, "Nucleation and Structure of Undercooled Melts" (to be published).
2. Y. Shiohara, M.G. Chu, D.G. MacIsaac, M.C.Flemings, "Solidification Mechanisms of Undercooled Metal Alloys," Proceedings of Materials Research Society, Boston Meeting, November 1981.
3. Y. Shiohara, M.G. Chu, D.G. MacIsaac, M.C. Flemings, "Structure of Undercooled Liquid Droplets," Dallas, AIME Meeting, February 1982.
4. C.G. Levi and R. Mehrabian, Technical Report to the Office of Naval Research, Contract No. N00014-78-V-0275, (190). C.G. Levi and R. Mehrabian, Met. Trans., Vol. 11B, 21 (1980).
5. P.R. Holiday, A.R. Cos and R.J. Patterson, in "Rapid Solidification Processing: Principles and Technologies," R. Mehrabian, B.H. Kear and M. Cohen (eds.), Claitor Pub., Baton Rouge, 246 (1978).
6. R.D. Field and H.L. Fraser, in "Rapid Solidification Processing: Principles and Technologies," R. Mehrabian, B.H. Kear and M. Cohen (eds.), Claitor Pub., Baton Rouge, 270 (1978).
7. T.F. Kelly, Sc.D. Thesis, MIT, December 1981.
8. R.E. Cech, Trans. AIME, 585 (1956).
9. J.H. Perepezko and I.E. Anderson, TMS-AIME, 1980 Symposium on Synthesis and Properties of Metastable Phases, T.J. Rowland and E.S. Machlin (eds.), in press.
10. J.H. Perepezko, D.H. Rasmusen, I.E. Anderson and C.R. Loper, Jr., Proceedings of International Conference on Solidification, The Metals Society, 169 (1977).
11. J.H. Perepezko, C. Galaup and D.H. Rasmussen, Proceedings of the 3rd European Symposium on Materials Science in Space (1979).
12. J.H. Perepezko and J.S. Smith, J. Non-Cryst. Solids, Vol. 44, 65 (1981).

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OF POOR QUALITY

13. J.H. Perepezko, "Rapid Solidification Processing-Principles and Technologies," R. Mehrabian, B.H. Kear and M. Cohen (eds.), Claitor Pub., Baton Rouge, 56 (1978).
14. W.R. Glickstein, R.J. Patterson II and N.E. Shockley, in "Rapid Solidification Processing: Principals and Technologies I," R. Mehrabian, B.H. Kear and M. Cohen (eds.), Claitor Pub., Baton Rouge, 46 (1978).
15. C.M. Adam, Interim Reports for Office of Naval Research, Department of the Navy, FR-15178, May 1981. (Reports heat transfer analyses by Mollendorf and Janz.).
16. D. Turnbull, "Thermodynamics in Metallurgy," American Society for Metals, Metal Park, Ohio (1949).
17. J.W. Cahn, Acta Met., Vol. 8, 554 (1960).
18. J.W. Cahn, W.B. Hillig, G.W. Sears, Acta Met., Vol. 12, 1421 (196).
19. M.E. Glicksman, R.J. Schaeffer, "The Solidification of Metals," Iron and Steel Institute Publ. No. 110 (1968).
20. J.C. Baker and J.W. Cahn, Solidification, American Society for Metals, Metals Park, Ohio, 23 (1971).
21. S.E. LeBeau and J. H. Perepezko, "Undercooling of Aluminum Alloy Droplets," Oral Presentation, Fall Meeting AIME (1981).

N82 27385

PROJECT A3: THE STRUCTURE AND PROPERTIES OF RAPIDLY SOLIDIFIED HIGH ALLOY ALUMINUM MATERIALS

Principal Investigator: Prof. N. J. Grant
Personnel: Mr. W. Wang

RESEARCH ABSTRACT

A series of 2024 type aluminum alloys modified by additions of 1 to 2% Li were studied to determine the role of the Cu:Li and the (Cu + Mg):Li ratios on resultant strength, ductility, notch-tensile behavior, and crack propagation rates. Ultrasonically gas atomized powders, with quench rates of 10^4 to 10^5 °/s, atomized in an argon atmosphere, produced yields of powder such that almost 100% was finer than 250 microns. The powders are free of gases and porosity, are quite spherical, have few satellites (adhering fine powder particles) and are of uniform microstructure. Strength properties are such that yield strength is 20% greater than for lithium-free 2024 ingot alloy, tensile strength is 10% greater than that of 2024 ingot material, and ductilities are comparable. In terms of specific strength and specific modulus, these RS 2024-Li alloys are significantly better than IM 2024.

RESEARCH SUMMARY

An examination of the ternary diagram Al-Cu-Li shows an exceedingly complex system with numerous ternary intermetallic compounds in addition to the expected $CuMgAl_2$ and Al_3Li (delta prime) phases. Small changes in the Cu:Li and (Cu + Mg):Li ratios can lead to the appearance of three ternary phases involving Al, Cu, and Li. The presence of Li in the ternary phases decreases the amount of Li available for formation of Al_3Li, one of the important

ageing phases in this system. The presence of 1.6% Mg, 0.5 Mn, and up to 0.25% Cd further complicates the prediction of which phases will form and in what quantities.

Accordingly, Cu was varied from 3.96 to 5.92%, Mg from 1.57 to 1.92%, and Li from 1.25 to 2.17%. Both Mn and Cd were omitted from one of the alloys. See Table 1 for final alloy compositions.

The high Cu alloy (5.92% Cu, 1.29% Li, 1.57% Mg, 0.36% Mn, and 0.13% Cd) had very poor ductility. Strength values were not importantly different than those for the lower copper content, but ductility was decidedly smaller. The presence of primary $CuAl_2$ was readily evident; unfortunately this primary phase coarsened during solution heat treatment and probably accounted in part for the poor ductility values. Measured values of notch toughness and da/dN values were the poorest of the three alloys studied.

To illustrate the room temperature tensile data, Table 2 shows for Alloy 3 values of YS, UTS, elongation, and reduction of area for various heat treatments; in addition YS and UTS values are listed after correction for the decrease in density due to the presence of 0.96% Li.

The decrease in density of Alloy 2 (1.63 wt pct Li) is 5% while the increase in Youngs modulus is 12.5% for a net gain of 18.3% in specific modulus.

Further, Table 3 shows representative values of the Notch Yield Ratio, the Notch Tensile Ratio and Fracture Toughness (these values are more nearly equal to K_Q rather than K_{IC} due to specimen geometry).

Overall, these Li-modified 2024 alloys demonstrate the importance of the Cu:Li ratio on mechanical properties, with

Li having a major positive effect on both specific modulus and specific strength. The high fracture toughness values and the excellent notched yield and tensile properties indicate that alloys based on the 2024 compositions can be expected to possess excellent commercial potential.

PUBLICATIONS

1. K. Sankaran and N.J. Grant, "The Structure and Properties of Splat Quenched Al Alloy 2024 Containing Li Additions." Mats. Sci. and Eng., 44, 1980, 213.
2. V. Anand, A.J. Kaufman and N.J. Grant, "Rapid Solidification of a Modified 7075 Al Alloy by Ultrasonic Gas Atomization." Proceedings Second International Conf. on Rapid Solidification, March 1980. Eds. R. Mehrabian, B.H. Kear and M. Cohen. Claitor's Publ. Div., Baton Rouge, La.
3. N.J. Grant, S. Kang and W. Wang, "Structure and Properties of Rapidly Solidified 2000 Series Al-Li Alloys." Aluminum-Lithium Alloys, Eds. T.H. Sanders, Jr. and E.A. Starke, Jr., Conf. Proc. The Mat. Soc. of AIME, May 1981.

TABLE 1

Compositions of the Alloys

Alloy	Cu	Mg	Li	Mn	Cd	Fe	Si	Zn	Cr	Ti	Al
1	(5.92)	1.57	1.29	0.36	0.13	0.18	.06	0.01	-	-	bal.
2	3.78	1.40	1.63	(0.01)	(-)	0.11	.13	0.02	(0.01)	(0.18)	bal.
3	4.16	1.80	0.96	0.50	0.18	0.14	0.02	0.02	(0.02)	-	bal.

( ) indicate variables in compositions

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TABLE 2

Room Temperature Tensile Properties of Alloy 3

Desig.	TMT	0.2% Yield Strength ksi (MPa) σ_Y	Tensile Strength ksi (MPa) σ_{UTS}	Elong. ε %	R.A. %	$\frac{\sigma_Y}{\rho \times 10^4 in}$	$\frac{\sigma_{UTS}}{\rho \times 10^4 in}$
3-AE	As extruded	26.6 (183.4)	43.0 (296.5)	13.6	20.0	27.4	44.3
3-T6 (510,1hr)	510°Cx1hr+W.Q.+190°C x2hr+W.Q.	26.6 (457.8)	79.0 (544.7)	7.4	10.0	68.5	81.4
3-T4 (510)	510°Cx0.5hr+W.Q.+R.T. x21hr+W.Q. >15 days	58.4 (402.7)	81.4 (561.3)	11.9	17.5	60.2	83.9
3-T6 (510)	510°Cx0.5hr+W.Q.+190°C x21hr+W.Q.	68.2 (470.2)	81.1 (559.2)	9.0	13.3	70.3	83.6
3-T817 (510)	510°Cx0.5hr+W.Q.+1.7% C.R.+190°Cx21hr+W.Q.	66.9 (461.3)	74.6 (514.4)	8.3	20.0	69.0	76.9
3-T84 (510)	510°Cx0.5hr+W.Q.+3.8% C.R.+190°Cx21hr+W.Q.	71.3 (491.6)	76.4 (526.8)	6.3	12.5	73.5	78.8
3-T815 (510)	1.5%C.R.+510°Cx0.5hr+ W.Q.+190°Cx21hr+W.Q.	69.0 (475.8)	81.5 (561.9)	7.6	10.0	71.1	84.0
3-T814 (510)	510°Cx0.5hr+1.4% stretch+190°Cx21hr	69.8 (481.3)	75.2 (518.5)	7.8	12.5	72.0	77.5
3-T6 (495)	495°Cx1hr+W.Q.+190°C x21hr+W.Q.	60.5 (417.2)	74.0 (510.2)	10.7	12.5	62.4	76.3

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TABLE 3

Notch Tensile Properties and Fracture Toughness Values

Alloy and TMT	Notch Tensile Strength ksi (MPa) σ_{NTS}	Notch Yield Ratio $\frac{\sigma_{NTS}}{\sigma_{\gamma}}$	Notch Tensile Ratio $\frac{\sigma_{NTS}}{\sigma_{UTS}}$	Fracture Toughness ksi $\sqrt{in}$ (MPa $\sqrt{m}$) K_{IC}
2-T4(510)	77.6 (535.1)	1.2	1.0	30.8(33.9)
2-T4(495)	75.1 (517.8)	1.4	1.1	---
3-T6(510)	71.9 (495.8)	1.1	0.9	22.7(25.0)
3-T4(510)	81.4 (561.3)	1.4	1.0	33.9(37.3)

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N82 27386

PROJECT A4: RAPID QUENCHING EFFECTS IN GLASSY POLYMERS

Principal Investigator: Prof. F. J. McGarry
Personnel: Dr. J. F. Mandell
Mr. A. Agrawal
Mr. H. D. Lee

RESEARCH ABSTRACT

Using a specially constructed microbalance for hydrostatic weighing, density changes in PVC thin film (with no additives, 30~100 μm thick), due to rapid quenching (~500°C/sec) through the glass transition temperature, have been observed. The more severe the quench, the greater is the free volume content. Isobaric volume recovery of PVC has also been studied by volume dilatometry. Both show aging of relaxing molecular rearrangements taking place as a linear function of logarithmic aging time at room temperature. Distribution of retardation times and Primak's distributed activation energy spectra have been applied to the volume recovery data. The concomitant changes in mechanical properties of PVC after quenching have been monitored by tensile creep and stress-strain to failure. All reflect the presence of excess free volume content, due to rapid quenching.

I. INTRODUCTION

Metallic glasses prepared by quenching molten alloys at the rate of approximately 10^6 °C/sec have been intensively studied.[1-6] Such materials are characterized by amorphous state, ductility, lower modulus of elasticity, high flow stress, superior fatigue resistance, higher electrical resistivity, superior corrosion resistance, etc.

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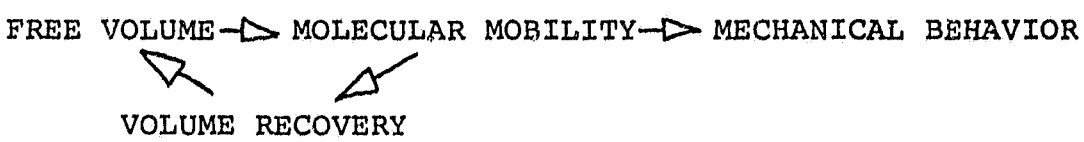
Compared to metals, polymers exhibit not only relatively poor thermal conductivity but also a narrower temperature range for quenching. Accordingly, similarly high quenching rates are not possible for polymers. Using thin film specimens of glassy polymers and selecting adequate quench media, however, relatively fast cooling rates in the range of 500-700°C/sec can be achieved. According to the concept of fictive temperature[7,8] it is believed that the fictive temperature, where glass formation begins, will be greater at increasing cooling rates.[7-9] In this connection, excess free volume that is required for segmental motion will be frozen in. Subsequently, when such a quenched glassy polymer is aged at a temperature below T_g, densification and change in the population of the various conformational isomers of the polymer chains will ensue in order to reach an equilibrium state. The reduction in the excess free volume, thus, results in a significant observed embrittlement of amorphous polymers.[10-12]

Theoretical and experimental results reported by Williams, Landel and Ferry[13], Turnbull and Cohen[14] and Kovacs[15] suggest that molecular transport mobility depends on free volume. The relationship between free volume, volume recovery, molecular mobility, and mechanical behavior can be illustrated by the following:



Various studies on the subject have not adequately defined the effects of free volume on mechanical properties, especially for rapid quenching effects. More specifically,

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the role of excess volume in the ductility of glassy polymers must be defined in order to gain further insight into the modes of molecular motion that contribute to the observed ductile behavior. Based on this understanding, it is hoped to predict the changes in material properties and further to utilize the benefits of rapid quenching effects for glassy polymers as engineering materials. Thus, study of rapid quenching effects on the mechanical properties of amorphous polymers has been undertaken.

II. MATERIALS AND EXPERIMENTAL METHODS

In order to achieve the highest cooling rates, thin film specimens of polyvinyl chloride (Geon 121) which contains no additives, are prepared either by solvent-casting in T.H.F. or by melt-molding. Typically, film thickness is in the range of 30μm to 130 μm. During annealing and quenching, the specimens were wrapped in aluminum foil (0.02 mm thick) and copper sheet (0.13 mm thick), in order to prevent surface contamination and to maintain good shape for mechanical tests. The temperature for annealing was in the range of 90°C to 160°C at atmospheric pressure. The time for annealing was 3-6 minutes. Quenching has usually been accomplished by plunging into ice water.

Among the methods available for density measurements, hydrostatic weighing is the best approach for fast measurement and accuracy. The use of thin film specimens has two serious disadvantages: the weight is only 100 mg and the large surface area causes serious static electricity problems. Accordingly, to monitor density changes to ± 0.0001 gms/cm^3, not only a very high sensitivity balance but a big chamber to minimize static between the specimen and chamber wall are required.

Following the ideas of Madorsky,[16] a microbalance was constructed to perform the hydrostatic weighing. This

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apparatus employs a quartz spring or a fine tungsten wire in the form of helical spring. In order to reduce the variability in the downward surface tension force, the suspension wire which has a diameter of 7 μm was treated by electrical heating under $1\sim10\times10^{-3}$ torr vacuum, yielding a uniformly granular coating of chromium oxide on the surface of the nichrome wire. Further, a precision thermoregulator was made to control the temperature of the distilled water within ±0.005°C. Consequently, using a cathetometer which reads to 10 μm, the balance can detect weight differences of 5×10^{-6} gms., giving the desired density sensitivity of 0.0001 gm/cm^3 or better.

The volume recovery behavior under various temperatures is also studied by a glass dilatometer described in detail by Bekkedahl.[17] This consists of a reservoir, containing the specimen of known mass, joined to an accurately calibrated capillary of known cross-sectional area. The technique of filling mercury has been improved by employing a specially designed mercury reservoir. The specimen is then subjected to different thermal treatments by immersing the dilatometer in a glycerine bath, which is thermostatically controlled to within ±0.05°C in the range of 80°C to 130°C, and the water bath, which is controlled by the thermoregulator within ±0.005°C in the range of 20° to 82°C. Finally, using a cathetometer reading to 50μ, this set-up can detect volume changes to 1×10^{-5} cm^3.

Because of the thin film nature of the specimens used, it was necessary to construct a special apparatus to perform creep measurements. This required careful temperature control and optical determination of strain because a mechanical extensometer would disturb the response of the specimen. Stress-strain curves were determined using standard procedures.

III. RESULTS

Typical densification results determined by hydrostatic weighing are given in Fig. 1. These data show the effect of quenching from various initial temperatures to ice water. More of the excess volume is retained when quenched from higher temperatures. The densification due to physical aging takes place almost as a linear function of logarithmic aging time in each case.

Dilatometry is used to provide volume relaxation data over a broader temperature range. To construct isochronal volume versus temperature curves it was necessary to carry out volume recovery at various final or aging temperatures. This is dilaometrically performed by quenching a PVC specimen from 99°C, where PVC is characterized by an equilibrium structure, to various temperatures below T_g. The volume recovery behavior in the temperature range of 20°C to 65°C, which is far below the glass transition temperature of PVC, is shown in Fig. 2. Similar results of volume recovery behavior near the glass transition temperature of PVC were also carried out. The relative excess volume $(V-V_\infty)/V_\infty$ represents a dimensionless measure of the departure from equilibrium. The straight lines of Fig. 2 plotted vs. log time indicate a tendency for the rate of contraction to become slower as contraction proceeds with time. Furthermore, the relative excess volume retained at various temperatures is proportional to the temperature difference.

Crossplots of the data yield two ischronal branches below the equilibrium state, at 1 minute and 200 hours after quenching from equilibrium at 99°C to various temperatures T, shown in Fig. 3. Both branches asymptotically approach two parallel straight lines with a slope of $\bar{\alpha}_g = (d\,v/d\,T)_t = 7.35\times10^{-5}$ cm^3/°C. These lines intersect the

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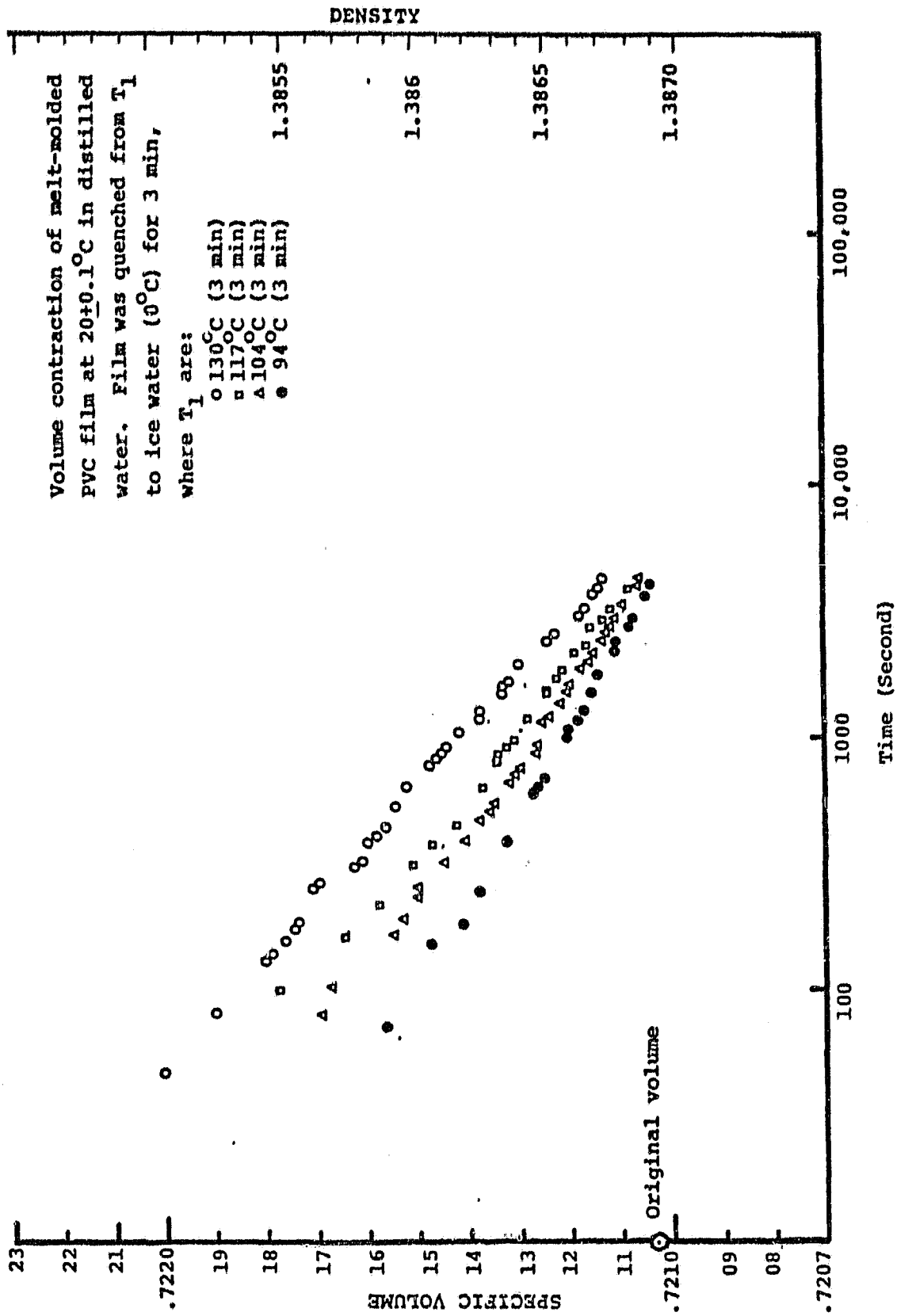

Figure 1: Effect of quenching PVC film specimen (Geon 121), from various initial temperatures to ice water, on the specific volume and volume contraction behavior at 20°C.

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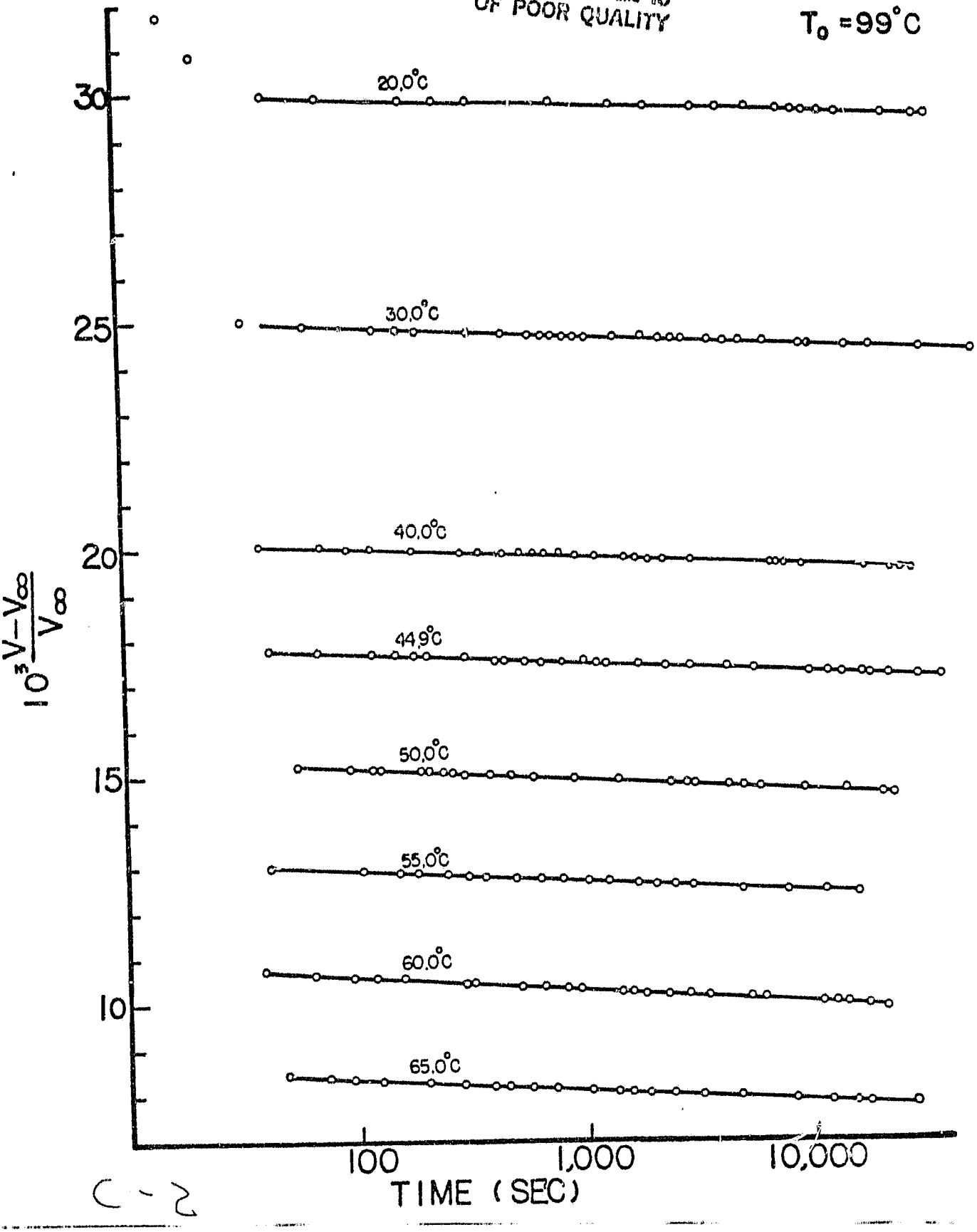

Figure 2: Isothermal volume contraction of PVC, quenched from equilibrium at 99°C to various final temperatures far below T_g.

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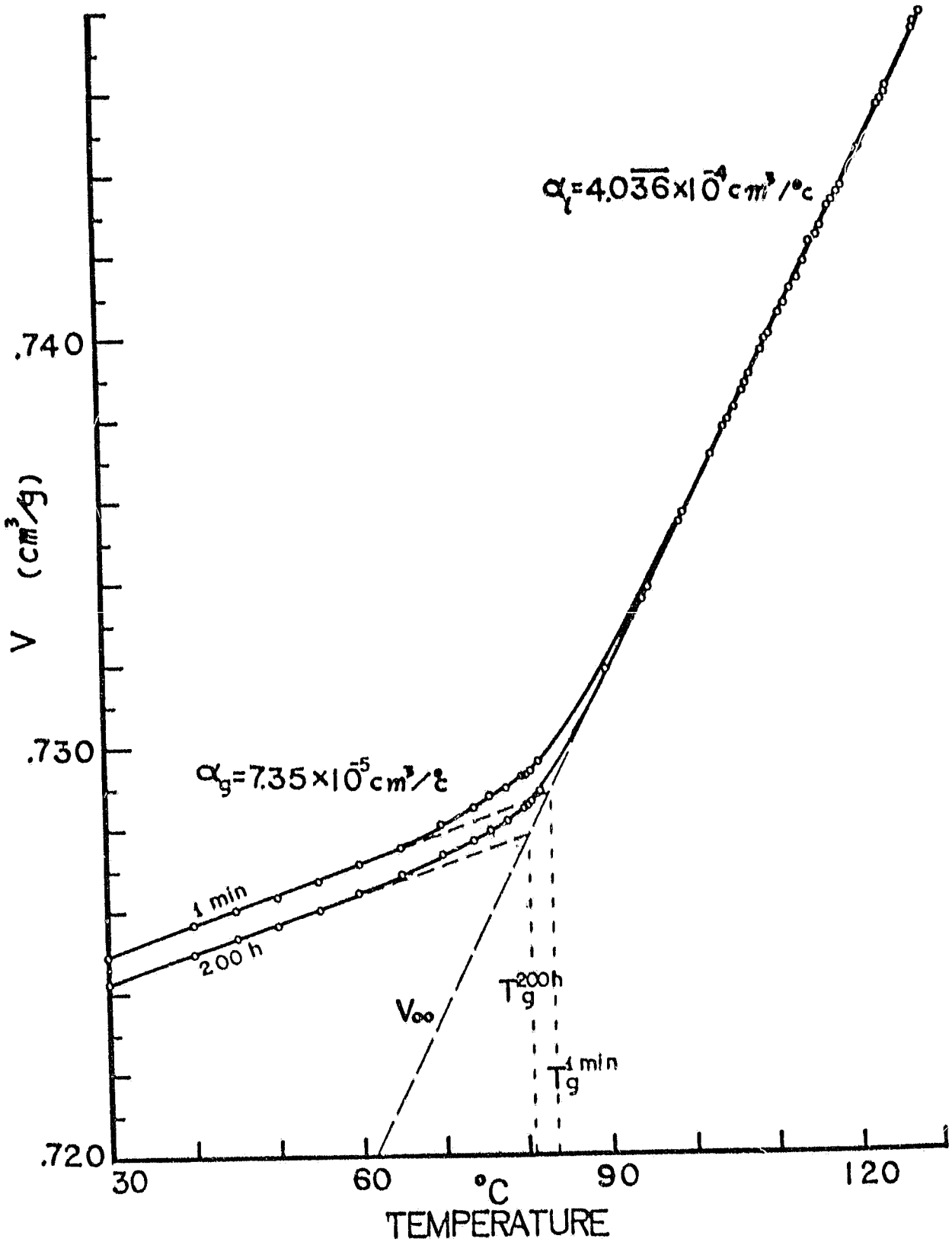

Figure 3: Isochronal specific volume vs. temperature for PVC showing glass transition temperature dependence upon aging time.

equilibrium volume line at 83.3°C and 80.9°C, which can be associated with the glass transition temperatures T_g at 1 min and 200 h, respectively.

Creep experiments show the effect of excess volume on the mechanical properties. The effect of quenching from various initial temperatures is shown in Fig. 4. The quench from 153°C to 0°C produces the least dense structure and the highest creep values, whereas the quench from 96°C to 0°C gives the most dense structure leading to the lowest creep. In essence, quenching from various temperatures above T_g to ice water clearly produces different levels of instantaneous creep as well as subsequent creep at the same aging time prior to loading. At higher stresses, the effect of excess volume has been found to enhance the ductility while reducing the yield stress. More high stress effects will be studied in the future because of their implications for cold forming operations.

IV. CONCLUSIONS

Hydrostatic weighing and volume dilatometry results clearly demonstrate the more severe the quench, the greater is the departure from equilibrium volume or the greater is the free volume content. Further, aging of relaxing molecular rearrangements, based on the studies of phenomenological events, takes place as a linear function of logarithmic aging time at temperatures far below T_g.

Studies of mechanical properties monitored by tensile creep reveal the dependence of the creep behavior on the trapped free volume content. The phenomena of aging and quenching are essentially thermoreversible. Further, a linear relationship of log (shift factor) vs. log (aging time) is observed from investigating the creep behavior of PVC film specimens at various aging intervals after quenching. This

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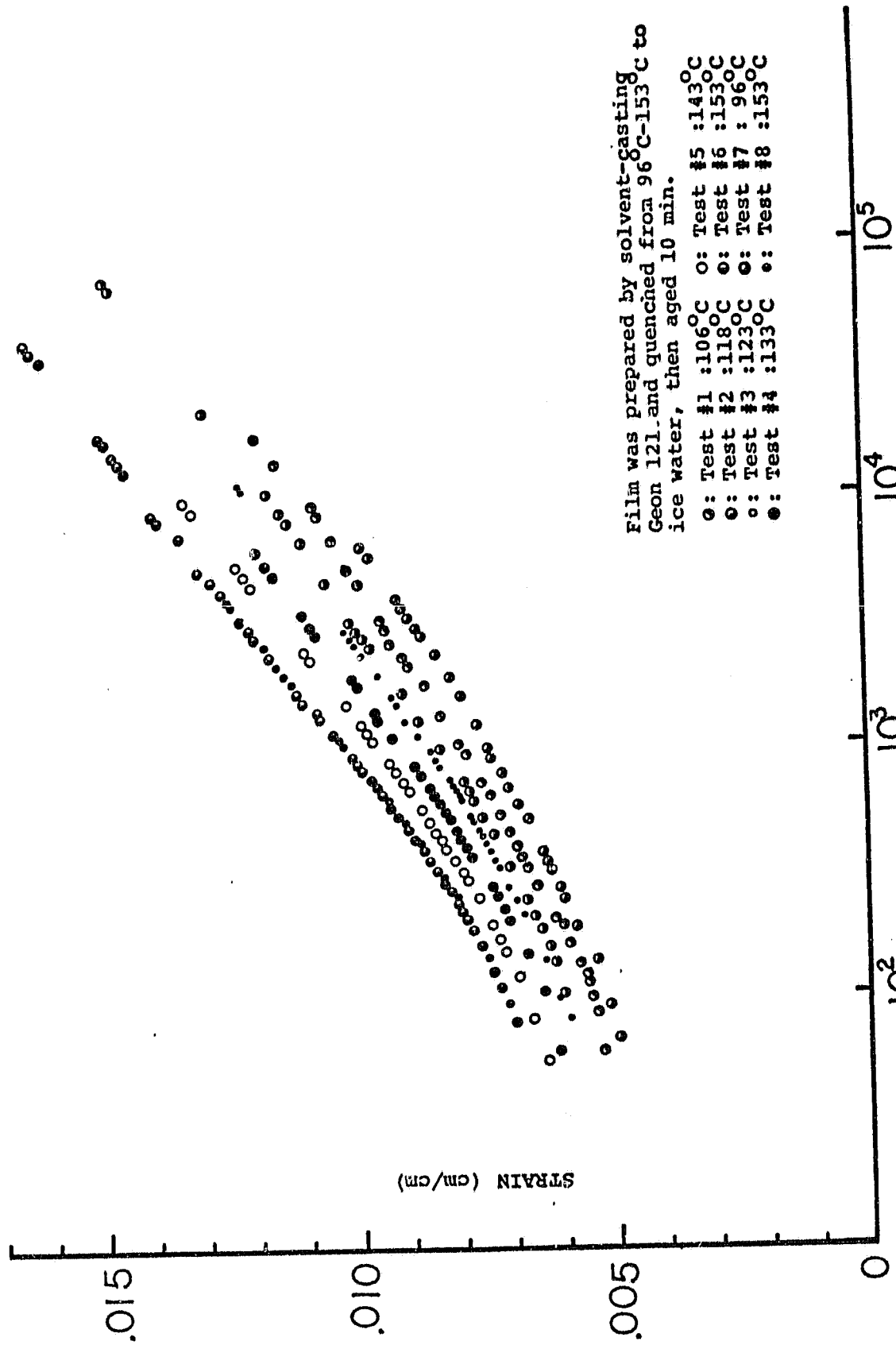

Figure 4: Effect of quenching from various initial temperatures above T_g to ice water on the creep behavior of PVC at the same aging interval.

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observation strongly corroborates the linear behavior of diminishing free volume. In addition, reduction in ductility is observed as aging proceeds. These observations indicate that the volume changes in the glassy matrix of PVC due to rapid quenching and subsequent aging are relatively small but they directly and strongly affect the mechanical properties.

REFERENCES

1. T.R. Anathataman and C. Suryanarayana, J. of Mat. Sci., 6, 1111 (1971).
2. H. Jones, "Rapidly Quenched Metals," N.J. Grant (ed.), 1, M.I.T. Press (1976).
3. H.A. Davies, "Rapidly Quenched Metals LLL," B. Cantor (ed.), 2, Chameleon Press, London (1978).
4. H. Warlimont, Phys. Technol., 11, 28 (1978).
5. J.J. Gilman, Sci., 208, 856 (1980).
6. P. Chaudhari, B.C. Gieseen, and D. Turnbull, Scientific American, 98, (April 1980).
7. A.Q. Tool, J. Amer. Cer. Soc., 29, 240 (1946).
8. A.Q. Tool, J. Res. Nat. Bur. Standards, 37, 73 (1946).
9. F.R. Schwarzl and F. Zahradnik, Rheological ACTA, 19, 137 (1980).
10. R.M. Mininni, R.S. Moore, F.R. Flick, and S.E.B. Petrie, J. Macromol. Sci.-Phys., B8 (1-2), 343 (1973).
11. R.J. Morgan and J. E. O'Neal, J. Polym. Sci., Polym, Phys. Ed., 14, 1053 (1976).
12. J.M. Hutchinson and C.B. Bucknall, Polym. Eng. and Sci., 20, 1973 (1980).
13. M.L. Williams, R.F. Landel and J.D. Ferry, J. Amer. Chem. Soc., 77, 4701 (1955).
14. M.H. Cohen and D. Turnbull, J. Chem. Phys., 31, 1164 (1959).
15. A.J. Kovacs, Rheologica ACTA, Band 5, Heft 4, 262 (1966).
16. S.L. Madorsky, Vacuum Microbalance Techniques, 2, 47 (1962).
17. N. Bekkedahl, National Bureau of Standards, 42, 145 (1949).

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PROJECT A5: DEVELOPMENT OF RAPIDLY SOLIDIFIED OXIDATION RESISTANT ALLOYS

Principal Investigator: Prof. G. J. Yurek
Personnel: Mr. D. Cocke

RESEARCH ABSTRACT

The objective of this program of research is to develop iron-base alloys that contain low concentrations of expensive and/or strategic metals, but that are very resistant to oxidation at elevated temperatures. Rapid solidification processing is being employed to make alloys that are uniform in composition, that comprise very fine grains (<10 μm) and that contain a uniform dispersion of very fine (<0.5 μm) nonmetallic inclusions. Each of these factors contribute to the oxidation behavior of alloys. The work in this program is directed to determining the compositional and processing variables that yield the optimum oxidation resistance.

I. INTRODUCTION

The oxidation of alloys in systems that operate at high temperatures limits their useful life by decreasing their load-bearing cross sections, by degrading their mechanical properties or by changing their shapes. The resistance of an alloy to oxidation at elevated temperatures is usually dependent on the formation of a thin scale of Cr_2O_3, Al_2O_3, or SiO_2 on its surface by reaction of CR, Al, or Si dissolved in the alloy with oxygen or oxygen-bearing molecules in the gas phase. Continuous, pore-free layers of these oxides inhibit oxidation because diffusion of reactants through them is slow. Good resistance to oxidation in actual practice requires that protective oxide scales maintain good adherence to the alloy substrate during

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observation strongly corroborates the linear behavior of diminishing free volume. In addition, reduction in ductility is observed as aging proceeds. These observations indicate that the volume changes in the glassy matrix of PVC due to rapid quenching and subsequent aging are relatively small but they directly and strongly affect the mechanical properties.

REFERENCES

1. T.R. Anathataman and C. Suryanarayana, J. of Mat. Sci., 6, 1111 (1971).
2. H. Jones, "Rapidly Quenched Metals," N.J. Grant (ed.), 1, M.I.T. Press (1976).
3. H.A. Davies, "Rapidly Quenched Metals LLL," B. Cantor (ed.), 2, Chameleon Press, London (1978).
4. H. Warlimont, Phys. Technol., 11, 28 (1978).
5. J.J. Gilman, Sci., 208, 856 (1980).
6. P. Chaudhari, B.C. Gieseen, and D. Turnbull, Scientific American, 98, (April 1980).
7. A.Q. Tool, J. Amer. Cer. Soc., 29, 240 (1946).
8. A.Q. Tool, J. Res. Nat. Bur. Standards, 37, 73 (1946).
9. F.R. Schwarzl and F. Zahradnik, Rheological ACTA, 19, 137 (1980).
10. R.M. Mininni, R.S. Moore, F.R. Flick, and S.E.B. Petrie, J. Macromol. Sci.-Phys., B8 (1-2), 343 (1973).
11. R.J. Morgan and J. E. O'Neal, J. Polym. Sci., Polym, Phys. Ed., 14, 1053 (1976).
12. J.M. Hutchinson and C.B. Bucknall, Polym. Eng. and Sci., 20, 1973 (1980).
13. M.L. Williams, R.F. Landel and J.D. Ferry, J. Amer. Chem. Soc., 77, 4701 (1955).
14. M.H. Cohen and D. Turnbull, J. Chem. Phys., 31, 1164 (1959).
15. A.J. Kovacs, Rheologica ACTA, Band 5, Heft 4, 262 (1966).
16. S.L. Madorsky, Vacuum Microbalance Techniques, 2, 47 (1962).
17. N. Bekkedahl, National Bureau of Standards, 42, 145 (1949).

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the application of external stresses and during thermal cycling. If a protective oxide scale spalls from the surface of an alloy, the alloy must be able to reform the protective oxide rapidly to avoid extensive oxidation of the bare alloy surface.

The adherence of an oxide scale to an alloy may be increased considerably by the presence of a fine, uniform dispersion of intermetallic or nonmetallic precipitates in the alloy. In general, the external protective scale tends to grow inward around the precipitates, thereby yielding intrusions of the scale into the alloy, which are effective in mechanically keying the scale to the alloy substrate.

The selective oxidation of an alloying element to form an external protective scale requires the formation of a critical volume fraction of the oxide near the alloy surface to cause a transition from internal to external oxidation of the alloying element. A higher concentration and a higher diffusivity of the alloying element favors external oxidation as does a lower solubility and diffusivity of oxygen in the alloy. Grain boundaries and dislocations that intersect the surface of an alloy promote the formation of a continuous layer of the most thermodynamically stable oxide (Cr_2O_3, Al_2O_3, or SiO_2) on the surface.

Very fine-grained alloys may be obtained by rapid solidification processing. The sizes (<10 μm) remain stable at elevated temperatures as long as the alloy contains a dispersion of very fine stable nonmetallic inclusions to inhibit grain growth. The combination of a stable, fine alloy grain size and a fine, uniform dispersion of nonmetallic inclusions should provide an excellent alloy microstructure for oxidation resistance, provided the alloy composition is adjusted properly.

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The purpose of this progra , is to use the principles outlined above to employ rapid solidification processing to develop iron-base alloys that are very resistant to oxidation at elevated temperatures and that contain very low concentrations of expensive and/or strategic metals.

II. RESULTS

The focus of the initial part of this program is the processing and testing of very fine-grained RS Fe-Al alloys containing 4-10 wt%Al and about 1 vol% MnS. The Al is present in these alloys to form an external scale of Al_2O_3 that will inhibit oxidation of the Fe. The purpose of the MnS which is supposed to be present as a uniform dispersion of very fine MnS inclusions, is to maintain the fine grain size of the alloy at elevated temperatures. Manganese sulfide was chosen because it is a very stable compound and because the diffusivity of sulfur in iron-base alloys is low. These two factors inhibit coarsening of the fine inclusions in the RS alloy at high temperatures, thereby maintaining their effectiveness in pinning grain boundaries.

The first rapidly solidified alloy produced in this program was an Fe-6wt%Al alloy. A master alloy was made by melting the elements in an Al_2O_3 crucible under an argon atmosphere in an induction furnace. Manganese and MnS were added to the master alloy in quantities that would yield a final composition of ~6wt%Al, ~1.6wt%Mn, and ~0.3wt%S. The final composition of the RS alloy was, however, 5.5wt%Al, 1.5wt%Mn and 0.075%S, thereby indicating that considerable sulfur was lost during the melting steps.

About three pounds of the RS alloy were produced by remelting the master alloy in a calcia-stabilized zirconia crucible under an argon atmosphere and allowing a thin

stream of the liquid alloy to fall between two molybdenum rolls that were rotating counter-currently to each other. The rolls were not cooled by external means. The RS alloy so produced was in the form of flakes that were ∿0.5 to 2.0 mils thick, ∿0.5" wide and ∿2 inches long. The flakes were cut into smaller pieces before being compacted in a mild steel can, which was subsequently evacuated and welded shut before being hot extruded. The hot extrusion was carried out at 1100°C with a 20:1 reduction ratio. The steel can was machined from the surface of the extruded rod to yield a bar of fully dense RS alloy that was ∿0.5 inches in diameter.

The as-cast master alloy and the RS alloy were characterized using optical and scanning-transmission electron microscropy (STEM). The as-cast alloy comprised large grains ∿0.1 to 1.0cm in diameter. The grain size of the RS alloy flakes depended on the thickness of the flakes, which reflects a variation of grain size with cooling rate; i.e., the thinner flakes comprised fairly uniform grains that were ∿1 to 6μm in diameter, while the thicker flakes contained both the fine grains and larger grains that were ∿20 to 40μm in diameter.

The extruded RS alloy contained a mixture of fine grains (2-10μm) and larger grains (20-50μm). An etched transverse cross section through the extruded bar had a marbled appearance caused by selective etching of the alloy around oxide films that had existed on the surfaces of the flakes before hot extrusion. The presence of the oxide film is attributed to the rather slow rate of cooling of the flakes after exiting the Mo rolls in the rapid solidification apparatus; i.e., the flakes were hot for a sufficiently long time to allow oxidation by the small amount of oxygen in the argon atmosphere. The RS alloy also contained a number of inclusions of Mo (∿100-500μm in diamter), which apparently were picked up from the Mo rolls.

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Examination of the extruded RS alloy with a STEM revealed the presence of very fine nonmetallic inclusions (~0.05 to 0.1 μm in diameter), which were identified by EDX analysis to be mostly MnS. A number of the precipitates were identified as ZrO_2 and (Mn,Zr)S. The source of the Zr was apparently the calcia-stabilized zirconia crucible used during the remelting process. Many of the precipitates were located along alloy grain boundaries, but once again, a considerable range of grain sizes was observed.

A thermogravimetric apparatus was constructed to conduct both isothermal and cyclic oxidation tests of the rapidly solidified alloys. Some preliminary isothermal oxidation tests were conducted with the alloys described above. The tests were run for 100h at 900°C in pure oxygen at 1 atm pressure. Both the as-cast and the RS alloy exhibited a rapid period of oxidation in the early stages of exposure, followed by a period of slow oxidation that is attributed to the formation of an Al_2O_3 surface film. The transition to passive behavior occurred more rapidly with the RS alloy, which is expected because of its finer grain size and its more uniform composition. The RS alloy also exhibited, however, accelerated oxidation around the inclusions of Mo. These results, although encouraging, are only preliminary in nature and are not considered to be a test of the goals of this program because the microstructure of the RS alloy did not meet fully the specifications of the program.

The problems encountered in the production of an RS Fe-Al alloy using uncooled, twin Mo rolls to achieve rapid solidification have prompted us to seek an alternative rapid solidification process. The current plan is to produce RS Fe-Al alloys using melt spinning with a water-cooled copper wheel. Such an apparatus is available in Prof. N. Grant's laboratory. We have designed and constructed a melting unit that will be employed with the spinner to produce continuous ribbons of the RS Fe-Al alloys.

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An Al_2O_3 crucible will be used in the melting unit, which will eliminate contamination of the melt from the crucible. The melt will be forced out of the crucible through a small hole in its bottom by pressurizing the crucible with purified argon. The atmosphere above the crucible will, ideally, be saturated with respect to sulfur, which will help to minimize losses of sulfur.

The melt spinning apparatus produces a ribbon (~0.2 mil thick, ~12.0 mils wide) that is both thinner and more uniform in thickness than the flakes produced by roll quenching, and the cooling rates are higher. Thus, the grain size of the RS alloy should be finer and more uniform. Also, because of the greater cooling rate, subsequent oxidation of the alloy directly after solidification should be less, which will help to eliminate the presence of prior foil boundaries in the extruded product.

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PROJECT A6: LASER MATERIALS PROCESSING FACILITY

Principal Investigator: Dr. J. S. Haggerty

RESEARCH SUMMARY

The ceramics group within the Materials Processing Center and the Advanced Energy Materials group in the Energy Laboratory have jointly supported construction of a laser facility which is specifically designed for materials processing research. It gives MIT research capabilities which are unique in academic institutions.

The facility uses a custom designed 1500 watt CO_2 laser (Photon Sources Model 1033) with controls which permit CW, repetitive pulse, and shaped power-time cycles. The controls are designed to be interfaced with numerically controlled positioning equipment. The laser is designed to emit two 600-650 watt Tm_{oo} mode beams, two 600-650 watt Tm_{01} mode beams, one 1200 watt Tm_{oo} mode beam or one 1500 watt Tm_{01} mode beam. In all configurations, the laser can be tuned to emit less than 20 watts. This power range will satisfy requirements from smaller diameter crystal growth up to modestly deep penetration welds in steel. The beams go from the laser to the experiment stations through conduits positioned at ceiling level. Removable mirrors are employed to direct the beam(s) to the different experiment stations.

The first experiment station consists of a machine designed for floating zone crystal growth. Four beams are directed onto the heated region. We will also install anvils for quenching molten drops to study new glass and nonequilibrium crystalline compositions. The laser heat source permits high purities, freedom to select ambient atmosphere, and extremely high melting points. This chamber and optics can also be

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used for powder synthesis at rates which are substantially higher than is possible with the optics and laser (150 watts maximum) we are presently using.

The second experimental station will consist of a large controlled atmosphere chamber with provisions for manipulating sample position. It will be used for a variety of cutting, welding, alloying, glazing, and heat treatment experiments. It can also be used for laser chemistry experiments.

The crystal growth station has been operational since October 1980. Since then it has been used to produce single crystals for several researchers at MIT and has undergone minor modifications to improve operational characteristics. Examples of crystals which have been grown include: $Ba_xSr_{1-x}Nb_2O$, LaB_6, LiF_2, Fe_2O_3, Fe_3O_4, FeO, Y_2O_3 stabilized ZrO_2, high purity Al_2O_3, TiO_2 doped Al_2O_3, and Sc_2O_3 stabilized Ta_2O_5. These crystals were grown for Professors Bowen, Cannon, Tuller, Coble, Yurek, and Linz. The equipment has also been used for preliminary cutting and shaping experiments with Si_3N_4 to displace diamond shaping processes. In addition to the research already completed, this laser heated crystal growth facility is the basis for several research proposals that have been submitted.

The funds for the laser heated crystal growth facility came from a combination of four sources, including this NASA grant.

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B. FLUID FLOW IN CRYSTALLIZATION PROCESSES

Project B1: FLUID FLOW IN CRYSTAL GROWTH: ANALYSIS OF THE FLOATING ZONE PROCESS

Principal Investigator: Professor R. A. Brown

Personnel: Mr. C.J. Chang
Mr. H.M. Ettouney
Mr. G.M. Harriott
Mr. L.H. Ungar
Mr. Y. Yamaguchi

SUMMARY

This research program is aimed at a fundamental understanding of the interactions of heat, mass, and momentum transport in crystal growth from the melt. Emphasis has been on studies of the small-scale floating zone process and on a prototype of the vertical Bridgman growth system. In both systems detailed numerical calculations are being used to disect the interplay between fluid convection and dopant segregation. These calculations are based on newly developed finite-element techniques that make feasible the complete solution of solidification problems which include convection. Other numerical methods have been developed for solving thermal models of crystal growth processes with melt/gas menisci and for simulating the microscale instabilities in solidification interfaces.

1. SCOPE OF RESEARCH PROGRAM

Our research program is a comprehensive theoretical and computational study ultimately directed towards a fundamental understanding of the interactions of heat, mass, and momentum transport in crystal growth from the melt.

Although special emphasis has been placed on the floating zone process, the techniques for analysis and the physical insights developed in this research have broad application to other problems in melt crystal growth and studies are underway into Bridgman Growth, Edge-Defined Film-Fed Growth, and into the microscale instabilities in directional solidification.

In each research project, a combination of analytical modelling and computer-aided calculation is being used to develop both a qualitative understanding of the relevant physics and quantitative models of the selected crystal growth processes. To do this, state-of-the-art numerical methods have been developed for handling solidification problems. These methods give us the capability for accurate calculation of the fluid flow and mass transfer near solidification interfaces.

The five research projects that are currently underway are:

1) Thermal modelling of crystal growth processes with melt/gas interfaces. (H.M. Ettouney)
2) The coupling between rotationally-driven convection, surface-tension-driven convection, and solute transfer in the floating zone process at low gravity. (G.M. Harriott and L.H. Ungar)
3) Fundamental studies of natural convection in low Prandtl number melts; effect of a magnetic field on the intensity of convection. (Y. Yamaguchi and C.J. Chang)
4) Effect of buoyancy-driven convection on melt/solid interface shape and radial segregation in vertical Bridgman growth. (C.J. Chang)
5) Microscale modelling of melt/solid interface dynamics. (L.H. Ungar)

RESEARCH SUMMARY

2.1 THERMAL MODELLING OF CRYSTAL GROWTH PROCESSES

In principle, the macroscopic shape of the interface separating melt and solid during solidification depends on the transfer of heat, mass, and momentum. The conservation statements for the transport of these quantities through both melt and solid phases and across phase boundaries are mathemically coupled to the location of the phase boundary. In turn, the location of the melt/solid interface is set by local statements of conservation of energy and mass along the phase boundary, each written in terms of fluxes extrapolated from the bulk phases, and by assumptions of equilibrium for concentration and temperature. The first goal of this portion of our research has been to develop numerical methods for solving solidification problems accurately and efficiently. This goal has been accomplished for steady solidification problems and the finite element methods that are preferred for these calculations are outlined in a manuscript[3] based on models that neglect fluid flow in the melt. The reasoning behind the use of these simple models is two-fold. First, they are good descriptions of heat and mass transport for many crystal growth geometries, especially in a low-gravity environment. More importantly, novel numerical methods are most efficiently developed for these less complicated models and then extended to account for bulk convection in the melt. This strategy has proven successful in the development of the finite element techniques outlined in Section 2.4 for treating natural convection near a melt/solid interface.

The Isotherm-Newton formulation, the most efficient finite element technique developed by Ettouney[2], has been extended to calculate simultaneously the temperature and concentration fields in a binary melt and to account for the

dependence of the melting temperature on concentration. Here the conservation equations for mass and energy are solved simultaneously with the condition for thermal equilibrium at the interface. Although this technique requires solution of a large set of nonlinear algebraic equations, it is not intrinsically limited to binary systems with small slopes of the solidus curve. These calculations have uncovered a primary difficulty in calculations of combined heat and mass transport in crystal growth systems. For liquid semiconductors, the region of variation of concentration in the melt is confined to a small layer near the melt/solid interface, whereas temperature variations are significant throughout both melt and solid. Concentration is best approximated by a finite-element basis that is concentrated near the solidification interface; however, approximations to the temperature distribution must be uniform. We have developed methods for simultaneous calculation of temperature and concentration on two different finite-element grids. These techniques establish the methodology necessary for detailed simulation of thermosolutal convection near a solidification interface.

Ettouney has extended the finite-element algorithms to calculate the shapes of melt/gas menisci and melt/solid interfaces in crystal growth systems where both types of boundaries are present. The menisci are located by solution of the equation of capillary statics and by satisfying the critical angle condition [Surek and Chalmers, J. Crystal Growth, 29, 1-11 (1975)] for steady crystal growth. The output of these calculations is the shape of the molten region along with the thickness of the grown crystal as a function of heat transfer conditions and growth rate. Applications to Edge-Defined Film-Fed Growth have defined limits in terms of growth rate and die temperature for steady operation. Similar studies of the floating zone geometry are underway.

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2.2 FLUID MECHANICS OF A ROTATING LIQUID ZONE

Research has focused on understanding the fluid mechanics of a liquid zone trapped between two cylindrical and differentially rotated solid rods and is aimed at describing the influence on the stability of the molten zone and on mass transfer of fluid flows driven by rotation of the feed and crystal rods. G.M. Harriott has developed asymptotic methods for calculating these flows and the deflection of the melt/gas meniscus when the Reynolds number $Re \equiv \Omega R H/\nu$ is small, where ν is the kinematic viscosity of the melt, R is the radii of the rods, and H is the height of the melt; see Fig. 1.

The details of this analysis are contained in a manuscript[6]. One major result shown in Fig. 2 is the cellular strcture of the flows produced by rotating the top surface at rate $s\Omega$ and the bottom surface at rate Ω. Depending on the relative rotations measured by s, and the aspect ratio of the zone $A \equiv R/H$, there may be either one or two toroidal cells in the zone. Sample streamlines for a zone with aspect ratio of one are shown in Fig. 3. The value s=-1 corresponds to exact counter-rotation. Here the stagnation streamline that separates the two cells is exactly a plane at the middle of the zone. For any other configuration this streamline is not a plane but a curve; see Figs. 3a-3f.

Harriott's analytical results have been compared to detailed finite element calculations that are possible for a wide range of Reynolds number. The asymptotic results agree within ten percent with the numerical results up to Re=50 and hence are very useful estimates of the fluid flow in a microzone. These flows have been used as the basis for calculations of radial dopant segregation under steady state conditions.

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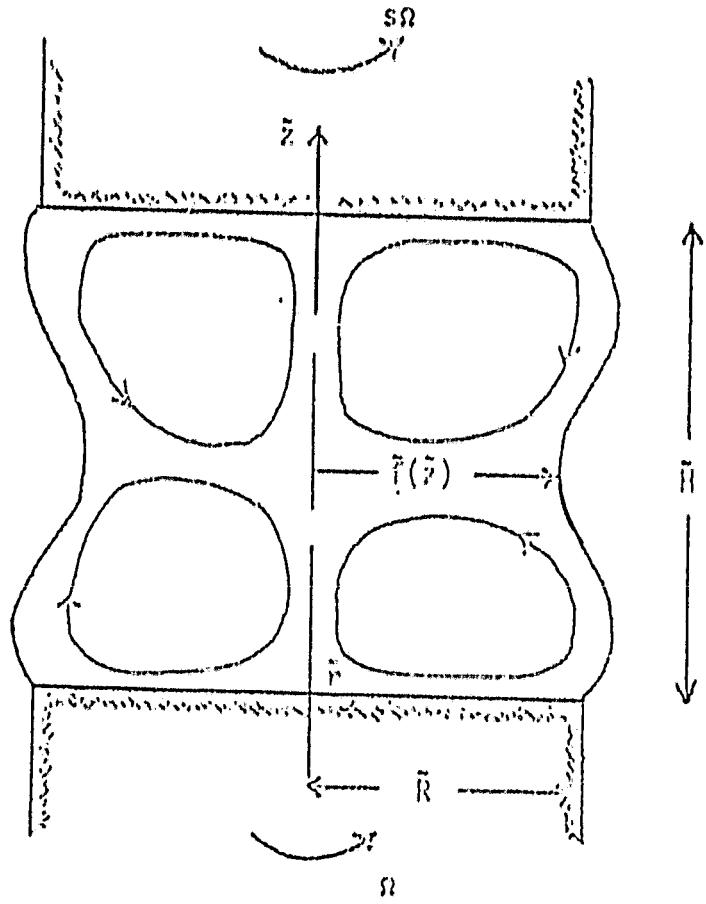

Figure 1. Geometry for model of rotating liquid zone.

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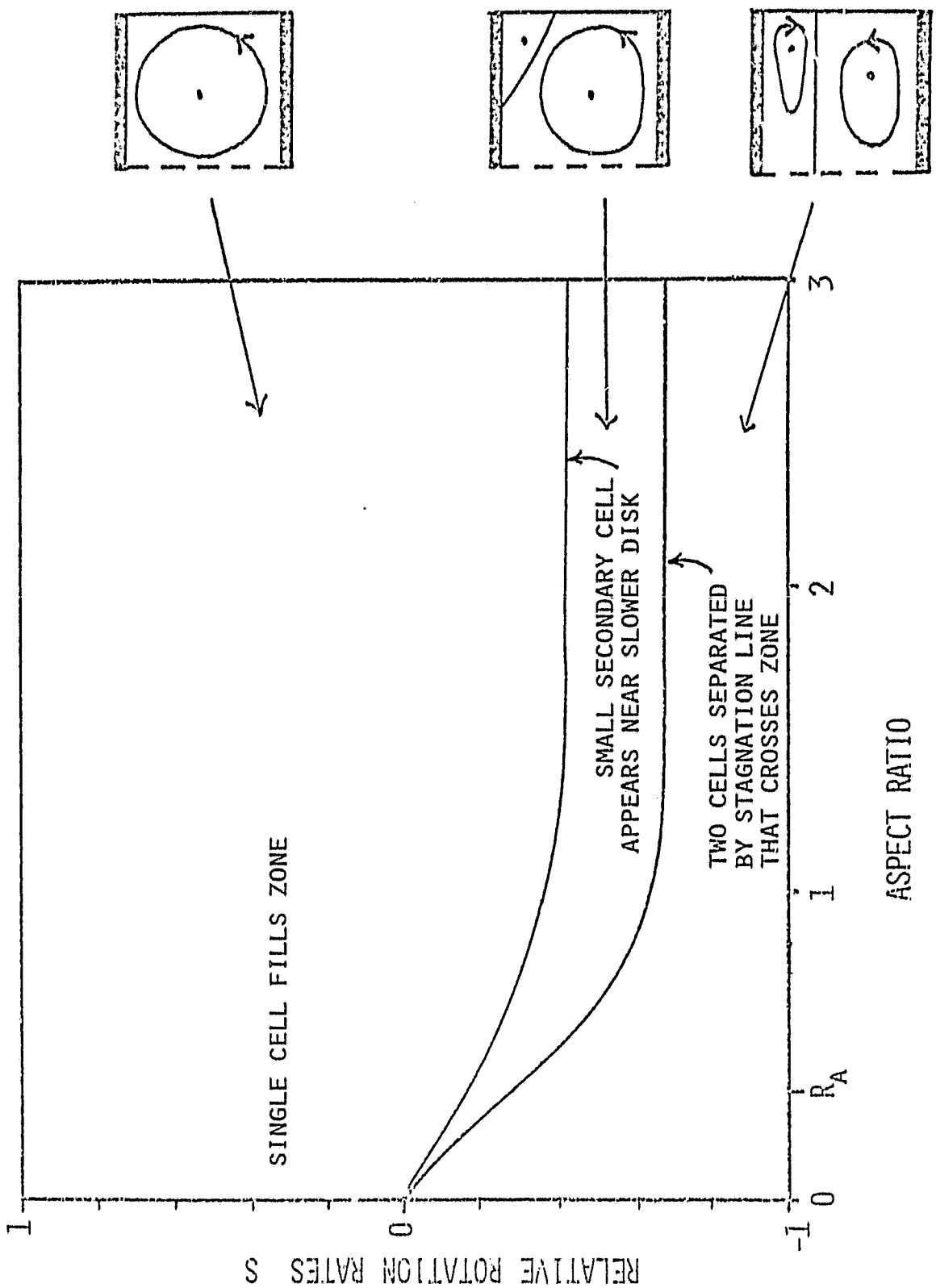

Figure 2. Variation of cellular structure of flow as a function of aspect ratio A and relative rotation of the end rods s.

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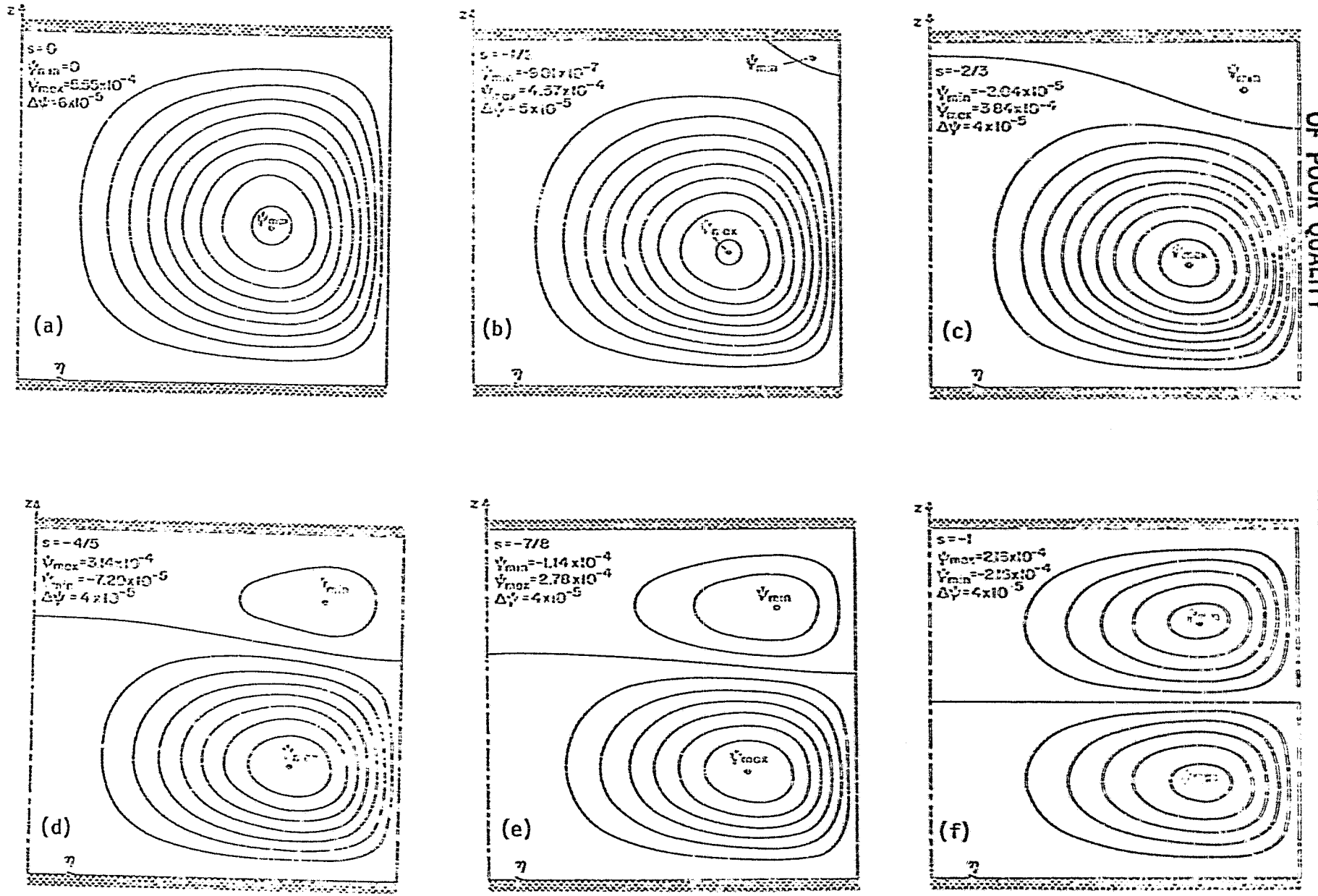

Figure 3. Streamlines predicted by analytical solution for a rotating liquid zone as a function of relative rotation rate s for A=1.0.

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Numerical investigations of the flow at higher Reynolds number have uncovered multiple steady flows beyond a critical value that depends on aspect ratio and rotation ratios. For exact counter-rotation the onset of these multiple flows occurs at a bifurcation point in Re; for Λ equal to one, the critical value of Reynolds number is approximately 109.5. As shown in Fig. 4, new families of flows with cells of unequal size start at this Reynolds number and evolve toward higher values of Re. The difference between these asymmetric flows and the original symmetric flow is brought out by the streamline plots in Fig. 5. Mathematical arguments indicate the stability of the fluid flow changes at the bifurcation point so that only the asymmetric flow would be observed experimentally. This prediction is being tested.

In another study[2], L.H. Ungar has mapped the stability of a rigidly rotating liquid zone held together by surface tension for a wide range of the volume of melt, gravitational acceleration, and rotation rates. This study is built on earlier efforts at modelling the stability of floating zones (Brown and Scriven, Philos. Trans. R. Soc. Land., 297, 51-79; Coriell, Hardy, and Cordes, J. Colloid Interface Sci., 60, 126-136) and is based on the application of bifurcation theory for analyzing the existence of multiple steady solutions and their stability. The mathematical insights that were gained in studying this relatively simple problem have paid great dividends in the studies of the rotating flows and buoyancy-driven convection; see Sections 2.3 and 2.4

2.3 FUNDAMENTAL STUDIES OF BUOYANCY-DRIVEN CONVECTION

The complicated buoyancy-driven flow patterns in vertical Bridgman and floating zone growth systems have emphasized the need for understanding the transitions from axisymmetric

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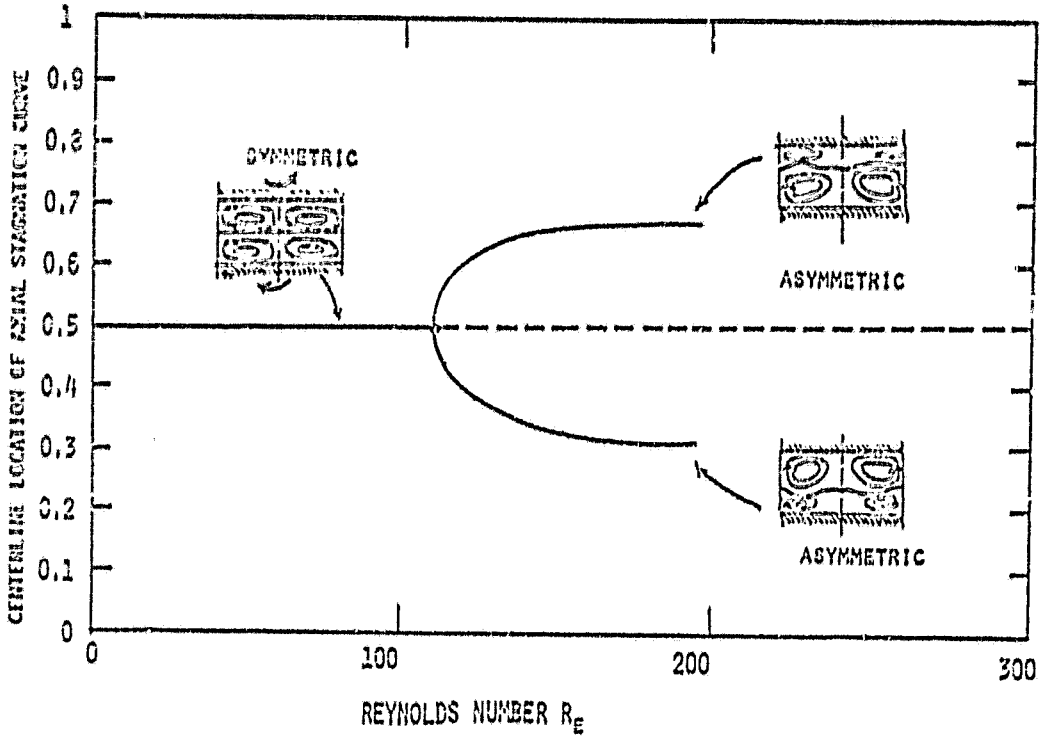

Figure 4. Multiple solutions calculated by finite element analysis for s=-1 and Λ=1.0.

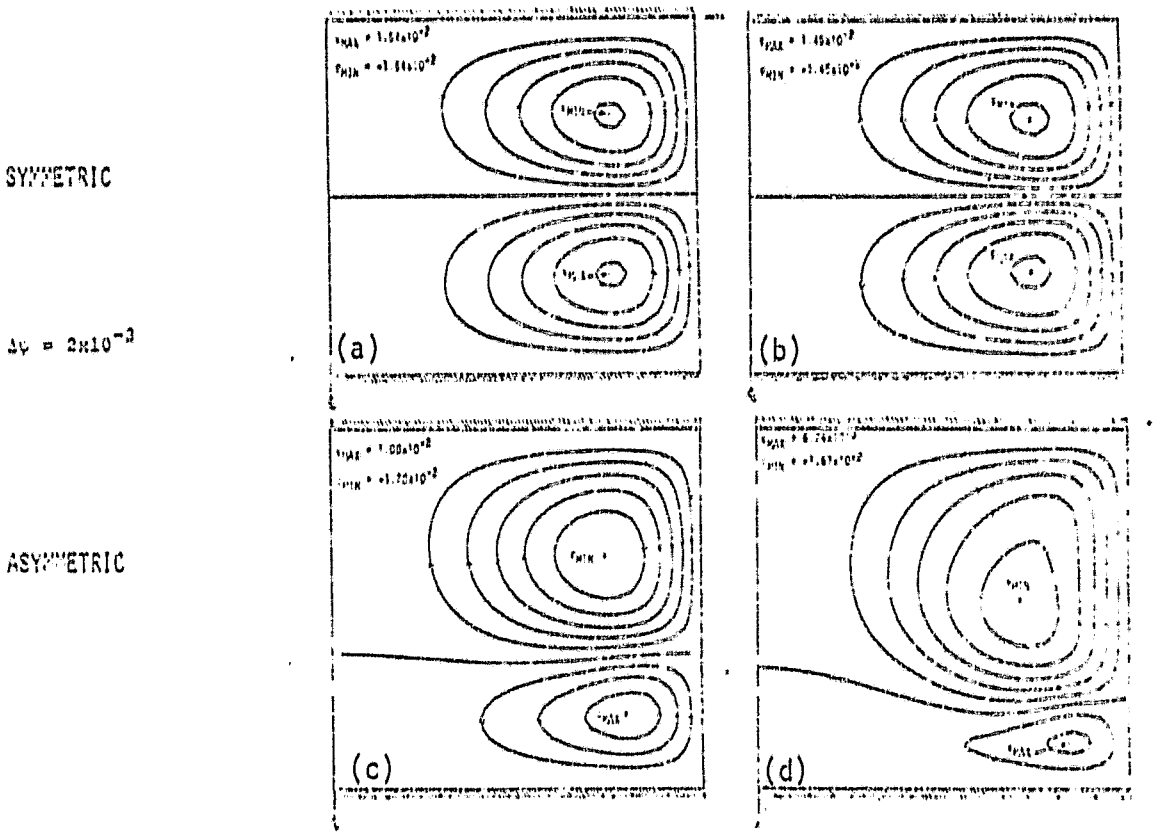

Figure 5. Comparison of streamlines for flows in families of symmetric and asymmetric solutions. Cases (a-b) are for Re=125 and (c-d) for Re=200.

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laminar flow to time-periodic flow in more simply defined heat transfer geometries. Our research has focused on axisymmetric flows in a vertical cylinder heated from below with either adiabatic or perfectly conducting sidewalls. This configuration was chosen for its geometrical similarities to the vertical Bridgman system and because results for the critical Rayleigh number for the onset of convection are also known (Charlson and Sani, Int. J. Heat Mass Transfer 13, 1479-1496 (1970) and Int. J. Heat Mass Transfer 14, (1971). Experimental investigations for this same geometry are also possible as has been demonstrated by Olson and Rosenberger (J. Fluid Mech., 92, 609-629 (1980)).

We have combined finite element methods with newly developed computer-aided methods for detecting and tracking multiple solutions to map out the steady axisymmetric flows that satisfy the Boussinesq equations for natural convection. A typical set of results is shown on Fig. 6 for a cylinder with height L twice its radius R and a conducting sidewall; here the Nusselt number for the top surface N_u of the cylinder is plotted against the Rayleigh number $Ra \equiv \beta g(T_H - T_c)L^3/\alpha\nu$ for each family of flow fields identified in our calculations.

The rest state corresponds to $N_u^T = 1$ and is the stable state up to the first critical value $Ra = 1.2 \times 10^4$ where two families of singlecelled flows are stable and equally probable in experiments. Our predicted locations for the critical point is within three percent of the value calculated by Charlson and Sani using linear stability analysis.

For a Prandtl number of one, the single-celled flows increase in intensity with increasing Ra until both families turn toward decreasing values of Rayleigh number at a limit point near $Ra = 6 \times 10^4$. This limit point marks the loss of existence of a single-celled flow and may well mark the

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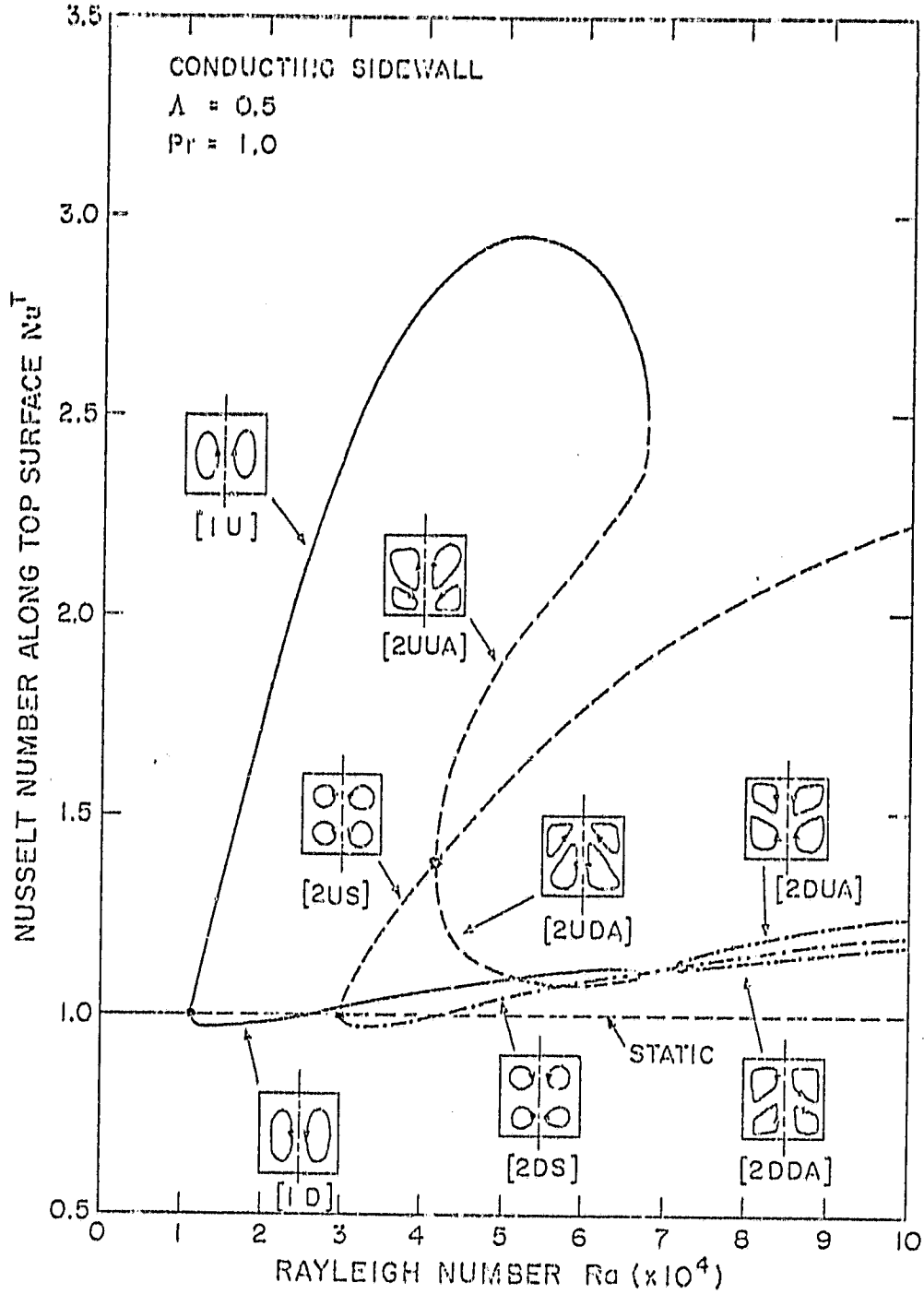

Figure 6. Flow families for buoyancy-driven convection in a vertical cylinder heated from below and with a conducting sidewall.

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upperbound for steady stable axisymmetric flows. As depicted on Fig. 6, the two families of single-celled flows join families of flows with two rolls stacked axially in the cylinder. These two cell flows branch from the static state at a second critical Rayleigh number $Ra=3.1\times10^4$. As explained fully in a recent manuscript[7], the flow structure of Fig. 6 is generic for Prandtl numbers between 100 and 0.01 and for either insulated or conducting sidewalls.

The detailed knowledge of the flow structure portrayed by Fig. 6 is a unique approach to understanding convection in melt crystal growth and is the basis for assessing the onset of fully three-dimensional steady and time-periodic convection, as well as determining precisely the effects of a magnetic field on the flow patterns in crystal melts.

2.4 BUOYANCY-DRIVEN CONVECTION IN VERTICAL-BRIDGMAN GROWTH

Calculations of natural convection in melt crystal growth have been extended to account for the dependence of the shape of the melt/solid interface on the convective flow pattern in the melt. C.J. Chang has done this by combining the Isotherm-Newton technique developed by Ettouney with finite element techniques for calculating buoyancy-driven convection. Chang's algorithm is the most efficient one yet developed for solving solidification problems involving fluid flow and will be widely used. The method has been reported in a recent publication[1] for the solution of a prototype solidification problem where a melt and solid are held in a cylindrical ampoule in a vertically destabilized linear temperature field. Just as for a vertical cylinder filled with melt, multiple steady flows and melt/solid interface shapes are possible for this two-phase system. The structure of these flows is currently being determined.

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More important applications of Chang's algorithm are to studies of convection and mass transfer in the thermally stabilized growth experiments of C. Wang in the Materials Science Department at MIT, to the Bridgman experiments proposed for the Solidification Experiment System of NASA, and to a similar system being designed at MIT. A prototype for a Bridgman system is shown in Fig. 7 and sample isotherms and streamlines for Prandtl number of 0.01 and Rayleigh numbers up to 10^5 are shown in Fig. 8 for a stationary ampoule.

The melt/solid interfaces in these calculations are not flat, but slightly curved because of radial temperature gradients at the edges of the gradient region and because of convective heat transfer. Interfaces are shown in Fig. 9 that correspond to the flow fields given in Fig. 8. These curved interfaces together with the convection in the melt cause radial segregation of the dopant in the crystal.

Chang has calculated the solute distribution in a steady-state analog of Bridgman growth, using the velocity fields and interface shapes predicted from his convection calculations. Fig. 10 shows the distribution of solute along the solidification interface for Rayleigh numbers up to 10^4 for the galliumdoped germanium system of Wang. The slight amount of radial segregation present in the absence of natural convection (Ra=0) is due to the curvature of the melt/solid interface as studied by Coriell and Sekerka [J. Crystal Growth, 46, 479 (1979)]. As the convection level is increased, the delivery of solute to the interface becomes more uneven radially until at Ra=10^3 the radial segregation of gallium is maximized. Further increases in the Rayleigh number causes the beginning of a solute boundary layer and decreases the amount of radial segregation.

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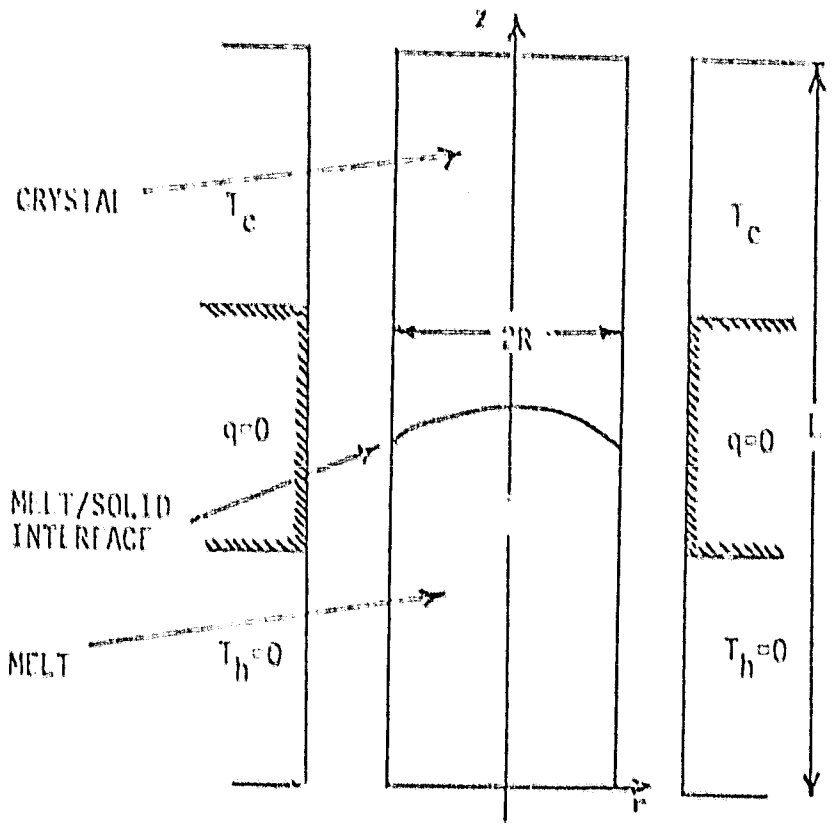

Figure 7. Prototype of vertical Bridgman system.

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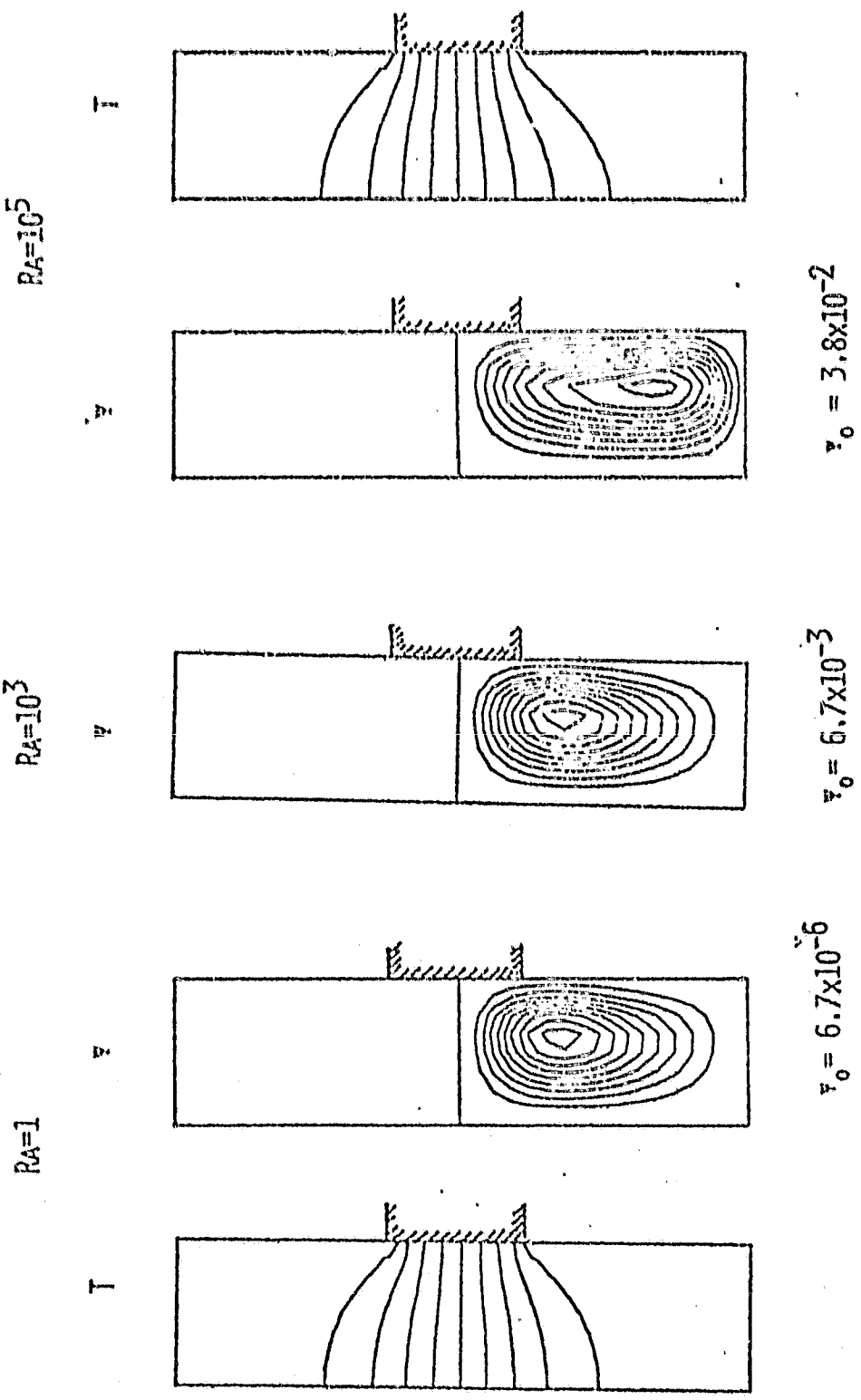

Figure 8. Temperature fields and streamlines for prototype of Bridgman solidification system with Pr=0.01 and Rayleigh numbers of 1, 10^3, and 10^5. In each case the right side of the vertical slice through the melt is shown.

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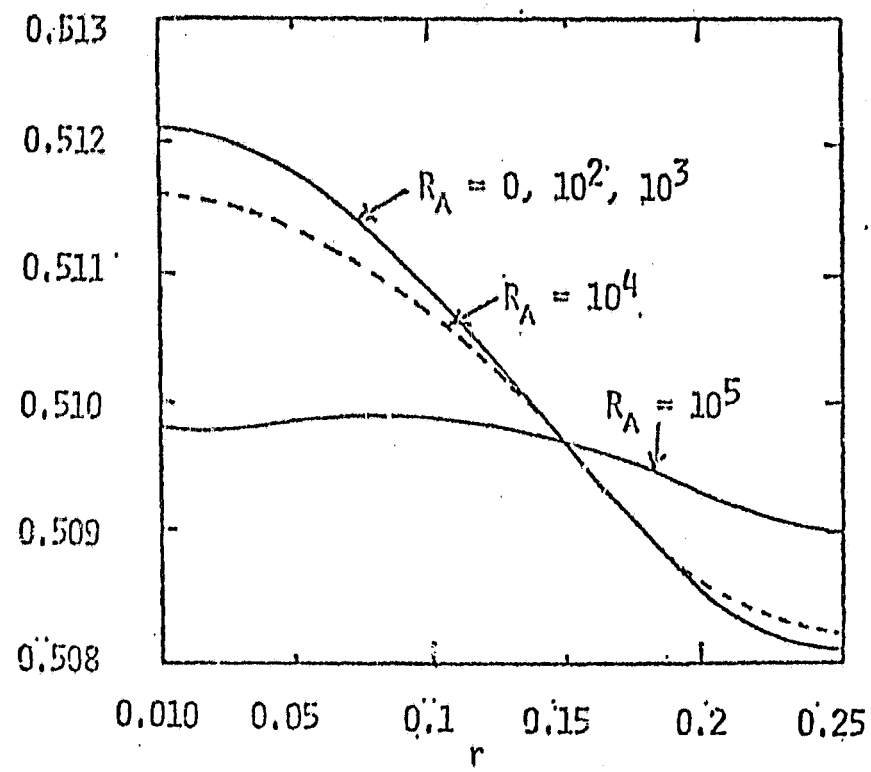

Figure 9. Melt/solid interface shapes calculated with flow fields in Figure 7.

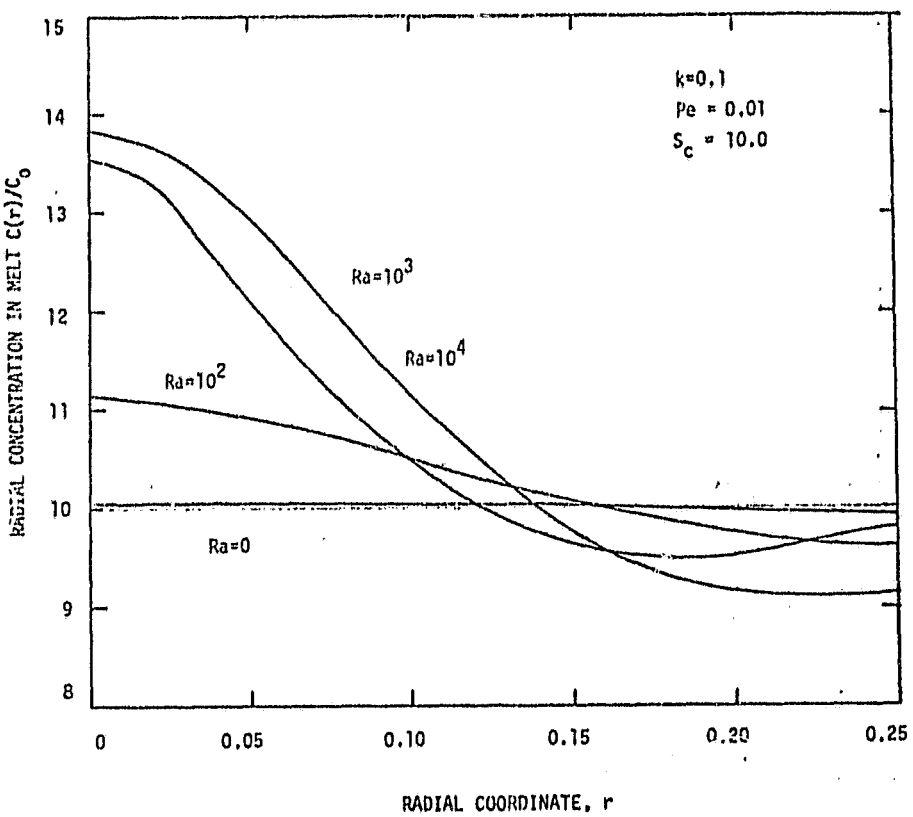

Figure 10. Radial concentration of dopant in the melt to the melt/solid interface.

2.5 MICROSCALE MODELLING OF SOLIDIFICATION DYNAMICS

The Isotherm-Newton method for solving steady solidification problems has been extended to account for the variation of melting point temperature with the shape of the solidification interface, where the condition for interfacial equilibrium depends on the shape of the interface through its mean curvature. This added complication is systematically handled because we write an explicit fbxbcdUelement representation for the location of the interface. Ungar is combining this new finite element formulation with methods for calculating the stability and multiplicity of steady solutions (see Ungar and Brown[2]) to analyze the evolution of microscale variation of an interface that is constitutionally unstable. So far, the linearized results of Mullins and Sekerka [J. Applied Physics, 35, 444-451 (1964)] have been reproduced and steady interfaces with finite amplitude cellular morphologies have been calculated.

Analytical methods developed in [7] have been applied to study an interface with a grain boundary. Contrary to previous analyses [Coriell and Sekerka, J. Crystal Growth, 19, 90-104 (1972) and 19, 285-293 (1973)] the presence of the grain boundary causes large changes in the amount of constitutional undercooling needed for an instability of a given wavelength. Ungar's analytical results are valid only for grain angles near 90° (as measured through the solid). Numerical calculations are being developed that are valid for all angles.

PRESENTATIONS

1. C.J. Chang and R.A. Brown, "Radial Segregation Induced by Natural Convection and Melt/Solid Interface Shape in Melt Crystal Growth." Fifth American Conference in Crystal Growth, San Diego, July 1981.

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2. C.J. Chang and R.A. Brown, "Finite Element Analysis of Convection and Mass Transfer in Directional Solidification." Invited paper at the 18th Annual Meeting of the Society of Engineering Science, Providence, September 1981.
3. C.J. Chang and R.A. Brown, "Finite Element Methods for Buoyancy-Driven Convection Near a Melt/Solid Interface." Second National Symposium on Numerical Methods in Heat Transfer, Maryland, September 1981.
4. G. Harriott and R.A. Brown, "The Fluid Mechanics of a Differentially Rotated Captive Drop." 74th National Meeting of the AIChE, New Orleans, November 1981.
5. Y. Yamaguchi, C.J. Chang and R.A. Brown, "Multiple Buoyancy-Driven Flows in a Vertical Cylinder." 34th Meeting of the Fluid Dynamics Division of American Physical Society, Monterey, November 1981. Abstract in Bull. Amer. Phys. Soc., 26, 1286 (1981).

REFERENCES

1. C.J. Chang and R.A. Brown, "Finite Element Calculation of Buoyancy-Driven Convection Near a Melt/Solid Phase Boundary." To appear in Proceedings of the Second National Symposium on Numerical Methods in Heat Transfer, Hemisphere Press (1981).
2. L.H. Ungar and R.A. Brown, "The Dependence of the Shape and Stability of Captive Rotating Drops on Multiple Parameters," Philos. Trans. R. Soc. Lond., in press (1981).
3. H.M. Ettouney and R.A. Brown, "Finite Element Methods for Steady Solidification Problems," J. Comp. Physics, submitted.
4. H.M. Ettouney and R.A. Brown, "Effect of Heat Transfer on Melt/Solid Interface Shape and Solute Segregation in Edge-Defined Film-Fed Growth: Finite Element Analysis," J. Crystal Growth, submitted.
5. C.J. Chang and R.A. Brown, "Effect of Steady Buoyancy-Driven Convection on Melt/Solid Interface Shape and

Radial Solute Segregation in Vertical Bridgman Growth," J. Crystal Growth, submitted.

6. G. Harriott and R.A. Brown, "The Fluid Mechanics of a Differentially Rotated Captive Drop," J. Fluid Mech., submitted.
7. Y. Yamaguchi, C.J. Chang and R.A. Brown, "Axisymmetric Buoyancy-Driven Convection in a Vertical Cylinder Heated From Below," J. Fluid Mech., to be submitted.

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N82 27390

PROJECT B2: NUMERICAL MODELING AND OPTIMIZATION OF POLYMER MELT PROCESSING OPERATIONS

Principal Investigator: Prof. David Roylance

Personnel: Mr. Brent Collins
Mr. Craig Douglas

RESEARCH ABSTRACT

This project has been concerned primarily with the application of finite-element computer analyses to polymer flows of the type encountered in melt processing operations. The finite element method is well suited to a wide variety of problem types, and is able to incorporate irregular boundary conditions and complicated fluid properties more conveniently than alternative methods. Our code as now developed is able to predict values of fluid velocity, pressure, shear stress, and temperature at any point within the flow field. As such, it is of value in diagnosing such processing problems as regions of fluid stagnation at which thermal degradation may occur, or regions of excessive shear deformation which lead to thermomechanical damage. It is further able to generate predictions of the forces which must be applied to the melt to achieve the desired flow, and this information is of value in designing processing equipment of optimal efficiency and minimum energy consumption. Ultimately, the project seeks to develop a versatile and easily implemented analytical tool which may be used routinely by processing engineers, as well as by researchers in rheology seeking solutions to presently intractable problems.

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RESEARCH SUMMARY

At the beginning of the current year, our finite element code had been developed so as to handle a wide variety of creeping flow problems, and some preliminary work on coupled temperature effects had been completed. The capability for coupled viscous flow-heat transfer problems was developed further during the current year, so that now many practical problems in nonisothermal polymer melt processing can be modeled numerically. Excellent agreement has been obtained between computed velocity and temperature fields and those available from theoretical closed-form solutions of selected problems. Finite element solutions have also been obtained in several cases in which closed-form solutions are not possible, such as the die entry problem. In all of these calculations, our code takes the momentum convection to be negligible (polymer melts have low Reynolds numbers), but it does have the capability to treat thermal convection. Convective terms are well known to introduce instability in computed results, and our code is able to avoid these problems either by successive grid refinement within the usual Galerkin method of finite element analysis, or by an "optimal upwinding" scheme in which a greater weight is attached to the upwind side of each element.

During the second half of the current year, attention turned to transient problems, in which temporal derivatives appear explicitly in the governing equations. A capability for such problems has been implemented by means of a versatile and unconditionally stable two-point scheme, known as the theta-method. We have been able to predict transient flow-heat transfer solutions with this algorithm which agree well with closed-form results, but it must be mentioned that selection of the proper spatial and time steps is highly important; even a versatile algorithm may fail unless the problem's parameters are carefully chosen.

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The code is presently written so that the various material properties - the viscosity, conductivity, density, etc., - may be computed as functions of the solution variables (velocity gradient, temperature, pressure etc.). Only little work has been done in computing these nonlinear problems, however, and a more detailed exploration of such effects will constitute a major portion of the effort during the coming year. Nonlinear problems can be coded and attacked by a number of iterative schemes, but in general no single scheme is guaranteed of success. One expects that numerical convergence will become more difficult as the strength of the nonlinearity increases, and it is likely that the very strong (usually exponential) dependence of the material parameters on the solution variables in polymer flows will prove a most difficult problem.

In addition to the further exploration of nonlinear problems, the code will be developed so as to include the capability for handling reactive flows such as occur in reaction injection molding or epoxy dry-blend compounding. These will be both nonlinear and transient, so that many serious problems in convergence are expected. However, we are confident that many of these problems can be circumvented, and that a novel and versatile analytical tool will result.

PUBLICATIONS:

1. Roylance, D., "Finite Element Modeling of Nonisothermal Polymer Flows," to appear in the ACS Symposium Series, "Computer Applications in Coatings and Plastics."
2. Collins, B., "A Finite Element Model of a White-Metzner Viscoelastic Polymer Extrudate," Technical Report T-733, Charles Stark Draper Laboratory, February 1981.

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PROJECT B3: STUDIES OF METALS ELECTROPROCESSING IN MOLTEN SALTS

Principal Investigator: Prof. D. R. Sadoway

Personnel: Mr. A. Abdelmassih
Mr. P. T. Rogers

RESEARCH ABSTRACT

Molten salts are very important solvent systems in which the electrodeposition of a wide variety of metals may be conducted. However, solid electrodeposits from molten salts are typically incoherent, powdery, and/or dendritic. To understand better the electrodeposition process, fluid flow patterns in the electrolyte are being observed in order to determine how mass transport affects the morphology of the metal deposit. Studies are being conducted on the same metal, both in aqueous electrolytes in which coherent solid electrodeposits are produced, as well as in transparent molten salt electrolytes. Process variables such as current density and composition of the electrolyte are adjusted to change the morphology of the electrodeposit and, thus, to permit the study of the nature of electrolyte flow in relation to the quality of the electrodeposit. The results of this work will be helpful in electrochemical cell design and will serve as a data base for subsequent mathematical modeling of fluid flow in such systems.

RESEARCH SUMMARY

It is generally true that electrowon metal is of better quality than the thermal reduction product. However, solid electrodeposits from molten salts are typically incoherent, powdery, and/or dendritic.

The novelty of the present study is its consideration of the effects of fluid flow of the electrolyte in seeking to explain the poor quality of solid electrodeposits in molten salts. The plan is to electrodeposit the same metal in separate experiments from aqueous solutions and molten salt electrolytes. Transparent cells allow observation of electrolyte circulation patterns by a laser Schlieren optical technique.

Zinc has been chosen as the metal to study. It can be deposited both from aqueous chloride and molten chloride electrolytes. Furthermore, both types of electrolyte systems are transparent to visible light, an important property which permits the use of noninvasive optical techniques of flow measurement.

As this project is the first of its kind at the Materials Processing Center, much effort was spent in building up a laboratory for electroprocessing. This year the facilities for flow visualization by laser Schlieren photography were added. These include a pneumatically supported optical bench measuring 4 x 6 feet.

Phase one of the zinc plating study was devoted to the electrorefining of zinc in aqueous acid chloride solutions. Working at room temperature without the need for furnaces and controlled atmosphere cells allowed one to concentrate on perfecting the optics of the system. Following a survey of the literature on acid zinc chloride solutions, a study of the chemistry of these solutions was conducted with the purpose of identifying the dominant ionic species present as a function of $ZnCl_2$ concentration, alkali chloride concentration, and pH. Then, the electrochemistry of these solutions was studied by polarography and other techniques in various concentration-pH regimes which had been identified earlier. The optical apparatus to permit fluid

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flow visualization by laser Schlieren and shadowgraph techniques was assembled and tested on simple electroplating cells. The present optical arrangement is capable of recording the laser images in any of these formats: 35 mm photographic film, 8 mm movie film, or 1/2 inch videocassette.

The results of the electrorefining of zinc in aqueous acid zinc chloride solutions can be summarized as follows. First, the laser Schlieren technique, while it does not provide quantitative information, is a very powerful tool in the study of fluid flow in electrochemical cells. The flow patterns observed under a variety of conditions show a significant amount of convection even at relatively low current densities. Such convection improves mass transport of zinc to the cathode well beyond the rate of diffusion, and thus, delays the onset of dendrite formation. This permits one to plate at higher deposition rates for a given surface quality. Furthermore, it is clear that the laser Schlieren technique can be used as a tool of analysis in electrochemical cell design.

The next phase of the work is the adaptation of a cell to permit similar fluid flow studies of zinc electrodeposition in molten chloride solutions for comparison with the results of the aqueous system.

N82 27392

PROJECT B4: HEAT FLOW CONTROL AND SEGREGATION IN DIRECTIONAL SOLIDIFICATION

Principal Investigator: Prof. A. F. Witt
Associate Principal Investigators: Prof. W. M. Rohsenow
Prof. P. K. Houpt

Personnel: Mr. C. Wang
Mr. T. Jasinski
Mr. M. Wargo
Mr. E. Bourret
Mr. C. Herman

RESEARCH ABSTRACT

The thrust of this NASA-sponsored research program is directed toward the optimization of the vertical Bridgman technique for growth of electronic materials in single crystal form with the intent of advancing electronic materials processing at large and establishing a single crystal growth configuration through which the potential of reduced gravity environment for semiconductor crystal growth can be properly assessed.

In the first phase of this research the limitations of the configuration were experimentally determined and heat transfer related deficiencies identified. Taking into account the necessity for complementary heat transfer calculations in order to arrive at an optimized Bridgman-type growth configuration, it was decided to base the design of an alternate system on the use of heat pipes separated by a gradient region since well-defined boundary conditions can thus be experimentally realized. Heat transfer analyses based on one- and two-dimensional models indicated the necessity of a flexible gradient zone configuration, a feature which was incorporated into the system presently under construction.

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In a parallel study, directional melting of binary systems, as encountered during seeding in melt growth was analyzed for concurrent compositional changes at the crystal-melt interface. It was shown that steady state conditions cannot normally be reached during seeding and that the growth interface temperature (which determines the location of the crystal-melt interface) at the initial stages of seeded growth is a function of back-melt conditions. The theoretical treatment was numerically applied to HgCdTe and Ga-doped germanium.

Considering the increasing use of direct current flow across the crystal-melt interface for both analytical purposes and growth and segregation control, a theoretical and experimental study of the thermal effects associated with current flow was conducted. It was found that experimental measurements of DC induced growth during crystal pulling can be used for the precise determination of the Peltier coefficient. The validity of the developed theoretical framework was verified by numerically solving the time dependent energy transport equations using an explicit finite difference technique. The results were found to be in good agreement with experimentally determined current induced changes in the microscopic rate of growth.

1. VERTICAL BRIDGMAN TYPE CRYSTAL GROWTH: A HEAT TRANSFER ANALYSIS

This work, part of a comprehensive approach to the optimization of semiconductor crystal growth by the vertical Bridgman technique, is a heat transfer analysis based on one- and two-dimensional models. The present treatment neglects radial temperature gradients within the charge to yield relatively simple solutions of the axial temperature distribution. The analysis focuses on the axial temperature

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gradient in the liquid at the growth interface and on the growth interface position within the furnace. Also considered are the effects of charge motion, thermal coupling to the furnace, charge length, generation of latent heat of solidification, conductivity change at the growth interface, geometry and material of the crucible.

Axial Temperature Distribution According to One-Dimensional Models

The one-dimensional model used for the analysis of axial heat transfer is shown in Fig. 1. Making the assumptions described in Table I, the equation for the axial temperature distribution of the charge is the same as for a moving fin.

$$\frac{d^2\theta}{d\zeta^2} - Pe\,\frac{d\theta}{d\zeta} - 4\,Bi\theta = -4Bi\theta_f \qquad [1]$$

where

ζ = z/D (non-dimensional axial coordinate)
θ = $(T-T_{ref})/(\Delta T_{ref})$ (non-dimensional temperature)
θ_f = non-dimensional furnace temperature
Pe = Peclet number = VD/α
Bi = Biot number = hD/k
α = thermal diffusivity
h = heat transfer coefficient (charge-furnace)
k = thermal conductivity of charge
D = charge diameter
V = mechanical charge displacement rate

Equation [1] is solved for each zone using boundary conditions of equality of temperature and continuity of flux at the zone boundaries.

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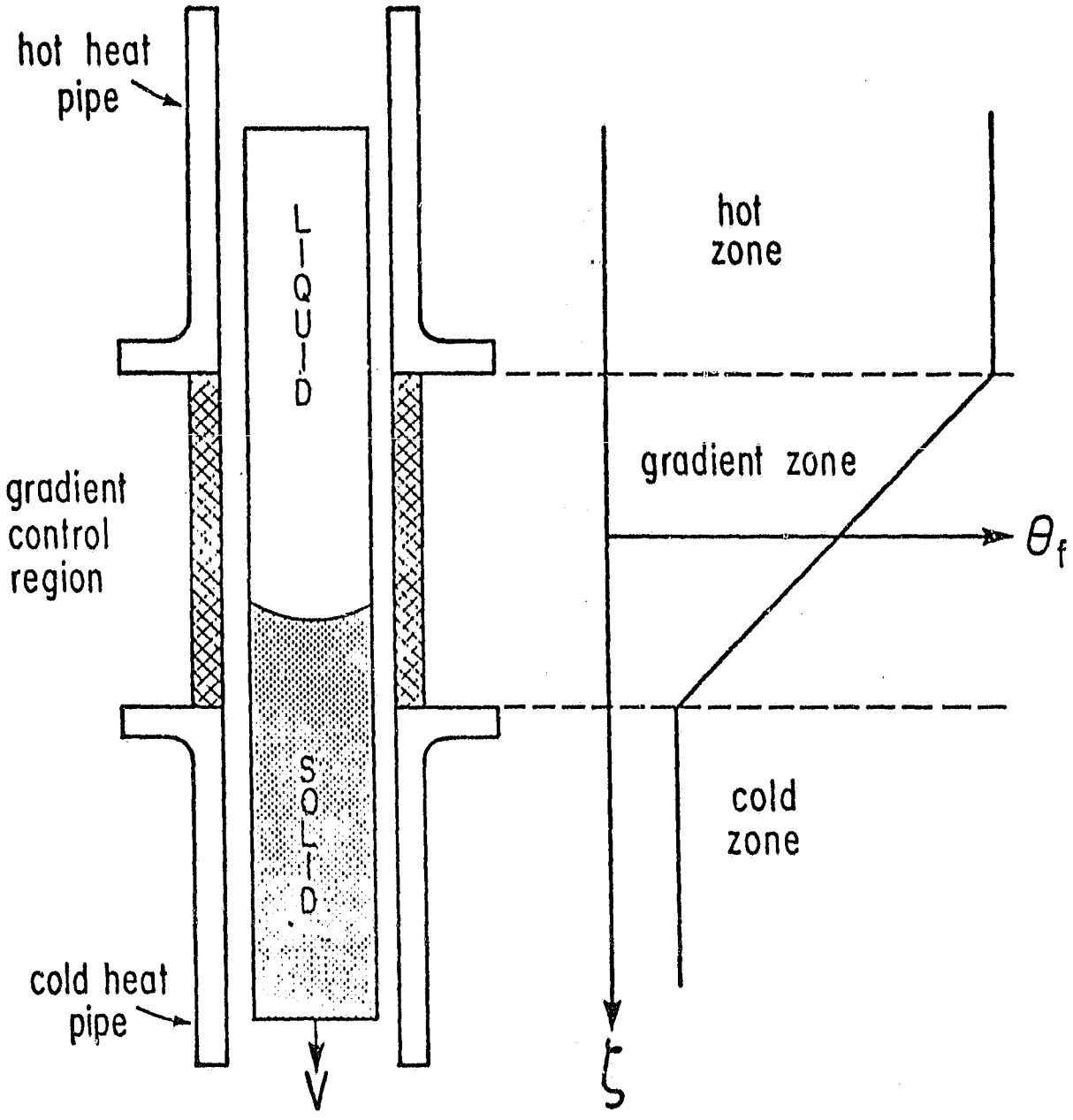

Fig. 1: One-Dimensional Model Used for Axial Heat Transfer Analysis

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"Infinite" Charge Length

The contribution to the solution of eq. [1] from the positive characteristic root is normally small and is zero for an infinite charge length. If the charge is not "infinite" in length, the interface location will change as the charge moves within the furnace. When most of the charge is in the hot zone, the interface will be displaced toward the cold zone and vice-versa. The charge appears

TABLE I

ASSUMPTIONS FOR THE ONE-DIMENSIONAL MODEL

(Equation [1] results from these assumptions.)

- Temperature not a function of radius.
- Hot and cold zone furnace temperatures uniform (heat pipe action).
- Gradient zone furnace temperature varies linearly.
- Heat exchange between the furnace and charge is governed by a heat transfer coefficient, constant within each zone.
- Transients are negligible.
- No thermal convection in the liquid.

"infinite" in length when the contribution from both the positive and negative roots become small. If the following criteria is chosen,

$$\exp\left[(m_{-})\zeta_{\infty}\right] < 0.01 \qquad [2]$$

(where ζ_{∞} = length of charge in hot or cold zone for charge to appear infinitely long) then,

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$$\zeta > \frac{5}{m_-} \qquad [3]$$

If Pe is small, the characteristic roots become:

$$m_{\pm} = \pm 2\sqrt{Bi} \qquad [4]$$

Substituting eq. [4] into eq. [3] results in a useful expression for determing ζ_∞.

$$\zeta_\infty > \frac{5}{2\ Bi} \qquad [5]$$

Motion of the interface may result in it being a location of unfavorable radial gradients. A method of stabilizing the interface location is to increase the length of the charge so that solidification in the center portion occurs with essentially infinite ends in the hot and cold zone.

Biot Number Effect

As Bi increases, the temperature follows more closely the furnace temperature distribution and the axial temperature gradient in the gradient zone increases. The relationship between Bi and axial temperature gradient can be demonstrated through the solution of eq. [1] which gives the axial temperature gradient zone as,

$$\frac{d\theta}{d\zeta} = -\left[\lambda + (2Bi_H^{1/2})^{-1} + (2Bi_C^{1/2})^{-1}\right]^{-1} \qquad [6]$$

where:

Bi_H = Bi in hot zone
Bi_C = Bi in cold zone

It is concluded that the establishment of large axial thermal gradients, frequently necessary to avoid constitutional supercooling, necessitate a large Bi.

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Latent Heat Effect

The latent heat of solidification enters the solution only in the boundary conditions at the interface. Assuming equal solid and liquid thermal conductivities, continuity of flux gives,

$$\left(\frac{d\theta}{d\zeta}\right)_{liq} = \left(\frac{d\theta}{d\zeta}\right)_{sol} + Pe\ R_H \qquad [7]$$

where:

$$R_H = \Delta H / C_p \Delta T_{ref}$$

ΔH = latent heat of solidification

The effect of the latent heat is small if,

$$Pe\ R_H << [\lambda + (2Bi_H^{1/2})^{-1} + (2Bi_C^{1/2})^{-1}]^{-1}. \qquad [8]$$

Otherwise, the latent heat will increase the temperature everywhere in the charge and the interface will move toward the cold zone.

Thermal Conductivity Change at the Crystal-Melt Interface

The charge phase with higher conductivity will have lower axial gradients due to lower thermal resistance to heat transfer in the axial direction.

The assumption of a large Bi forces the temperature drop from hot to cold zone to occur entirely in the gradient zone. The axial temperature gradient in the liquid becomes:

$$\left(\frac{d\theta}{d\zeta}\right)_{liq} = \frac{2}{\lambda} \bullet \frac{1}{1+R_K} \qquad [9]$$

where:

$$R_K = K_{liquid}/K_{solid}$$

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In materials where R_K is greater than 2 or 3, a large reduction in axial gradient in the liquid at the interface results. It is found that, for example in germanium, the difference in thermal conductivity between the solid and the liquid phase results in a reduction of 43% in the axial temperature gradient of the liquid in the gradient zone.

Crucible Effect and Radial Resistance in the Charge

Containment of the charge always decreases axial gradients. A crucible of low thermal conductivity adds thermal resistance between the charge and furnace effectively decreasing Bi; one of high conductivity "short-circuits" heat from the furnace within the crucible itself, again decreasing axial temperature gradients. The heat flow in the crucible are approximated by solving the heat conduction equation in the crucible:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\Theta}{\partial r}\right) + \frac{\partial^2\Theta}{d\zeta^2} = 0 \qquad [10]$$

with the assumption that the $\partial^2\Theta/\partial\zeta^2$ term is equal to that of the charge in eq [1] and Pe approaches zero. Reformulating eq [1] results in a modified Bi number.

$$\frac{Bi_{eff}}{Bi_C} = Bi_C\left\{\left[\frac{1}{4}\left(\frac{D_C^2}{D^2}-1\right)-\frac{1}{2}\ln\frac{D_C}{D}\right]+1+\frac{k_C}{k}\left(\frac{D_C^2}{D^2}-1\right)+ \right. \qquad [11]$$

$$\left.\frac{k}{k_C}\left(\frac{1}{2}\,Bi_C\ln\frac{D_C}{D}\right)\right\}^{-1}$$

where:

D_C = crucible diameter
k_C = crucible thermal conductivity
Bi_C = $h_C D_C/k$

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Bi_{eff} = Biot to be used in eq. [1]
h_c = heat transfer coefficient between furnace and outer crucible surface
k = conductivity of the charge (either solid or liquid)

According to this relationship, the value of the conductivity ratio k_c/k, which maximized the effective Bi is:

$$\left(\frac{k_c}{k}\right)_{max} = \left\{\frac{Bi_c \ln\left(\frac{D_c}{D}\right)}{2\left[\left(\frac{D_c}{D}\right)^2 - 1\right]}\right\}^{1/2} \qquad [12]$$

For typical values of Bi_c and D_c/D the optimum conductivity ratio is between 0.1 and 1.0. Increasing Bi_c and decreasing D_c/D serve to increase the optimum conductivity ratio.

An analysis similar to the one above is made for radial thermal resistance in the charge. The result of this analysis indicates that the Biot number should be modified as follows:

$$Bi_{eff} = \frac{Bi}{1+\frac{Bi}{8}} \qquad [13]$$

where:

Bi = Biot not accounting for radial temperature gradients in the charge
Bi_{eff} = Biot accounting for radial temperature gradients in the charge

It is found that if Bi/8 is small compared to unity, radial gradients are small enough so that eq. [1] reasonably predicts the axial temperature profile. If Bi/8 is not small

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compared to unity, the above relationship can be used to approximate the effect of the radial gradients on the axial temperature distribution.

2. VERTICAL BRIDGMAN TYPE CRYSTAL GROWTH: AN EXPERIMENTAL STUDY OF GROWTH AND SEGREGATION

The presently reported experiments were designed to establish the limitations of conventional, vertical Bridgman growth and to identify heat transfer controlled deficiencies of this growth configuration in conventional form. For this purpose, gallium-doped germanium crystals, approximately 7 cm long, were grown in a vertical single-zone Marshall tube furnace. Two types of cooling were imposed at the bottom end of the crystal: direct cooling of the seed, for which the temperature at the bottom of the seed is expected to remain constant throughout the growth experiment, and indirect cooling, for which the temperature at the bottom of the seed is determined by the thermal environment, which changes continuously.

Growth Behavior

Depending upon the type of cooling, the microscopic growth rates are found to differ significantly from the lowering rate of the crucible and to never reach a steady state value. Consequently, during growth the position of the solid-liquid interface moved within the furnace. It is found that with direct seed cooling, the interface displacement (out of the furnace) for growth of 7 cm exceeds 8 mm. With indirect seed cooling, the growth interface displacement was in the opposite direction, i.e. into the furnace. The results for a lowering rate of 4 μm/s are summarized in Fig. 1. Heat transfer considerations support that an

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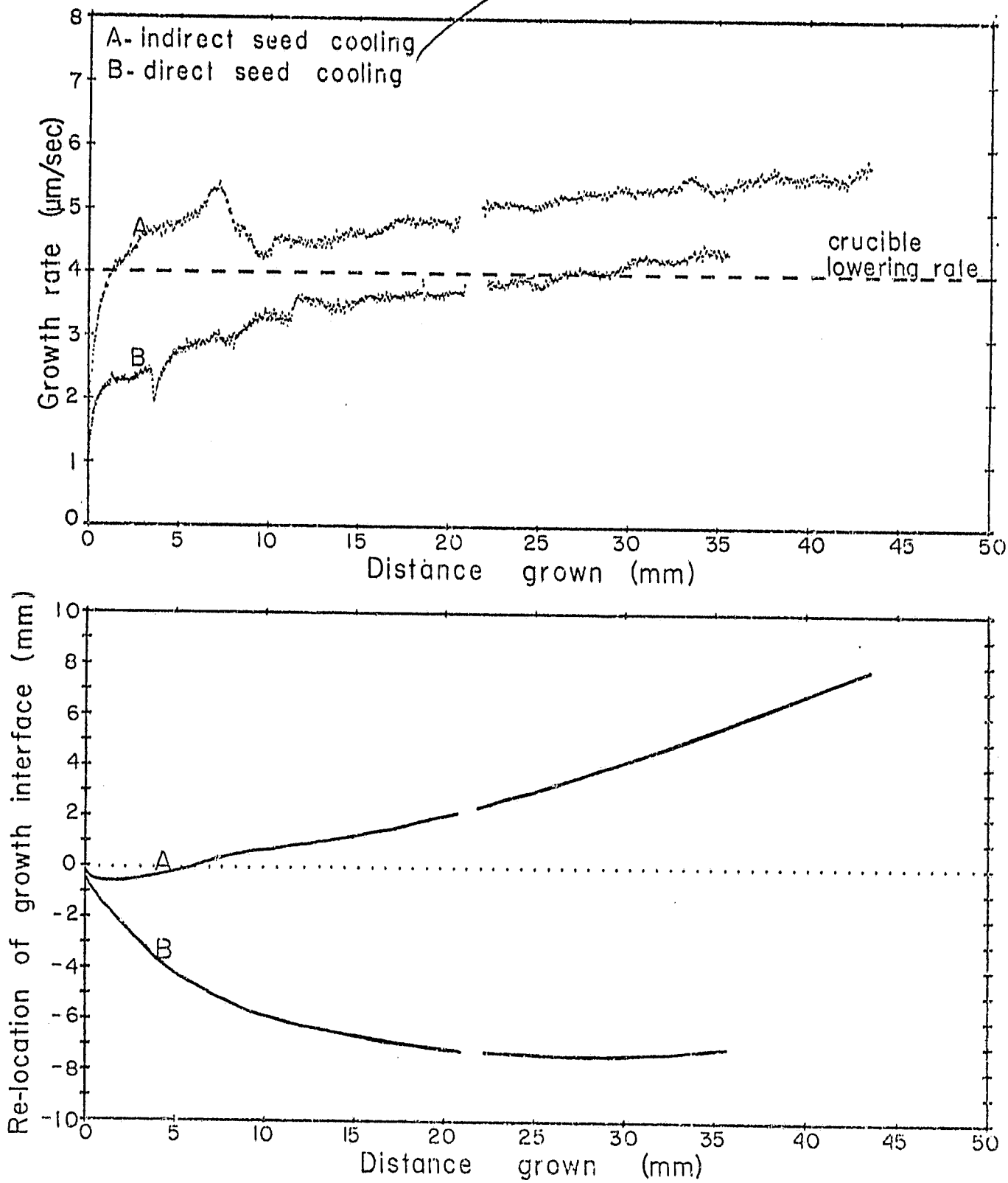

Fig. 1: Top: Comparison of Growth Rate as a Function of Distance Grown for Different Seed Cooling Conditions. Bottom: Differential Change in Growth Interface Position in the Furnace as a Function of Distance Grown

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increase in the rate of lowering increases the Peclet number (convective effect due to motion), thus increasing the temperature of the charge everywhere, and causing greater deviations from the initial interface position in the furnace. This effect was confirmed during a growth experiment with a lowering rate of 8 μm/s; the interface displacement was found to be 18 mm. The (experimentally determined) continuously changing growth rates are interpreted primarily as transients due to end effects.

Segregation Effects

Anomalous segregation of gallium in germanium was observed in all instances where the microscopic rate of growth assumed very low values. During the initial stages of all seeded growth experiments, the concentration of Ga is found to decrease under a steadily increasing growth rate (Fig. 2). After approximately 50 μm of growth, the segregation behavior is observed to exhibit the expected rate dependence. Since seeding involves backmelting of the seed, this anomalous behavior was suspected to be related to varying seed concentrations. Consequently, seed concentrations ranging from 0.1 to 10 times the equilibrium concentration for the solid in contact with the doped melt were studied. In all instances the anomalous gallium incorporation was observed.

The anomalous segregation behavior of gallium in germanium was observed also in all instances where growth was temporarily arrested and resumed after varying equilibration periods. For these experiments it was found through interface demarcation and spreading resistance measurements that, following the arrest, the microscopic growth decreased (as expected) and that initially the associated segregation increased (Ga concentration decreased). However, a gradual

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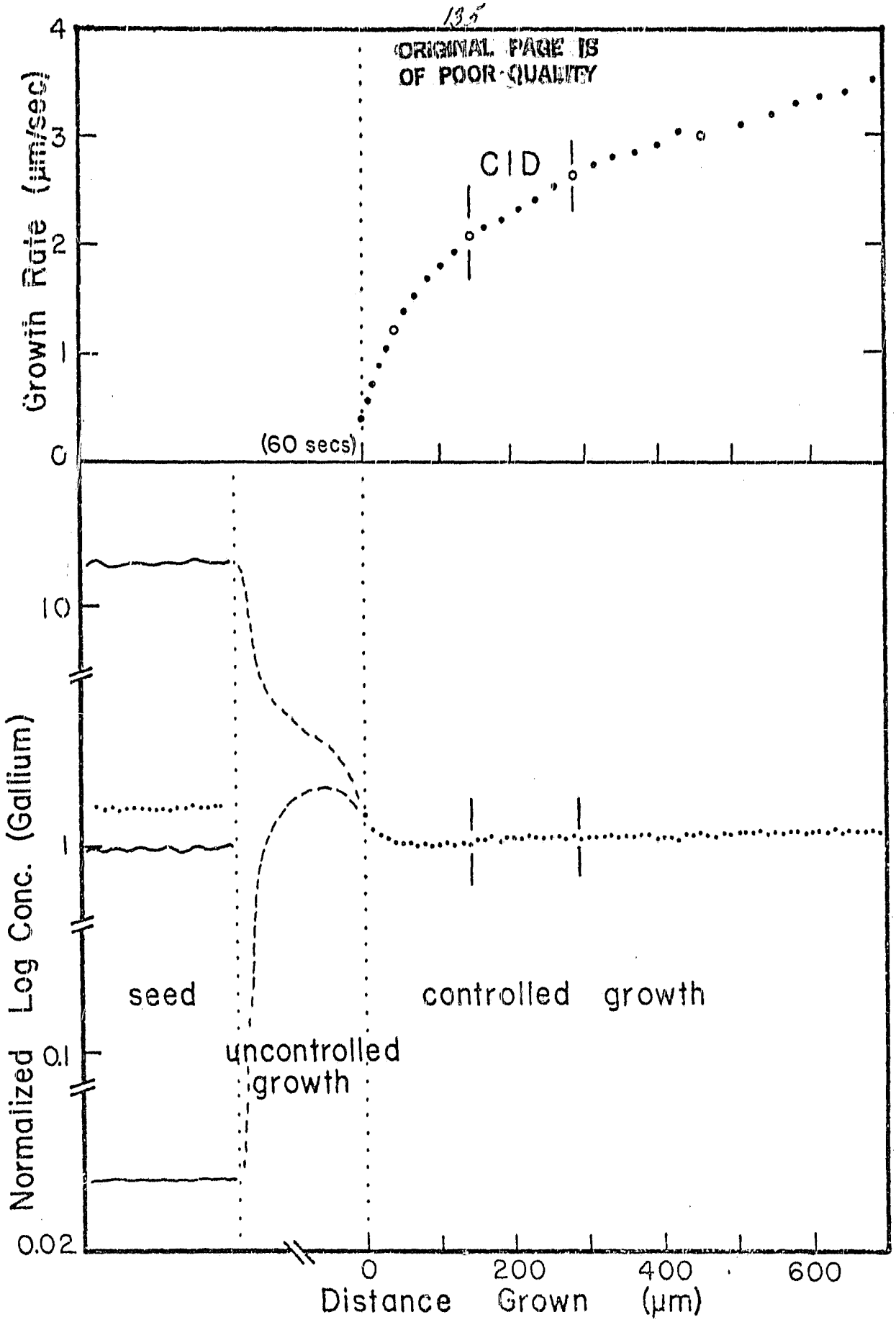

Fig 2: Growth Rate and Segregation During Seeding. Note Period of Uncontrolled Growth and Anomalous Segregation at Oneset of Growth

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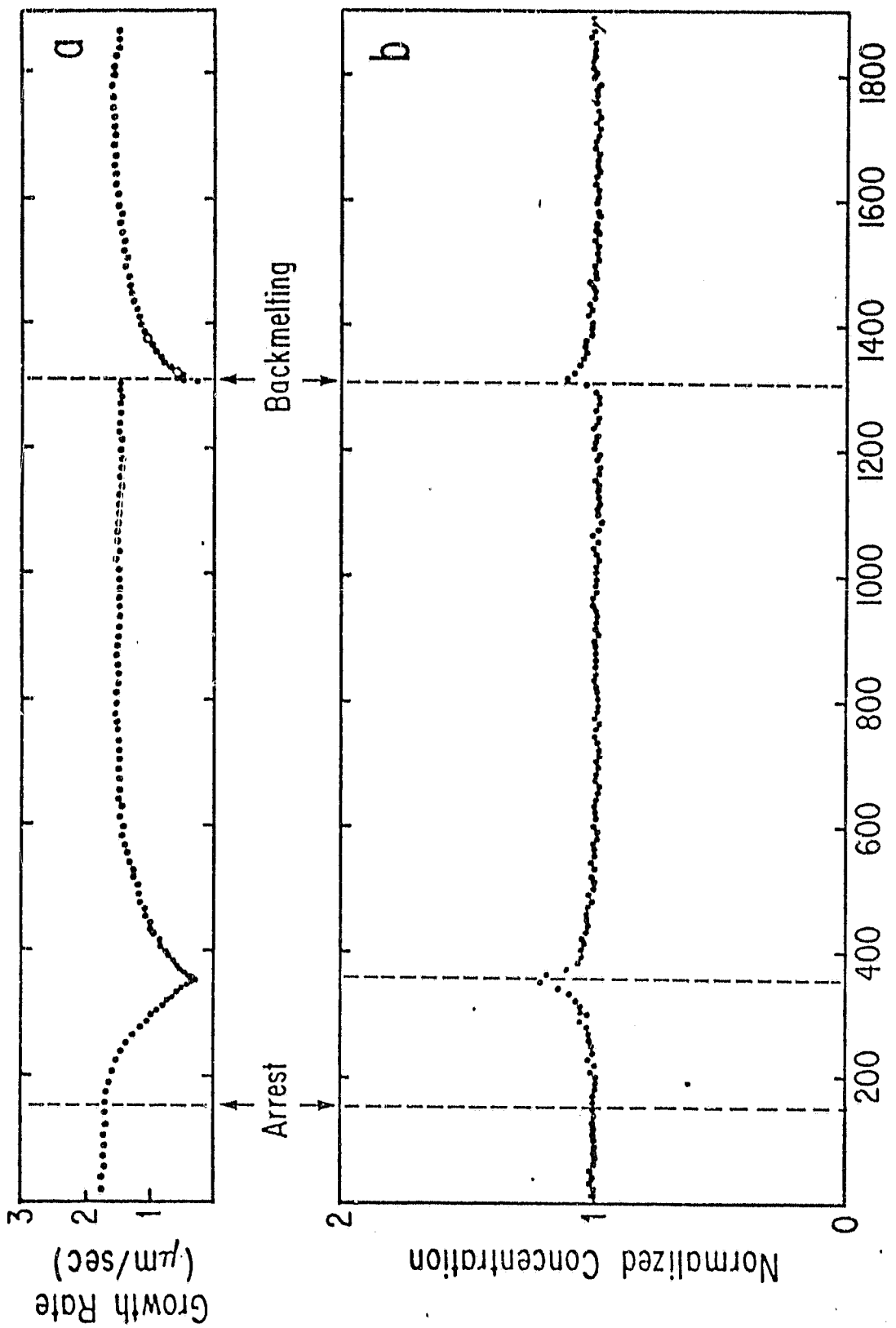

Fig 3: Growth Rate and Segregation During Equilibration. Note Anomalous Segregation for Growth Rates Less than Approximately 1 μm/sec.

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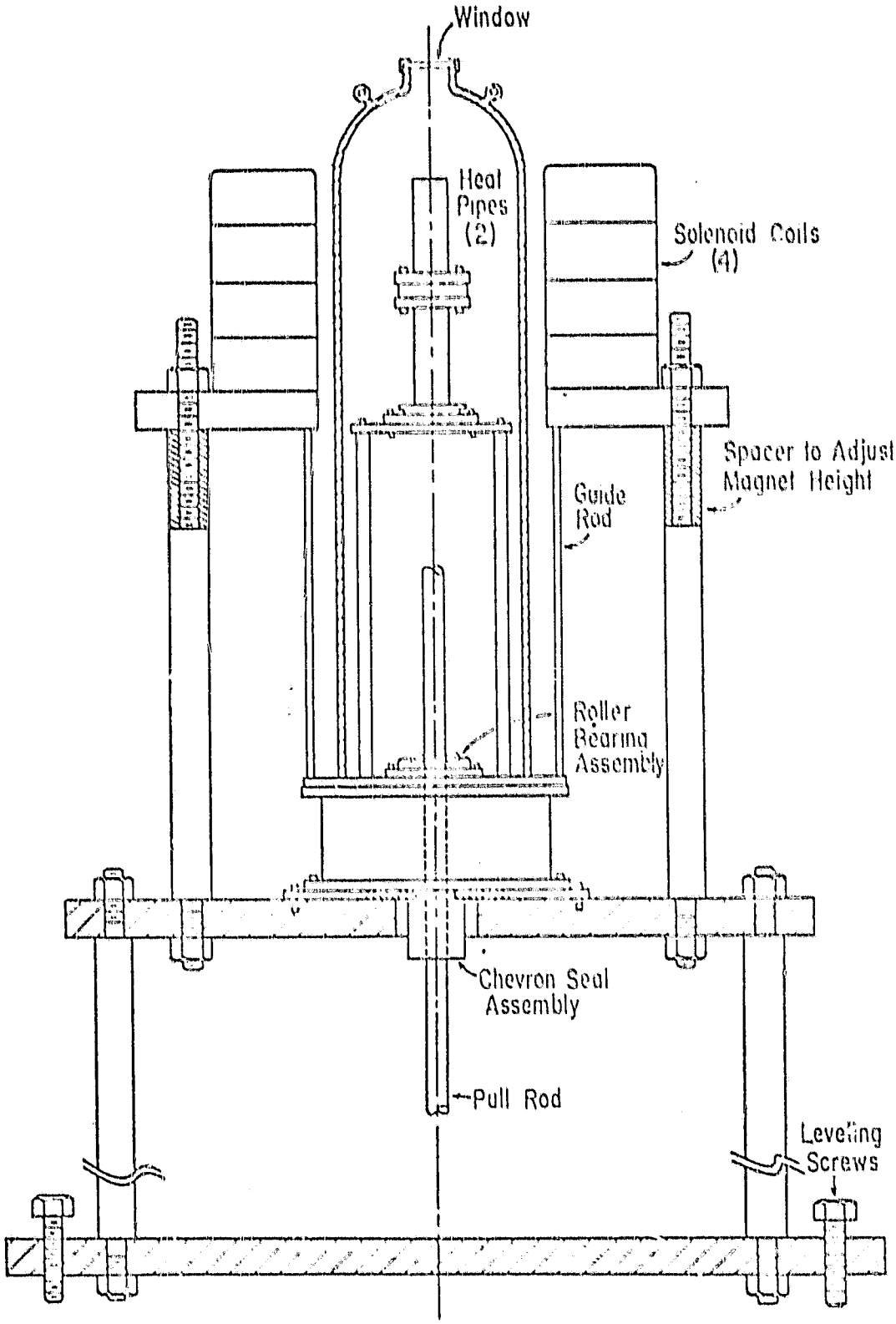

Fig 4: Schematic of Modified Bridgman Furnace Configuration

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increase in Ga concentration was observed as the transient growth rate during the arrest period decreased to less than 1 μm/s. Similarly, a decrease in Ga concentration was observed when growth was resumed and the growth rate increased from 0 to about 1 μm/s. As the growth rate exceeded about 1.5 μm/s, the segregation behavior was found to be normal (Fig. 3). Experiments were made for varying lengths of arrest times, ranging from 5 minutes to 12 hours; in all instances, the same anomalous segregation was observed. The most conspicuous evidence of anomalous segregation is provided by Ga concentration maxima centered about growth rate convergences to zero. It should, moreover, be noted that the dopant concentration maxima assume values significantly in excess of values encountered during steady state growth at rates in excess of 6 μm/s.

The presently reported "end effects" as well as the earlier uncontrollable, changing non-planar crystal-melt interface morphology, both of which have adverse effects on crystal growth and segregation, are heat transfer related deficiencies which appear to be inherent to growth by the Bridgman technique in conventional vertical configuration The elimination of these identified deficiencies have evolved as primary criteria in the conceptual design of a growth system currently under construction (Fig. 4).

3. THEORETICAL ANALYSIS OF SEGREGATION DURING DIRECTIONAL MELTING OF SEMICONDUCTOR CRYSTALS WITH LARGE LIQUIDUS-SOLIDUS SEPARATION AND ITS IMPLICATIONS ON SEEDED GROWTH

All seeded crystal growth from the melt involves as a first step a varying degree of backmelting of a crystal. This approach, generally successful in systems with small liquidus-solidus separation such as doped semiconductors,

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must, however, be expected to be problematic if binary or multicomponent systems with large liquidus-solidus separation ($Hg_{1-x}Cd_xTe$, $Pb_{1-x}Sn_xTe$, Ge-Si and the like) are involved. Any changes in composition that occur during melting at the crystal-melt interface are of fundamental importance since they will control the growth interface temperature and its stability. Both parameters affect the system's behavior during equilibration (melting arrest) and may control the degree of crystalline and compositional perfection achievable during ensuing solidification. Seeded crystal growth experiments, for example by the Bridgman and Czochralski techniques, involve boundary conditions which were not considered in earlier treatments. It is the purpose of this work to analyze the evolution of the solute concentrations, $C_S(t)$ and $C_L(t)$, at a crystal-melt interface and the related interface temperature during melting, with emphasis on the initial transient behavior. The analysis applies to seeding during crystal growth of binary systems in a configuration where a charge of known composition C_L is directionally melted in contact with a seed of composition C_S. The theoretical treatment is carried out in non-directional form; it is numerically applied to $Hg_{1-x}Cd_xTe$ and Ga-doped Ge to provide for comparative analysis of systems with small and large liquidus-solidus separation.

Theoretical Analysis of Solute Redistribution During Directional Melting

Making use of a series of basic assumptions, Fick's second law, formulated for a coordinate system which moves with the interface, assumes the form:

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$$D_S \frac{\partial^2 C_S}{\partial z^2} + \frac{\partial C_S}{\partial z} = \frac{\partial C_S}{\partial t} \qquad [1]$$

$$D_L \frac{\partial^2 C_L}{\partial z^2} + R\frac{\partial C_L}{\partial z} = \frac{\partial C_L}{\partial t} \qquad [2]$$

Solute flux conservation through the interface yields:

$$D_S \left.\frac{\partial C_S}{\partial z}\right|_{z=0^+} - R\, C_S^* = D_L \left.\frac{\partial C_L}{\partial z}\right|_{z=0^-} - R\, C_L^* \qquad t > 0 \qquad [3]$$

Using the change of scale:

$$\overline{C} = C - C_o \qquad [4]$$

and the dimensionless variables:

$$y = \frac{Rz}{D_L} \qquad \tau = \frac{R^2 t}{D_L} \qquad \alpha = \frac{D_S}{D_L}$$

The system of eqs. [1] and [2] becomes:

$$\alpha \frac{\partial^2 \overline{C}_S}{\partial y^2} + \frac{\partial \overline{C}_S}{\partial y} = \frac{\partial \overline{C}_S}{\partial \tau} \qquad [5]$$

$$\frac{\partial^2 \overline{C}_L}{\partial y^2} + \frac{\partial \overline{C}_L}{\partial y} = \frac{\partial \overline{C}_L}{\partial \tau} \qquad [6]$$

This set of equations, with the appropriate boundary conditions and the initial conditions, can be solved using the Laplace transforms:

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$$\tilde{\gamma}_S = \int_D^{\infty} \overline{C_S}\, e^{-st}\, dt$$

and

$$\tilde{\gamma}_L = \int_D^{\infty} \overline{C_L}\, e^{-st}\, dt$$

yielding:

$$\alpha \frac{d^2\tilde{\gamma}_S}{dy^2} + \frac{d\tilde{\gamma}_S}{dy} - s\tilde{\gamma}_S = 0 \qquad [7]$$

$$\frac{d^2\tilde{\gamma}_L}{dy^2} + \frac{d\tilde{\gamma}_L}{dy} - s\tilde{\gamma}_L = -q \qquad [8]$$

with

$$q = C_o\left(\frac{1}{K} - 1\right)$$

Taking the general solutions:

$$\tilde{\gamma}_S = A\, e^{-ay/\alpha}$$

$$\tilde{\gamma}_L = B\, e^{-by} + \frac{q}{s}$$

we obtain:

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$$\tilde{\gamma}_S = \frac{kq}{\delta} \frac{\exp\left(-\frac{1}{2} - \sqrt{\frac{1}{4} + \delta\alpha}\right)\frac{y}{\alpha}}{k - \frac{k}{2\alpha} - \frac{1}{2} - \frac{k}{\alpha^{3/2}}\sqrt{\frac{1}{4} + \delta\alpha} - \sqrt{\frac{1}{4} + \delta}} \quad [9]$$

and

$$\tilde{\gamma}_L = \frac{q}{\delta}\left[1 + \frac{\exp\left(-\frac{1}{2} + \sqrt{\frac{1}{4} + \delta}\right)y}{k - \frac{k}{2\alpha} - \frac{1}{2} - \frac{k}{\alpha^{3/2}}\sqrt{\frac{1}{4} + \delta\alpha} - \sqrt{\frac{1}{4} + \delta}}\right] \quad [10]$$

These relationships depend mainly on the two parameters k and $\alpha = D_S/D_L$. The inverse Laplace transforms are obtained in the general case by a numerical method. Analytical solutions were obtained for particular values of α.

The inverse Laplace transform is made by approximating the integral:

$$\bar{C}(\gamma,\tau) = \frac{1}{2\pi i}\int_{C-i\infty}^{C+i\infty} e^{\delta\tau}\tilde{\gamma}(\delta)d\delta$$

by a trapezoidal rule using discrete values of the Laplace transform $\tilde{\gamma}(\delta)$ along the integration paths $= c + i\omega$. For this purpose the integral [26] is approximated by Fourier cosine series which are evaluated using the Fast Fourier transform algorithm. The numerical inversion of [9] gives $C_S(y,\tau)$ for given values of α and k. Figure 1 is a plot of $\tau_{0.99}$, the time necessary to reach 99% of steady state as a function of k, for four different values of α.

[The real time (t) is related to the dimensionless time τ through $t = D_L\tau/R^2$.]

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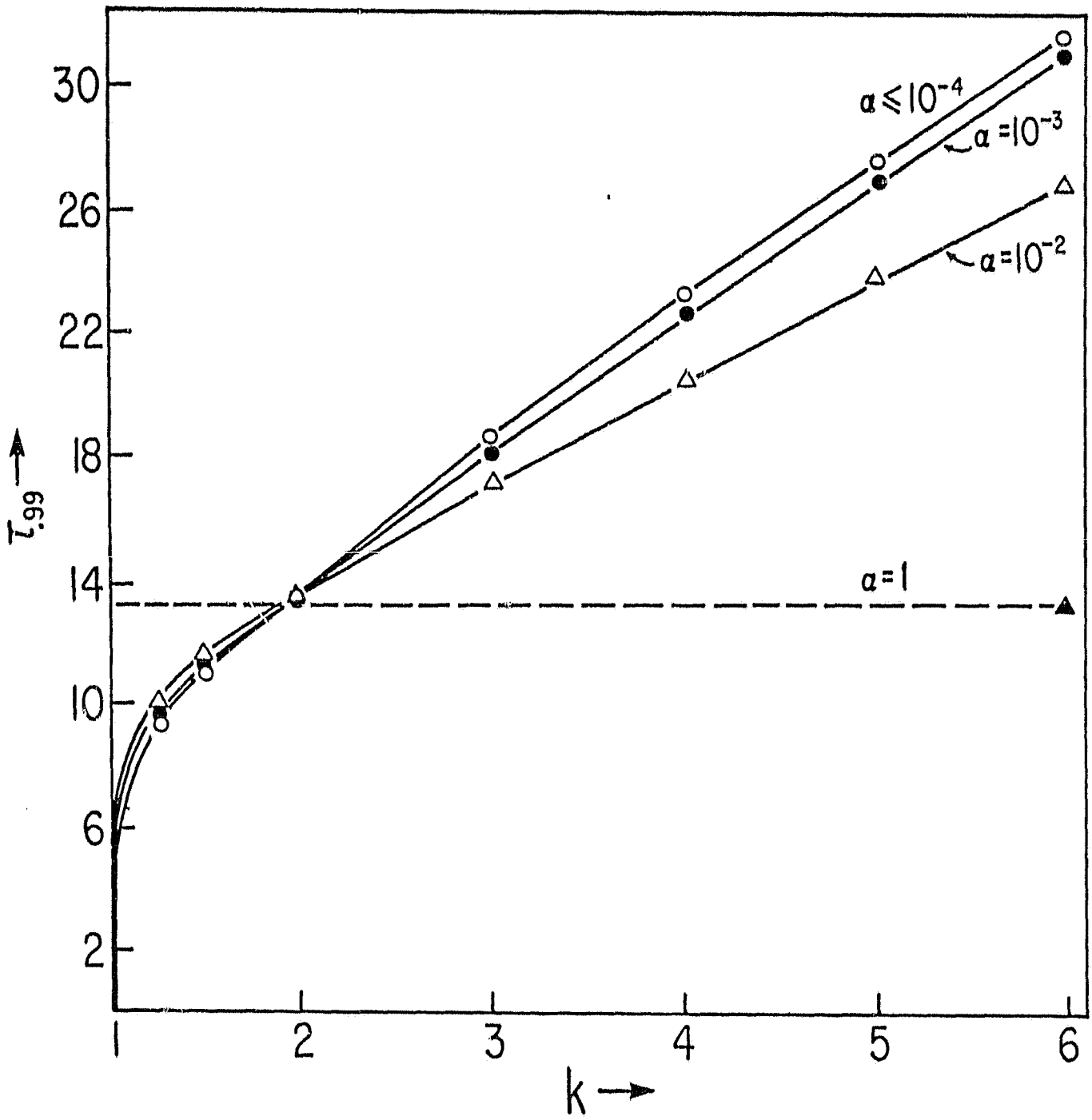

Fig. 1: Functional Dependence of $\tau_{0.99}$ on k for Various Values of α. ($\tau_{0.99}$ in non-dimensional form is the time required for C_s^* to reach 99% of the steady state value.)

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At the hypothetical upper limit ($\alpha=1$), the liquid and the solid behave symmetrically and a corresponding solution is given by:

$$\overline{C_S}(y,\tau) = \frac{C_o}{2}(1-k)\,\mathrm{erfc}\left(\frac{y}{2\sqrt{\tau}} - \frac{\sqrt{\tau}}{2}\right)\exp(-y) - \frac{C_o}{2}\,\mathrm{erfc}\left(\frac{y}{2\sqrt{\tau}} - \frac{\sqrt{\tau}}{2}\right)$$

which reduces at the interface to:

$$\overline{C_S^*}(0,\tau) = C_o(k-1)\,\mathrm{erf}\,\frac{\sqrt{\tau}}{2}$$

This relationship confirms the plotted data, 99% of steady state ($\mathrm{erf}\,\sqrt{\tau}/2 = 0.99$) is reached for all values of $k \neq 1$, with $\tau = 13.4$. The corresponding curve on Fig. 1 is used as a reference line to determine the variation of $\tau_{0.99}$ with for any given value of k.

Considering the special case of $\alpha \to 0$, the inversion of [9] yields:

$$\overline{C_S}(y,\tau) = \frac{C_o}{2}\left\{(1-k)\,\mathrm{erfc}\left(\frac{y}{2\sqrt{\tau}} - \frac{\sqrt{\tau}}{2}\right)\exp(-y) + \frac{1}{k}\,\mathrm{erfc}\left(\frac{y}{2\sqrt{\tau}} + \frac{\sqrt{\tau}}{2}\right)\right.$$

$$\left. - \left(\frac{2-k}{k}\right)\exp\left(\frac{2-k}{2k} - \frac{1}{2}\right)y\,\exp\left(\frac{1-k\tau}{k^2}\right)\,\mathrm{erfc}\left(\frac{y}{2\sqrt{\tau}} + \frac{2-k}{2k}\sqrt{\tau}\right)\right\} \qquad [11]$$

and

$$\overline{C_S^*}(0,\tau) = \frac{C_o}{2}\left\{(1-k)\,\mathrm{erfc}\left(\frac{-\sqrt{\tau}}{2}\right) + \frac{1}{k}\,\mathrm{erfc}\left(\frac{\sqrt{\tau}}{2}\right)\right.$$

$$\left. - \left(\frac{2-k}{k}\right)\exp\left(\frac{1-k}{k^2}\,\tau\right)\,\mathrm{erfc}\left(\frac{2-k}{k}\,\tau\right)\right. \qquad [12]$$

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Discussion of Segregation Analysis

The relationships [10] and [11] can be applied to solidification using the transform S defined by $k \xrightarrow{S} 1/k$, $S \xrightarrow{S} L$, $L \xrightarrow{S} S$. It yields a solution which is identical with that given by Smith et al, where D_S is considered negligibly small. Figure 1 shows that τ curves drawn for different values of α converge to equation [10] for $\alpha \leq 10^{-4}$. Generally accepted values for D_S and D_L in semiconductors lie in the range $10^{-10} - 10^{-8}$ cm^2/sec for D_S and $5 \times 10^{-4} - 10^{-5}$ cm^2/sec for D_L. Therefore the Smith et al. solution (or its equivalent for melting [10]) must be considered a good approximation. It should be pointed out, however, that there are as yet only limited data (of reasonable precision) for diffusion coefficients at melting point temperatures. While the uncertainty concerning the magnitude of D_L is not expected to have a noticeable effect on the value of α, D_S can be considerably lower than assumed, as a consequence of the temperature controlled increase in vacancy concentration, for example, and may thus have a significant effect on the value of α. The data show that already for $\alpha = 10^{-3}$ the Smith et al. approximation no longer applies, and that for any given interface displacement rate, the compositional transients in the solid ($\tau_{0.99}$) (and in the liquid) increase with increasing α for $k<2$ and decrease for $k>2$.

Implications of Segregation Behavior on Seeded Crystal Growth

It is of interest to consider the present analysis in terms of real time (t) behavior, i.e. to consider, for example, the specific effect of the rate of directional melting (R)

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on the time required to reach steady state. For this purpose, it is convenient to analyze the behavior of specific systems. An arbitrary choice is $Hg_{1-x}Cd_xTe$ of the composition $x = 0.2$ ($C_o = 0.2$). Fig. 2 presents the concentration of CdTe in the solid (HgCdTe) at the crystal-melt interface (C_S) as a function of τ for k_S and k_L. In real time (t), the CdTe concentration (C_S) is dependent on the rate of melting (R) which, in order to be meaningful, must satisfy the stability criteria. At the beginning of melting, the system is at equilibrium [$C_S(z,0) = C_o, C_L(z,0) = C_o/k$], and therefore under conditions of absolute stability. As melting proceeds, the interface stability is affected by out-diffusion and the subsequent formation of the boundary layer in the solid. Thus, while for $C_L(0,z) = C_o/k$ melting can be initiated at any rate, out-diffusion and interface breakdown must be anticipated if the rate exceeds a critical value. If the stability criteria is strictly applied to a steady state melting configuration, the G_S/R ratio required for stability is very high ($\simeq 10^8$ C/sec for $Hg_{0.8}Cd_{0.2}Te$). Such a high value is achieved by either a very high thermal gradient or a very slow rate of interface displacement. Making use of Fig. 2 and applying numerical values for HgCdTe, the present analysis shows that under neither condition will steady state be reached during seeding in Bridgman or Czochralski growth where the seed is back-melted for several millimeters only; the crystal-melt interface temperature during melting must therefore be expected to lie somewhere between the solidus and the liquidus temperatures. Considering the back-melting of an ingot of $Hg_{0.8}Cd_{0.2}$ Te for half an hour at the rate of 3.7×10^{-2} μm/sec (the rate required for absolute stability at steady state if $G_S = 1000^oC/cm$), the value at the end of back-melting (i.e. after half an hour) is 4×10^{-4} and, according to Fig. 2, the concentration in the solid (C_S) will be essentially unchanged at C_o and the interface temperature will remain at about T_S.

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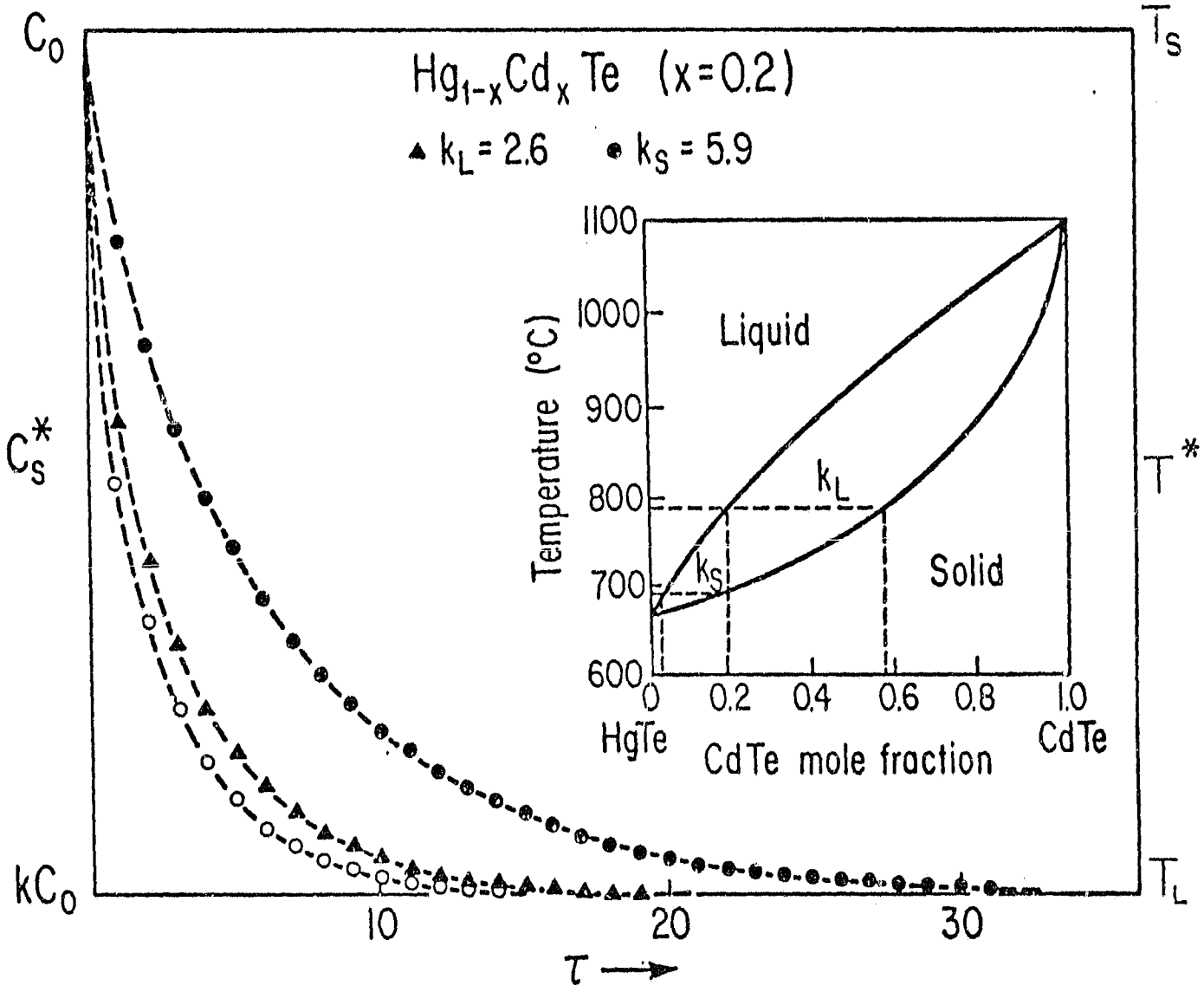

Fig 2: Functional Dependence of C_S^*, the Interface Composition in Solid $Hg_{0.8}Cd_{0.2}Te$ on τ for k_L (▲) and k_S (●). (α is assumed to be 4.7×10^{-5}; to assess the uncertainty associated with the assumed D_S value, the limiting case for α = 1 is also presented.)

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It is noteworthy that for systems with a liquidus-solidus separation smaller in $Hg_{0.8}Cd_{0.2}Te$ but larger than in very dilute systems, the temperature of the interface (T^*) at the end of the backmelting is expected to be somewhere in between T_S and T_L. Its value, at a given time, can be calculated from γ curves of particular systems. The interface temperature is related to the composition at the interface through the relation $T^* = T_m + m_t C_S$, where T_m is the melting temperature of the major constituent (for example, HgTe in $Hg_{0.8}Cd_{0.2}Te$) and m_t is the slope of the straight line joining T_m and the point on the solidus curve corresponding to the concentration C_S on the phase diagram. Therefore, the deviation of the interface temperature from the solidus temperature during transient melting ($\Delta T^* = T^* - T_S$) in dimensional notation is given by:

$$\Delta T^* = m_t C_S - m_{t=0} C_o$$

As C_S^* approaches the value of kC_o, ΔT^* approaches a maximun value for which $T^* = T_L$.

Segregation and Growth Interface Temperature

As a consequence of segregation during transient melting or solidificaiton to growth interface, temperature (T^*) is subject to change and the interface displacement rate (R) varies with time and differs from the mechanical displacement rate of the system (R_{syst}) provided either through the translation of the charge relative to the furnace or through a shift in the imposed thermal gradient. A simple expression for R can be obtained in system with a constant axial thermal gradient ($G = dT/dz$) . R can be broken down into the two components: $R = R_{syst} + R_{int}$, where R_{int} represents the incremental rate due to the change in the interface temperature induced by the change in the

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interface concentration $[(\partial C/\partial t)_{z=0} \neq 0]$ during the transient. At any given time t, the interface temperature is

$$T^*(t) = T_m + mC_S^*(t) \qquad [A.1]$$

and its displacement rate of the interface due to its change in temperature is:

$$R_{int} = \frac{dz}{dt} = \frac{dz}{dT} \cdot \frac{dT}{dt} \qquad [A.2]$$

From [A.1]:

$$\frac{dT}{dt} = m \left.\frac{dC_S}{dt}\right|_{z=0}$$

and

$$\frac{dz}{dT} = \frac{1}{G}$$

Therefore,

$$R_{int} = \frac{m}{G} \cdot \left.\frac{dC_S}{dt}\right|_{z=0} \qquad [A.3]$$

and,

$$R_{int} = R_{syst} \left.\frac{m}{G} \cdot \frac{dC_S}{dt}\right|_{z=0} \qquad [A.4]$$

Equation [A.4] shows that $R = R_{S\ st}$ if steady state is reached $[(dC_S/dt) = 0]$, if $G \to \infty$ or if $m = 0$ (no temperature change with composition).

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4. THE EFFECT OF DIRECT CURRENT ON CRYSTAL GROWTH FROM THE MELT: InSb

Experiments were conducted to investigate the effect of direct current on the growth of doped InSb. The results indicate that the growth rate is controlled on the microscale by the absorption of heat at the crystal/melt interface due to the Peltier effect. This effect is superimposed on longer time variations in growth rate caused by heat input imbalances due to Joule heating in the hot zone. A theoretical framework developed on the basis of conduction controlled heat flow predicts that the Peltier coefficient of InSb in contact with its melt can be calculated from the current induced microscopic growth rate change. The results obtained using this technique are in agreement with the values of the Peltier coefficient calculated (using the Kelvin relationship) from the published Seebeck coefficient. The theoretical framework was further verified by numerically solving the time dependent energy transport equations (with appropriate boundary conditions) using an explicit finite difference technique. The results are in good agreement with the experimentally determined current induced microscopic growth rate changes.

The Effect of Long Duration (20 s) Current Pulses on Crystal Growth

To determine the effect of current over long time periods, direct current pulses of 20 s duration were passed across the liquid/solid interface at 120 s intervals. While application of direct current in the form of short pulses has been shown to enhance the microscopic growth rate (for Peltier cooling), with pulses of long duration the perturbed interface velocity must, with time, relax to the steady state pulling rate as the temperature distribution in the liquid and solid adjust to accomodate the new equilibrium

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energy balance at the interface. Without flow of current, conservation of energy at the crystal/melt interface requires:

$$k_S \left.\frac{dT_S}{dX}\right|_{x=0} - k_L \left.\frac{dT_L}{dX}\right|_{x=0} = \rho \Delta H R$$

During growth with the flow of current:

$$k_S \left.\frac{dT'_S}{dX}\right|_{x=0} - k_L \left.\frac{dT'_L}{dX}\right|_{x=0} = (\rho \Delta H R)' + (\Pi J)$$

where:

Π = Peltier coefficient
J = current density

The primed values of the interfacial temperature gradients indicate that their magnitudes have changed to accomodate the new heat production (absorption) term ΠJ.

Theoretical Framework for Calculating the Peltier Coefficient of InSb (in Contact with its Melt) from Current Induced Layer Thickness

It has previously been shown by Lichtensteiger et al. that application of short duration (1 s) pulses of direct current across the liquid/solid interface of InSb during Czochralski growth caused an instantaneous increase in the microscopic growth rate which remained constant for the duration of the pulse. In addition, during current off growth conditions (3s), the microscopic growth rate also remained constant, but at a reduced magnitude. Their results were reproduced using experimental conditions that were the same as those employed to produce the previously discussed current induced layers: the graphite crucible was used with the temperature control

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thermocouple located at the base of the crucible. The observation of constant growth rate in both current-on and current-off regions was verified for a variety of duty cycles (t_{on}/t_{off}) and current densities. Interface demarcation (5 A, 10 ms duration, 100 ms interval) was superimposed on the current pulses. For values of current density below 25.4 A/cm^2 it was shown that the microscopic growth rate is effectively modulated between two values which remain constant for the duration of a pulse cycle.

It could be shown experimentally and confirmed theoretically, however that when a current pulse (Peltier cooling) is terminated, the liquid/ solid interface is repositioned to a point removed from its equilirium steady state (without current flow). The result is a change in the temperature distributions in the liquid and solid which will influence the net heat balance at the interface and thus affect the microscopic growth rate.

The change in growth rate, dR_o, caused by this change in temperature gradients (dG_S, dG_L) is given by:

$$dR = \frac{k_S dG_S \cdot k_L dG_L}{\rho \Delta H}$$

and is found to be -0.50 μm/s for one second pulses and a pulling rate of 12 μm/s. This effect is beyond the resolving capabilities of the interface demarcation technique as applied here. For a single pulse cycle, the temperature gradients in the vicinity of the crystal/melt interface therefore remain virtually unchanged and it follows that the microscopic growth rate changes observed during current pulsing are the direct result of interface motion accomodating the absorption of heat due to the Peltier effect. The balance of heat at the interface in the absence of direct current is:

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$$k_S G_S - k_L G_L = \rho \Delta H R_1$$

When current is applied, a term πJ, appears on the RHS, accounting for the Peltier effect:

$$k_S G_S - k_L G_L = \rho \Delta H R_2 + \Pi J$$

(R_1 and R_2 are the growth rates during current-off and current-on conditions respectively.) In the previous analysis it was shown that during a single pulse cycle the temperature gradients at the crystal/ melt interface remain virtually unchanged. Therefore, a direct relationship between the absorbed Peltier heat and the difference in microscopic growth rates (current-on vs current-off) is established:

$$\Pi J = \rho \Delta H (R_1 - R_2)$$

Since the current density, J, is a predetermined parameter, it follows that the Peltier coefficient can be directly calculated from the experimentally determined, contiguous values of R_1 and R_s:

$$\Pi = \frac{\rho \Delta H (R_1 = R_2)}{J}$$

The absolute magnitude of the Peltier coefficient, as calculated from this relationship, is directly dependent on the heat of fusion, H. The published values range from 67.7 J/g to 213.4 J/g. Consequently, the heat of fusion of InSb was measured using a Perkin-Elmer DTA 1700 differential thermal analyzer with a Perkin-Elmer System 7/4 thermal analysis controller. The heat of fusion was measured to be 238.1 J/g (13.48 kcal/mole).

The Peltier coefficient was calculated for contiguous pulse sequences. The results are presented in Table I.

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TABLE I

LISTING OF EXPERIMENTALLY DETERMINED
VALUES OF THE PELTIER COEFFICIENT

Sample	t_{ON}/t_{OFF}	A	$J(A/cm^2)$	$\Pi_p(V)$
I-38a	2/6	18	16.8	-0.0822
I-43	2/6	20	13.0	-0.0844
I-64-10	1/3	10	9.8	-0.0968
I-64-20	"	20	19.7	-0.0927
I-64-30	"	30	29.6	-0.0989
I-64-40	"	40	39.7	-0.0871
I-68-10	20/100	10	9.5	-0.1064
I-68-20	"	20	17.3	-0.0960
I-69-10	20/100	-10	-12.2	-0.1134
I-69-20	"	-20	-25.1	Remelt

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C. ADAPTIVE MATERIALS PROCESSING

PROJECT C1: ADAPTIVE CONTROL OF WELDING PROCESSES

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RESEARCH ABSTRACT

Growth of automated welding is limited at present by applicable sensor technologies. This project involves study of new sensors for both arc welding and resistance spot welding processes. For arc welding, the arc itself is used as the sensor. Minor changes in both composition and geometry of the plasma result in fluctuations in the arc voltage. These fluctuations can be studied at frequencies from 50 to 20,000 Hz by recording the signal on audio equipment and later digitizing and analyzing the results with a computer. While the process as currently employed is an off-line system, development of an on-line process controller would be possible once the optimum analysis technique is developed. For resistance spot welding, it has been shown that the dynamic resistance of the weld joint can be correlated to growth of the fusion zone. Previous investigators have used similar techniques, but they have not analyzed the structure of the dynamic resistance curve in detail nor have they correlated the results with actual weld geometry. Studies during the past year indicate that this technique is not as useful for projection welds as for spot welds.

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RESEARCH SUMMARY

1. Arc Welding

This project was initiated during the past year. As a result much of the effort has been devoted to acquiring, setting up, and developing software for the new computer which is being used for signal analysis of the weld noise voltage. The system has both A/D and D/A converters capable of operation to 10 kHz. Faster sampling rates should be possible with further developments in the system software. Most of the sampling and graphing programs are now operational.

Isolator and filtering circuits have been developed for interfacing the arc with the audio recorder and the computer. Work has begun on circuits which will allow direct recording of the arc to the computer, thus eliminating the need for the audio recorder.

Much of the noise resulting from the welding arc is due to voltage fluctuations in the welding power supply. These fluctuations are uniform and reproducible, hence it should be possible to eliminate the power supply noise thereby improving the signal to noise ratio of the fluctuations resulting from the arc. A Thevenin equivalent circuit for a commercial welding power supply was developed and an attempt was made to incorporate this into a Kalman filter. The results were not encouraging so subtraction of signals using FFT techniques is now planned.

During the past year it has been shown that welding over disturbances as small as 1.5 mm will produce measurable differences in the welding noise voltage. The optimum method for analysis of these fluctuations remains to be studied. Following this, the sensitivity, selectivity, and reproducibility of these disturbances will be investigated.

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This work is being performed in conjunction with an Office of Naval Research study of compositional changes in welding arc plasmas. That program has provided a transistorized welding power supply which will be used in future studies. This power supply will introduce much less extraneous noise into the arc voltage which should aid significantly in analysis of the data.

2. Resistance Spot Welding

During the past year the resistance spot welding machine has been instrumented with equipment for monitoring dynamic resistance, dynamic force, and electrode displacement. Acoustic emission equipment will be acquired in the near future. All of this information is being or will be used to study the mechanics of weld nugget formation. Studies on projection welds during the past year suggest that dynamic displacement may be the most useful technique for monitoring projection welds. The equipment is being modified for studies in the coming year of spot welding of galvanized steels.

PUBLICATIONS

1. E. Elias and T. W. Eagar, "Signal Analysis of Voltage Noise in Welding Arcs," to be published in Proc. of ASM Conference on Welding Consumables and Process Developments, Peoria, IL, September 1981.
2. J. G. Kaiser and T. W. Eagar, "The Effect of Electrical Resistance on Nugget Formation During Spot Welding," submitted to the Weld. J.

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IV. MATERIALS PROCESSING RESEARCH, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

This section summarizes ongoing Materials Processing research at Massachusetts Institute of Technology being conducted in a variety of Departments, Laboratories, and Centers. The research involves a total of 54 faculty members, 76 staff, 15 graduate students, and 57 undergraduates. The Table of Contents at the beginning of this report lists the projects and the page on which the research abstract will be found.

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A. RAPID SOLIDIFICATION PROCESSING

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SUMMARY

Rapid solidification continues to comprise a major thrust area of Materials faculty and staff at MIT. Work is proceeding on crystalline and non-crystalline metals, and on polymers. Work is planned on ceramics. Research includes fundamental studies on solidification mechanism and resulting structure, innovative processing techniques, properties and applications.

Professor Grant and co-workers continue their broad program focused on alloys which offer high strength at elevated temperatures, and on the processing methods necessary to achieve these goals. Professor Cohen and co-workers are concentrating on structure and structureproperty relations in ferrous alloys. Professor Vander Sande, interacting with most other faculty working in this area, continues his work on structure. Professor Latanision is working on corrosion

related aspects and Professor Yurek is studying the high-temperature oxidation resistance of fine-grained alloys. Professor Flemings and co-workers are concentrating on relation of solidification theory to structures produced, on innovative processes for rapid solidification, and on solidification at high undercoolings. Professor McGarry has initiated studies on rapid solidification of polymeric materials. Some current research activities are given below.

1. STRUCTURE AND PROPERTY CONTROL BY MEANS OF RAPID SOLIDIFICATION TECHNOLOGY: GLASSY AND MICROCRYSTALLINE METASTABLE ALLOYS

A rather broad range of programs constitutes the activities of this group. Emphasis remains focused on alloys which offer high strength at elevated temperatures and the processing methods necessary to achieve such goals. The application and study of rapid solidification (RS) to produce new classes of alloys and to achieve superior structures and properties are broadly applied to both microcrystalline and glassy alloys.

Numerous microcrystalline alloy systems have been studied to date, including Al, Cu, Fe, stainless steels, Ni-base superalloys and Co-base superalloys. Glassy alloys are based on transition metal-transition metal combinations and on transition metal-nonnetal alloys. Phenomena of interest include strength, plasticity, toughness, corrosion resistance, superplasticity, fatigue improvements, irradiation damage resistance (fusion reactors), etc., etc.

Brief paragraphs follow which attempt to attach a flavor to the specific programs underway.

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Glass Formation, Alloying Effects on the Glass Transition and Crystallization Temperature of Ni-Nb Alloys

Alloys in the 60-40 to 40-60 atom pct. range for Ni and Nb were carefully studied for embrittlement on heating and on crystallization, with measurement of attendant properties. Major alloying studies were undertaken to determine causes of increases or decreases in Tg, Tx and on toughness. Ease of glass formation through alloying and the effect of alloying on mechanical behavior were of particular interest.

Stabilization and Strengthening of $Pd_{80}Si_{20}$ Metallic Glasses

The effect of composition on thermal and mechanical stability was studied by adding B and Zr to $Pd_{80}Si_{20}$ singly and in combination. Combined additions of B + Zr of 3 and 1.5 at. pct., respectively, result in a stable glassy structure with an increased T_g of 73 K. Additionally, high-temperature strength was significantly improved.

Deformation Induced Dilatancies in Metallic Glasses at Low Temperatures

As a means of studying the deformation and fracture of glassy alloys, the compression mode was chosen since failure in the tension mode leads to infinitesimally small strain values. Using a PdSiCu alloy, it was possible to produce 2 mm diameter fully glassy rods which were ideal for miniature compression specimens. Deformation values up to almost 75% were readily attained, without cracking, and with very large numbers of shear bands. The fine structures of these highly deformed specimens are undergoing further study. Large changes in free volume on crystallization have been observed as a function of the amount of prior deformation.

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Production and Study of Superfine Crystalline Alloys Produced by Conversion of Selected Glassy Alloys

The attainment of grain sizes as fine as 100 to 500 A is demonstrated from prior glassy (homogeneous) alloys. Resultant grain sizes are very uniform. The aim is to produce ductile, tough, strong alloys which may also have other attractive characteristics such as corrosion resistance, for example. The alloys are of the Fe-Cr-Ni-Mo-B type with low boron content.

The Structure and Properties of RS Lithium Modified 2024 Aluminum Alloys

Lithium contents up to 3 percent are readily possible in RS atomized alloys and result in fine-grained (2 to 3 microns), high specific modulus alloys. Studies include measurements of tensile properties, fatigue behavior, fracture toughness, crack propagation rates, etc. The ratio of Cu:Li is a major alloying variable.

The Structure and Properties of RS 2618 Aluminum Alloy

This alloy, one of the best high-temperature ingot alloys, is being studied as RS atomized and hot consolidated material, and again after RS atomization plus attrition grinding to fine flakes to produce an oxide-dispersed 2618 product, which is expected to have significantly improved strength properties from 150 to 250°C.

The Structure and Properties of RS X2020

The X2020 type of alloy (Al-Cu-Mn-Li) is recognized as having particularly attractive properties, such as a high specific modulus and high specific strength. This continuing study attempts to optimize such properties while

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maintaining or improving such other features as notch toughness, notch fatigue behavior, etc. The Cu:Li ratio is a major variable since this ratio controls the amount and type of ternary intermetallic compounds formed.

The Structure and Properties of RS Al-Mg-Li Alloys

Whereas the Al-Mg-Li alloys have not shown comparable strength values to those of RS X2020 (Al-Cu-Li), the potential for major gains in specific strength and modulus favors the low specific gravity Al-Mg-Li alloys. Detailed studies of structure-property relationships are underway with special emphasis on notched strength values and fracture toughness behavior.

The Structure and Property Relationships in X7091, 705 with Zr + Ni, and Other Alloys

Maximum strength values are synonymous with the 7XXX alloys. Major additions of transition metals have been shown to be effective in RS 7XXX alloys by changing the chemistry of the phases formed and their size and distribution. In particular, additions of Fe, Ni, Ti, Zr, Mn, Co in various combinations and amounts have had beneficial effects especially on strength, with evidence that toughness and fatigue performance can be maintained at high levels. A number of these alloying combinations is being studied.

High-Strength, High-Temperature, High-Conductivity Copper-Base Alloys

Three distinct areas are being investigated:

A. MZC Type Alloys (Cu-Mg-Zr-Cr). These alloys with excellent strength at 20°C and excellent strength at 400°C in creep rupture are being examined as conven-

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tional ingot product, RS atomized powders, and RS atomized and attrition milled flakes. The latter two conditions represent oxide-dispersed alloys at two oxide contents. Thermal conductivity values are near 80 percent of those of pure copper. The presence of small amounts of ZrO_2 has been observed to prevent softening (at 20°C) after exposures as high as 1000°C for 1 hour.

B. Cu-Ni-Ti Alloys. These alloys in ingot form are stronger than the MZC alloy, but have only about 60 percent of the conductivity of pure Cu; they are also a bit weaker in creep at 400°C. As RS alloys, both in powder form and as fine attrited flakes, they have exhibited unusually attractive strength and ductility at 20°C and outstanding creep-rupture properties at 400°C. Studies of thermomechanically processed structures are continuing in a search for further improvements. These alloys with small amounts of TiO_2 due to particulate surface oxidation do not soften at 20°C even after one hour at 1000°C.

C. The Solution Treating, Ageing and Overageing Behavior of MZC and Cu-Ni-Ti Alloys Produced by Rapid Solidification. These copper alloys undergo complex ageing behavior patterns. The MZC alloy, with precipitates of both Cu_3Zr and Cr, presents additional structural complication when ZrO_2 and Cr_2O_3 are also formed during powder and flake processing. The Cu-Ni-Ti alloys, which harden unusually during quenching from the solution temperature, are further complicated when prepared from RS powders and attrited flake materials which produce TiO_2. The presence of the fine oxide dispersions serves to pin dislocations and thus to retain the energy of cold work due to extrusion. The structures are thus fully stable up to 1000°C, do not show re-crystallization and maintain strength in spite of such high temperature exposure.

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The Development of Cu-10Ni- and Cu-30Ni-Base Alloys by Tertiary and Quarternary Alloying Additions

These alloys, produced by rapid solidification (ultrasonic gas atomization), are being studied to establish the role of alloying elements such as Fe, Cr, Ti, Mn and others on strength, toughness, salt water corrosion, etc. A number of the alloying elements enhance salt water corrosion as long as they do not form coarse excess phases. The RS approach is being used to enhance the control of structure. First results show significant increases in strength and ductility over current commercial ingot-based alloys. Thermomechanical treatments and corrosion studies are just getting under way.

The Structure and Properties of Highly Alloyed Nickel-Base Superalloys Prepared from RS Atomized Powders

The aim here is to determine if fully alloyed, superfine RS powders can be suitably attrited to near-micron thick flakes to provide, for example, 1 to 2 vol pct of Al_2O_3 in a complex alloy such as IN-100. Additionally, fully alloyed, RS IN-100 of very fine powder size is mechanically blended with fine yttria powders to attempt to produce a homogeneous oxide dispersion. The application, broadly, of O.D. type alloys is restricted by extreme costs and inability to readily reproduce the best reported properties of such alloys made by more conventional processing methods.

The Superplastic Behavior of Duplex Ferrite-Austenite Stainless Steels

This study has as its aims the determination of the optimum content of ferrite to austenite on superplastic deformation, on strength of the final product, on corrosion resistance and other properties. The role of composition is equally

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important since the various ratios of ferrite to austenite can be achieved by many alloying combinations. The limited solubility of the ferrite for carbon and nitrogen will permit precipitation of carbides and nitrides in the ferrite. The RS process guarantees a fine grain size (3 to 20 μm) in the extruded product. Thus a broad variety of structures and structural characteristics will be studied for their influence on superplasticity.

The Initiation and Growth of Intercrystalline Cracks in δ-δ' Nickel-Base Superalloys, in δ-Carbide Cobalt-Base Superalloys, and in δ-Oxide Nickel-Base Oxide-Dispersed Alloys

Following the characterization of crack initiation and early growth in the creep mode, over a range of temperatures and stresses, samples will be prepared for fatigue testing as pre-cracked specimens to determine the further growth modes of cracks under a wide range of conditions of temperature, fatigue cycle frequency, hold times, etc. The aim is to determine which of these three basic alloy systems is better suited for further alloy development for service from 650 to 1200°C.

First-Wall Fusion Reactor Materials Prepared by RS Technology

The extreme demands on materials to operate as first-wall materials with high dpa, helium generation and precipitation, radiation creep, etc., call for unusually stable, strong alloys. RS techniques can produce fine-grained, homogeneous alloys with selected second-phase precipitates or dispersions uniformly distributed in the matrix, and of controlled particle size and shape. Extensive alloying, far beyond that possible through ingot technology, has already been denonstrated. Selected experimental alloys suitable

for fission reactor exposure to simulate a fusion reactor is another important issue. Using RS technology, a range of type 316 stainless steels with increasing TiC content have been prepared and are in test; type 316 SS with a fine dispersion of Al_2O_3 has also been prepared; ferritic Fe-BeO alloys, and selected copper-base alloys, have also been prepared and are undergoing neutron irradiation and heavy ion irradiation. Further plans call for study of several RS ferritic alloys with and without oxide or carbide dispersions.

New Magnetic Metallic Glasses with Reduced Metalloid Content

A series of new magnetic metallic glassy alloys of the types $Co_{80}Nb_{14}B_6$, $Co_{84}Nb_{10}B_6$ and $Fe_{81}Nb_5B_{14}$ is being studied for magnetic properties and stability against crystallization. These alloys are observed to exhibit a larger correlation length (approx. 2.0Å) which is shorter than is typically observed in "late transition$_{80}$-metalloid$_{20}$" glasses containing more than one transition metal species (approx. 2.3 to 2.5Å). the magnetic behavior of these alloys will also be studied in the crystalline form, it is hoped as a ductile, formable shape.

Magnetic Properties of Some New Co-Nb-B Metallic Glasses

These new glasses show attractive soft ferromagnetic properties as do the more common transition metal/metalloid glasses, while retaining ease of fabrication and good thermal stability despite the significantly reduced metalloid content. One of the patterns observed is that the presence of boron in the nominally Co_{85}-Nb_{15} alloy increases the moment reduction due to Nb. Extensive studies of the magnetic moments and hybridization in Co-Nb alloys are continuing.

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Publications:

1. N.J. Grant, S. Kang and W. Wang, "The Structure and Properties of Rapidly Solidified 2000 Series Al-Li Alloys," Eds. T.H. Sanders, Jr. and E.A. Starke, Jr., Conference Proceedings, The Met. Soc. of AIME, May 1981.
2. J. Megusar and N.J. Grant, "Stabilization and Strengthening of $Pd_{80}Si_{20}$ Metallic Glass," Mats. Sci. and Eng. 49, No. 3 (1981) 275.
3. J. Megusar, L. Arnberg, J.B. Vander Sande and N.J. Grant, "Optimization of Structure and Properties of Path A Prime Candidate Alloy (PCA) by Rapid Solidification," Jour. Nuclear Materials, Vol. 99, Nos. 2 & 3, September 1981.
4. J.P. Clark, N.J. Grant and T.B. King, "The Market for Manganese Derived from Deepsea Nodules," Natural Resources Forum, 5, (1981) 249.
5. J. Megusar, A.S. Argon and N.J. Grant, "Deformation Induced Dilatations in Metallic Glasses at Low Temperatures," presented at 4th International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981.

6. N.J. Grant, J. Megusar, and L. Arnberg, "Structure and Properties of Rapidly Solidified Austenitic Stainless Steels for the Fusion Reactor Environment," presented at 4th International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981.
7. L. Arnberg, J. Megusar, D. Imeson, H.J. Frost, J.B. Vander Sande, O.K. Harling, and N.J. Grant, "The Microstructure of Neutron Irradiated Rapidly Solidified Path A Prime Candidate Alloys," presented at Materials Research Society meeting on Rapid Solidification, November 1981.

2. RAPID SOLIDIFICATION PROCESSING OF IRON-BASE ALLOYS

The Office of Naval Research (ONR) has been supporting a research effort to determine the relationships between metallurgical structure and properties in rapid solidification processed iron-base alloys. This research program involves three faculty, one senior staff member, and four students.

The research work being undertaken in this program can be divided into four parts: microstructural characterization of rapidly solidified (RS) steels, grain growth retardation in RS steels, fracture toughness of RS steels, and decomposition of Fe-base amorphous alloys. Each of these areas is briefly described below.

Microstructural Characterization of Rapidly Solidified Steels

In an effort to obtain a qualitative assessment of the fundamental solidification variables associated with solidification at rapid solidification rates, two austenitic steels have been observed in the form of powders and after

consolidation. The two steels, a high-sulfur, 303 stainless type and a high-phosphorous steel (Fe-Cr-Ni-P) have been prepared by the centrifugal atomization technique pioneered by Pratt and Whitney Aircraft, West Palm Beach, Florida.

Scanning transmission electron microscopy (STEM) has been used for microstructural and microchemical analysis of these steels. Both fcc and bcc are found to be primary solidification phases in the as-solidified powder, where the smaller powder particles (<70μ dia.) tend to be bcc. In the high-sulfur steel, cellular solidification structures with sulfide precipitates (100 to 200 nm dia.) at the cell walls are observed in both fcc and bcc particles. The bcc structure, however, has many small sulfide precipitates (10 to 20 mm dia.) in the cell interior with few larger sulfide precipitates at the cell walls. The small precipitates, observed only in the bcc structures, form on cooling from a supersaturated solid solution that results from reduced solute partitioning during solidification. Partitioning of chromium and nickel is minimal in these cellular structures. A noncellular bcc structure is also observed with small sulfide precipitates throughout the entire structure. This non-cellular bcc structure results from smooth-front massive solidification. Analysis of the nucleation process for solidification indicates that a transition from fcc nucleation to bcc nucleation occurs with increasing wetting angle in heterogeneous nucleation. Thus bcc should nucleate in the smaller droplets of a liquid dispersion where catalytic surfaces of low potency (large wetting angle) tend to be the only heterogeneous nucleants available.

After hot consolidation, the high-sulfur steel contains a uniform dispersion of fine sulfides with an average sulfide size two to three orders of magnitude finer than conventionally-processed material.

In addition to the fcc and bcc primary solidification phases, rapid solidification of the high-phosphorus steel produces a fine cellular phase at the cell walls. The amorphous phase, which is stable to ~500°C, is enriched in phosphorus and chromium, but contains significantly less phosphorus than conventional glass-forming alloys. Hot consolidation of powders produces a chemically-uniform metastable austenite which can be effectively precipitation hardened by phospho-carbides.

Grain Growth in Rapidly Solidified Steels

Rapidly solidifed steels have been found to exhibit an unusual resistance to grain coarsening at high temperatures. Comparison of conventionally processed and rapidly solidified 9Ni-4Co and 2Mo steels revealed that the rapidly solidified material retains a grain size of ~20 μm at 1200°C, where conventionally processed material coarsens to several hundred microns. Thus far the only possible boundary pinning nechanism suggested by transmission and scanning transmission electron microscopy analysis is a fine dispersion of inclusions, principally MnS. Analysis of the grain coarsening behavior in terms of the theory of grain boundary pinning and particle coarsening indicates that the observed inclusion dispersions can account for the grain coarsening resistance. A thermodynamic survey of potential stable dispersed phases, based on both available experimental information and estimated subregular solution interaction parameters for austenitic iron, has identified TiN and rare-earth sulfides as particularly promising for alloy development via rapid solidificaton. Application of TiN dispersions is being examined in rapidly solidified microalloyed steels.

Fracture Toughness of Rapidly Solidified Steels

The use of high austenitizing temperatures is known to increase the sharp crack toughness (K_{IC}) of some steels, attributed primarily to dissolution of void initiating particles; simultaneously, the blunt notch toughness (C_V) and ductility are found to decrease due to excessive grain coarsening. The high temperature grain coarsening resistance of the rapidly solidified steels described above may allow improvement of K_{IC} without loss of C_V energy and ductility. Preliminary toughness measurements on 9Ni4C°-0.6C and 4M°-0.3C steels indicate that the KIC of rapidly solidified material is equal to or superior to that of conventionally processed material (after high austenitizing treatment). Furture efforts will focus on 4340, 300M, and HP310 steels where the benefits of high austenitizing treatments are well established. Both K_{IC} and Charpy C_V energy will be studied as a function of austenitizing treatment. The behavior of matrix tool steels (based on M-2 and M-50 matrix compositions) is also being investigated.

Decomposition of Fe-Base Amorphous Alloys

The prospects for using the glassy phase of materials as the starting point for achieving (by thermomechanical treatment) technically advantageous phases and phase-morphologies which cannot be attained otherwise have provided the motivation for this work. Research has been focused on Fe-based alloys, especially Fe-B alloys, which are of intrinsic interest in the glassy state because of their unique magnetic properties.

The as-quenched Fe-B glass is found to possess tetragonal Fe_3B -type short range order by Mossbauer Spectroscopy. Stress relaxation in the glass has been studied by the changes of stress-induced magnetic anisotropy visible in the

Mossbauer spectra. The anisotropy is affected by thermal relaxation and crystallization.

The overall transformation kinetics have been studied by Differential Scanning Calorimetry (DSC). There are two crystallization steps involved in glasses with boron concentration less than 17%, while only one crystallization step is apparent in the glasses with boron concentration more than 17%. The primary crystallization of α- Fe in a $Fe_{84.5}$ $B_{15.5}$ glass was also studied by Mossbauer Spectroscopy and Transmission Electron Microscopy (TEM). The growth of isolated Fe_3B particles was studied in-situ on the hot stage of a TEM in the $Fe_{81}B_{19}$ glass. In low boron glasses, the crystallization of α - Fe is characterized by a diffusion-controlled mechanism (activation energy ~2 ev/atm) with a limited particle size and decreasing nucleation rate. A transformation model with decreasing nucleation rate and limited particle size has been developed. The polymorphous crystallization of Fe_3B in low boron alloys is controlled by an interfacial mechanism. In high boron alloys the process is diffusion controlled with near simultaneous crystallization of Fe_3B and α- Fe.

From analysis of diffuse features in the electron diffraction patterns of Fe_3B crystallized from the glass, a defect structure is proposed, which is comprised of rod shaped domains of ε1 structure in a matrix of ε. While only the tetragonal forms of Fe_3B are obtained by crystallization from the glassy state, the orthorhombic form crystallizes from the melt.

α - Fe crystallized from the glass exhibits a smaller lattice parameter than pure α - Fe and, in the Mossbauer spectrum, evidence of a perturbed Fe- atom site. These effects are attributed to the metastable extension of solid-solubility of boron in α - Fe, reaching about 6% boron (in the $Fe_{84.5}$ $B_{15.5}$ alloy).

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Sponsors: AMAX Foundation, Bethlehem Steel Corporation, Office of Naval Research

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Publications:

1. M. Cohen, B.H. Kear, and R. Mehrabian, "Rapid Solidification Processing - An Outlook," Proceedings on Rapid Solidification Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p.1.
2. K.S. Tan, T. Wahl, and R. Kaplow, "Monitoring Metastable Phases and Grain Structures Derived from Glassy Alloys," Proceedings on Rapid Solidif .ation Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p.112.
3. M. Suga, J.L. Goss, G.B. Olson, and J.B. Vander Sande, "Austenitic Grain Crowth Characteristics in Rapidly Solidified Martensitic Steels," Proceedings on Rapid Solidification Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p. 364.
4. T.F. Kelly and J.B. Vander Sande, "A STEM Analysis of Two Rapidly Solidified Stainless Steels," Proceedings on Rapid Solidification Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p. 100.

N82 27395

3. IRRADIATION EFFECTS IN RAPIDLY AND CONVENTIONALLY SOLIDIFIED ALLOYS

Phase Stability in Rapidly Solidified Ni-Nb under Ni Ion Irradiation

Two alloy compositions in the Ni-Nb system ($Ni_{60}Nb_{40}$ and $Ni_{85}Nb_{15}$) were produced by rapidly quenching from the melt with the piston-anvil technique. The $Ni_{60}Nb_{40}$ samples (originally amorphous) were transformed to a metastable, partially crystalline state by heat treatment in a differential scanning calorimeter. The $Ni_{85}Nb_{15}$ samples were fully crystalline, with the majority of the grains composed of collections of primary dendrite arms. Samples of both compositions were irradiated with 4 MeV Ni^{++} ions in a Van de Graaff accelerator at temperatures from .48 to .62 T_L for $Ni_{60}Nb_{40}$ (698 to 898 K) and at two dose levels: 2 and 20 displacements per atom.

The resulting irradiation induced microstructures were examined by transmission electron microscopy and compared with thermally aged samples. Under thermal aging conditions, the $Ni_{60}Nb_{40}$ samples evolved towards the equilibrium twophase microstructure (NiNb and Ni_3Nb). Ni ion irradiation at 698 and 708 K produced a marked change in crystallite morphology, giving a greatly increased aspect ratio of the Ni_3Nb crystallites. The thermal evolution was arrested by ion irradiation in the temperature range studied, possibly by inhibiting the nucleation of the NiNb phase. No irradiation-induced voids were observed for this composition.

Thermal aging of $Ni_{85}Nb_{15}$ at up to 1 hour at 898 K produced no sifnificant changes in the microstructure. Aging for longer ties or at higher temperatures produced a complicated precipitate structure composed of large plate (rod) -like

Ni_3Nb precipitates in a Ni matrix. The ion irradiated $Ni_{85}Nb_{15}$ samples showed an increase in stacking fault and dislocation density, breakup of the grains into smaller collections of dendrite cells, dissolution and redistribution of the ordered Ni_3Nb precipitates and formation of oriented dislocation tangles in the dendrite cell walls. Ion irradiation under the above conditions was found to drive the microstructure along a different path than thermal evolution.

Feasibility of Studies of Ion Irradiation-Induced Phase Stability Changes in Fe-Ni-C Alloys

Neutron and ion irradiation experiments have shown that liquid metal fast breeder reactor and fusion reactor irradiations can be expected to produce changes in the phase stability of candidate alloys. The focus of this research is on the contribution of the chemical vacancy effect to phase stability. Excess vacancies are expected to contribute to the thermodynamic driving force for precipitation primarily when the microcluster:matrix interface is partially or wholly disordered and able to furnish a vacancy sink and when the atomic volume of the precipitate is larger than the atomic volume of the matrix. The high vacancy supersaturations produced by irradiation may provide a sufficient thermodynamic driving force to induce precipitation at alloy compositions and temperatures at which a single phase is normally present. We are presently investigating this effect in Fe-32 wt % Ni-C alloys (0.03, 0.1, 0.3 wt % C) by irradiation of transmission electron microscopy (TEM) disks with high energy Ni ions.

These Fe-Ni-C compositions were chosen for several reasons. First, for alloys containing 32 wt% Ni the martensite start temperature is approximately -100°C even at very low C contents and thus martensite formation (which might deform the

TEM disk surfaces, making the location of the narrow damage region within the disk difficult), will be suppressed. Second, austenitic steels are of practical interest for radiation environment applications and an Fe-32 wt% Ni-C alloy will remain austenitic at the temperatures of interest to this project. Third, in Fe-Ni-C alloys possible precipitates include graphite and $(Fe,Ni)_3C$ whose nucleation rates should be considerably enhanced by the excess vacancy concentration due to irradiation.

Preliminary calculations have shown that at 500°C a vacancy supersaturation of $1x10^{5}$ may be obtained with a displacement rate of $1x10^{-3}s^{-1}$. Further nucleation rate calculations indicate that the thermodynamic chemical vacancy driving force under heavy ion irradiation conditions may provide a sufficient driving force for nucleation in the single phase austenitic region of the Fe-Ni-C phase diagram.

Sponsors: National Science Foundation through CMSE, National Science Foundation

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4. RAPID RATE SOLIDIFICATION PROCESSING

These programs are on (1) development and application of solidification theory to rapid solidification and solidification at high undercoolings, (2) experimental studies on structures obtained by rapid solidification, and relation to theory, and (3) development of innovative processes for producing rapidly solidified materials.

The research is sponsored by National Aeronautics and Space Administration, National Science Foundation, and Army Materials and Mechanics Research Center.

Rapid Solidification of Binary Alloys

Simple binary alloys are being rapidly solidified by splat cooling, ribbon quenching, and laser or electron beam surface melting. Cooling rates and interface growth velocities are calculated and structures produced related to solidification theory. As example, the amount of residual second phase is measured in rapidly solidified aluminum-copper alloys, using the SEM and quantitative metallography; also by using X-ray methods. Composition profiles in other binary alloys are measured using STEM. Results are compared to the developing theories of solidification of rapidly solidified alloys.

Undercooling and Rapid Solidification

One Part of this study comprises dispersion of droplets of molten metal alloys in fluxes and slag to obtain large degrees of undercooling following the methods of Turnbull and Perepezko. Methods are being studied of combining the large undercoolings obtained with rapid solidification. Structures are examined by electron microscopy and related to solidification theory. Work to date is on both low melting point alloys and on high temperature iron and nickel base alloys. A second part of the study involves levitation melted samples which are undercooled by varying and controlled amounts in inert gas, or in a surrounding fluid slag. The levitation work is being conducted on nickel base alloys.

Sponsors: National Science Foundation, National Aeronautics and Space Administration, Army Materials and Mechanics Research Center

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Publications:

1. M.C. Flemings, "Segregation and Structure in Rapidly Solidified Cast Metals," Metallurgical Treatises, Co-editors, J.K. Tien and J.F. Elliott, Metallurgical Society of AIME, 1981.
2. L.J. Masur and M.C. Flemings, "Solute Redistribution in Rapidly Solidified Al-Cu Alloys," Presented at 4th International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981.
3. Y. Shiohara, M.G. Chu, D.G. MacIsaac and M.C. Flemings, "Solidification Mechanism of Highly Undercooled Metal Alloys," presented at Materials Research Society Meeting on Rapid Solidification, November 1981.

5. OXIDATION AND CHEMICAL STABILITY OF RAPIDLY SOLIDIFIED MATERIALS

A broad range of programs are underway in the corrosion laboratory on corrosion resistance, hydrogen embrittlement, chemical stability, and oxidation behavior of rapidly solidified crystalline and non-crystalline materials.

Corrosion Resistance of Microcrystalline Fe-Base Alloys

In some instances microcrystalline alloys produced by rapid quenching are found to have superior corrosion resistance when compared to otherwise equivalent wrought or cast alloys of the same composition. During the past year we have extended our study of microcrystalline stainless steels having grain diameters ranging from 2 (microcrystalline) to 100 μm (conventional wrought material). Alloys, produced with the aid of Professor N.J. Grant, were either fully austenitic or of an austenitic/ferritic duplex microstructure. The microcrystalline alloys are found to be consistently more resistant to localized corrosion in acid

chloride environments than their wrought counterparts. Metallographic examination indicates that pitting initiates more uniformly on microcrystalline surfaces, but pits do not propagate. We believe that the high degree of chemical homogeneity characteristic of the microcrystalline alloys, which resulted from rapid solidification, is the principal reason for their resistance to localized corrosion.

Hydrogen Permeation and Embrittlement in Metallic Glasses

Metallic glasses are considered to represent a good structural and compositional analog of grain boundaries in polycrystalline metals and alloys. Structurally, grain boundaries and glassy alloys may both be modeled atomically in terms of the packing of polyhedral units. Likewise, transition metal-metalloid type glasses are similar in composition to solute segregated grain boundaries. During the past year we have continued our examination, by means of electrolytic hydrogen permeation experiments, of the absorption and transport of hydrogen in $Ni_{81}P_{19}$ and $NiSi_{4.5}B_{2.8}$ glasses. These glasses approximate grain boundaries in polycrystalline nickel and nickel-base alloys (Incenel 600, Hastelloy C-276, for example) in which P segregation has been observed by Auger electron spectroscopy through the use of the Central Surface Analytical Facility in CMSE. We had observed that such glasses absorb considerably more hydrogen than is typical of bulk polycrystalline material because, we believe, of the effect of metalloids such as P in stimulating hydrogen absorption. More recent work shows evidence of hydrogen trapping in these glasses when the charging overpotential exceeds a critical value.

Chemical Stability of Metallic Glasses

Glassy metals have remarkable mechanical, magnetic and electric properties, and, accordingly, great potential

commercial utility. Without chemical stability in the environments to which these alloys may be exposed while in service, their unusual properties may not, however, be appreciated. Some metallic glasses are remarkably inert chemically. The objective of this program is to examine the corrosion resistance of such alloys and to develop a fundamental basis for understanding this behavior. In particular, studies are underway to evaluate the role of structure (crystalline vs. glassy), homogeneity, and alloy composition (the large concentration of metalloids in some inert glasses, the role of film forming alloy additions, etc.) on the kinetics of anodic and cathodic reactions on a variety of glassy surfaces. During the past year we have examined film growth kinetics on Fe-Cr-Ni-P-B and Fe-Ni-P-B glassy alloys by means of ellipsometry. Likewise, the composition and valence states of the elements present in thin passive films have been characterized by means of Auger electron spectroscopy and ESCA. We have observed that P is present in the passive films. This is in contradiction to earlier work in Japan which suggests that P stimulates initial reactivity of the surface and subsequent formation of a protective film but is not itself incorporated into the film. At any rate, matters appear rather complex and our current effort is oriented toward separating the effects of metalloid elements, such as P, from the influence of film formers, such as Cr, with regard to passivation and film growth kinetics. Work is in progress to examine resistance to localized corrosion and stress corrosion cracking.

A Study of the Relationship Between the Microstructure and Chemical Stability of Rapidly Quenched Iron Base Alloys

The principal objective of this research is to examine the possibility that through rapid quenching technology and subsequent microstructural manipulation, microcrystalline iron-base alloys with improved corrosion resistance might be

developed. The alloys of interest at this stage include the Fe-Ti and Fe-Ti-P systems. Research is just underway.

The Oxidation Behavior of Fine-Grained Rapidly Solidified Iron-Base Alloys

This program, which began on 1 September 1981, is directed to determining the oxidation behavior of very fine-grained alloys produced by compaction and heat treatment of rapidly solidified alloys. The rapidly solidified alloys will be made by both melt spinning and gas atomization. The advantages and disadvantages of these two techniques will be evaluated relative to the structure and the properties of the compacted alloy. Compaction will be accomplished by hot extrusion. The alloy systems to be investigated will be based on Fe-Cr-Al, with and without additions of rare-earth elements (e.g., Y) and with and without dispersions of very fine (<0.5 μm) nonmetallic phases (e.g., TiC, AlN, etc.)

Sponsors: Bethlehem Steel Corporation, National Science Foundation (DMR), National Science Foundation (MRL Program at MIT)

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Publications:

1. R.M. Latanision and R. Courtel, Eds., Advances in the Mechanics and Physics of Surfaces, Vol. 1, Harwood Academic Press, N.Y., 1981.
2. S. W. Smith, Jr. and R. M. Latanision, "The Redistribution of Cathodic Activity on an Aluminum Surface in Seawater upon the Introduction of Copper Ions", CORROSION 81., NACE, Houston (1981).
3. G. S. Was and R. M. Latanision, "Synergistic Effects of Thermal Treatment and Cathodic Polarization on the

Fatigue Crack Growth Behavior of Inconnel 600", Proc. 8th Int'l. Congress on Metallic Corrosion, p. 400. DECHEMA, Frankfurt, 1981.

4. R. M. Latanision, M. Kurkela and F. Lee, "The Role of Grain Boundary Chemistry and the Environment on Intergranular Fracture", Proc. Third International Conference on Effects of Hydrogen on Behavior of Materials, in press.
5. B. J. Berkowitz, M. Kurkela and R. M. Latanision, "Effect of Ordering on the Hydrogen Permeation and Embrittlement of Ni_2Cr", Proc. Third International Conference on Effects of Hydrogen on Behavior of Materials, in press.
6. G. S. Was, H. H. Tischner, R. M. Latanision and R. M. Pelloux, "Fatigue Crack Growth Behavior of Inconel 600 at Cathodic Potentials", Metallurgical Transactions, in press.
7. G. S. Was, H. H. Tischner and R. M. Latanision, "The Influence of Thermal Treatment on the Chemistry and Structure of Grain Boundaries in Inconel 600", Metallurgical Transactions, in press.
8. T. Tsuru and R. M. Latanision, "The Corrosion Resistance of Microcrystalline Stainless Steel," Proc. H. H. Uhlig Symposium Denver ECS Meeting, October 1981, in press.
9. R. M. Latanision, "General Overview: Atomistics of Enviromentally-Induced Fracture," in Proc. NATO Advanced Research Institute on Atomistics of Fracture, in press.
10. R. G. Ballinger, R. M. Latanision, W. C. Moshier and R. M. N. Pelloux, "The Role of Uncertainty in the Measurement of Crack Length by Compliance Techniques", Proc. IAEA Specialists Meeting on Subcritical Crack Growth, held 13-15 May 1981, at Frieberg, FRG.
11. R. B. Diegle, N. R. sorensen, T. Tsuru and R. M. Latanision, "The Corrosion Resistance of Glassy Alloys," in volume on Corrosion: Treatise on Materials Science

and Technology, ed., J. C. Scully, Academic Press, in press.

6. OTHER RELATED PROJECTS

1. Rapid Solidification of Thermoplastics
   F. J. McGarry
   See -- Effect of Processing on Polymer/Composite Structure and Properties, page 192.

2. The Modelling of Rapid Solidification Processes
   J. Szekely
   See -- Mathematical and Physical Modelling of Materials Processing, page 236.

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B. EFFECT OF PROCESSING ON POLYMER/COMPOSITE STRUCTURE AND PROPERTIES

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SUMMARY

After many decades of regarding polymer processing as a series of unrelated, often empirical, disciplines dealing with the formation and shaping of materials, the industry has come to realize that further advances in the vitality and economic health of the field will require a more consistent and rational point of view in which processing is viewed as a participant in the underlying triad of relationships which comprise materials science and engineering. This triad includes processing as it influences material structure, and ultimately properties. Although several MIT faculty are presently involved in research dealing with various aspects of what might be termed polymer processing, a group of faculty has formed under the auspices of the Department of Materials Science and Engineering whose work is centered specifically around the theme of processing-structure-properties, and this group has developed enough coherence to justify its inclusion in this report under a common heading. Their work spans the full range of subdisciplines of polymer science and engineering: Professor Wnek is concerned primarily with polymer chemistry and

synthesis, Professor Sung treats structure modification and optimization through processing as the unifying theme of her research; Professor Roylance has been developing methods of melt flow modeling as an important aspect of his work in processing structure-property relations of polymers; Professor McGarry's longstanding interest in mechanical properties of composites has always included processing as an important aspect; and Professor Rose has extended his expertise in biomedical materials research to include polymer processing effects. Although any classification of the diverse research interests of this group is of course somewhat arbitrary, they are in fact unified by a common interest in processing and its role in shaping structure, and the following descriptions are intended to summarize their principal goals and approaches.

An analysis of the design technology of advanced graphite/epoxy composites being conducted by Professors Mar, Dugundji, Pian, and Crawley of the Department of Aeronautics and Astronautics is also reported herein.

1. POLYMER SYNTHESIS

Electrically Conductive Polymers

Composites of polyacetylene and low density polyethylene (LDPE) have been prepared by impregnating the LDPE with a Ziegler-Natta catalyst followed by exposure to acetylene gas. The resulting materials soften upon heating provided that the polyacetylene content is <ca. 5 wt% and remain flexible and tough indefinitely. The composites can be doped with iodine to afford conductivities as high as 10 $\Omega^{-1}cm^{-1}$. Their conductivities decay less rapidly upon air exposure compared with I_2-doped polyacetylene film. The construction

of batteries from the composites having open circuit voltages of ca. 2.2V has been demonstrated. The microwave absorption characteristics of the composites are being investigated.

We are currently exploring the generality of our synthetic approach with regard to the types of polymeric materials which may act as media for the in-situ polymerizations of acetylene. The properties of composites prepared by simply dispersing polyacetylene powder in various matrices are also being studied.

Polymeric materials are also being synthesized in which rigid, conjugated pendant groups are attached to an aliphatic backbone. The goal is to produce materials which are processable (at least before doping) and which can be doped to high conductivities with both electron doners or acceptors. The potential influence of ordered domains derived from the rigid pendant groups on electrical properties will be addressed.

Sponsor: MIT Center for Materials Science and Engineering

Faculty: G. E. Wnek

Graduate Students: M. E. Galvin, A. Guiseppi-Eli, D. P. Whelan

Publications:

1. A. Feldblum, Y. W. Park, A. J. Heeger, A. G. MacDiarmid, G. E. Wnek, F. E. Karasz and J. C. W. Chien, "Microwave Properties of Low Density Polyacetylene," J. Polym. Sci. Polym. Phys. Ed., 19, 173 (1981).
2. J. C. W. Chien, G. E. Wnek, F. E. Karasz and J. A. Hirsch, "Electrically Conducting Acetylene-Methylacetylene Copolymers - Synthesis and Properties," Macromolecules, 14, 479 (1981).
3. G. E. Wnek, J. Capistran, J. C. W. Chien, L. Dickinson, R. Gable, R. Gooding, K. Gourley, F. E. Karasz, C. P.

Lillya and K.-D. Yao, Adv. Chem. Series, Las Vegas ACS Meeting, in press.

4. J. C. W. Chien, G. E. Wnek, F. E. Karasz, J. M. Warakomski, L. C. Dickinson, A. J. Heeger and A. G. MacDiarmid, "Electron Paramagnetic Resonance Saturation Characteristics of Pristine and Doped Polyacetylenes," Macromolecules, in press.
5. M. E. Galvin and G. E. Wnek, "Electrically Conductive Polymer Composites. Polymerization of Acetylene in Polyethylene," Polymer, in press.

2. PROCESSING-STRUCTURE RELATIONS IN POLYMERS

Characterization of Polymer Surface Structure

In order to characterize polymer surface structure as a function of different processing conditions (injection molding, compression molding, etc.), last year we developed a modified attenuated total internal reflection FT-IR dichroism technique by using a symmetrical double-edged internal reflection crystal. We have now extended our work to measure three-dimensional orientation and other structural parameters, by rotating the polarizer and further improving the optical arrangements on the ATR set-up for increased sensitivity and accuracy. By using uniaxially orientated polypropylene and polyethylene terephthalate films, we demonstrated that we can obtain not only three-dimensional orientation functions for each absorption band (crystalline as well as amorphous), but also other surface structural information such as degree of crystallinity of trans/gauche conformer content.

When the surface of the polymer is rough or brittle, FT-IR ATR technique is difficult to apply. In collaboration with

Dr. Krishnan at Digilab, we developed an FT-IR photoacoustic (PA) dichroism technique to determine molecular orientation from such surfaces. In order to demonstrate the feasibility of this new technique, we used uniaxially drawn PET and compared PA and ATR dichroism techniques. For three well-known parallel bands, the dichroic ratio is greater than unity in both ATR and PA, as expected from the drawing process.

Sponsor: Office of Naval Research
Faculty: C. S. P. Sung
Graduate Student: J. P. Hobbs
Publications:

1. C. S. P. Sung, "A Modified Technique for Measurement of Orientation from Polymer Surfaces by Attenuated Total Reflection IR Dichroism," Macromolecules, 14, 591 (1981).
2. J. P. Hobbs, C. S. P. Sung, K. Krishnan and S. Hill, "Three Dimensional Characterization of Polymer Surface Structure by Modified Attenuated Total Reflection IR Dichroism," Proceedings of the 40th Annual Technical Conference, Soc. Plastics Eng., May 1982 (San Francisco).
3. K. Krishnan, S. Hill, J. P. Hobbs and C' S. P. Sung, "Orientation Measurements from Polymer Surfaces Using Fourier Transform Infrared Photoacoustic Spectroscopy," Applied Spectroscopy, May-June, 1982.

Mechanistic Studies of Adhesion Promoters in Al_2O_3 /Polyethylene Joint

Several spectroscopic techniques (FT-IR, ESCA, SEM and SEM-EDX) were employed to characterize the molecular structure of a deposited organo silane-type adhesion promoter and to probe the interactions at the polymer/silane interface as

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well as at the sapphire/silane interface. This structural information was correlated to properties of the dry joint by evaluating joint strength and failure mode and locus. Results are; first, direct confirmation of the heterogeneous, multimolecular nature of deposited silane on sapphire; second, a strong possibility of interdiffusion at the polyethylene/silane interface; third, the possible presence of a covalent bond at the sapphire/silane interface; and fourth, reasonable correlation with joint strength and failure mode.

Sponsors: Air Force Office of Scientific Research, Army Research Office

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Publications:

1. N. H. Sung, A. Kaul, S. Ni, C. S. P. Sung and I. J. Chin, "Role of Organo Silanes and Organo Titanate in Promotion of Adehsion Strength of Al_2O_3/Polyethylene Joint", Proceedings of 36th Annual Technical Conference, Reinforced Plastics/ Composites Institute, SPI, Session 2-B, 1981.
2. A. Kaul, N. H. Sung, I. Chin and C. S. P. Sung, "Mechanism of Adhesion Promotion Through Organosilanes in α-Al_2O_3/ Polyethylene Joints," Proceedings of 37th Annual Technical Conference, Reinforced Plastics/Composites Institute, SPI, Session 2-E, 1982.

Molecular Understanding of Physical Aging Phenomenon via Azochromorphoric Labelling Studies

As far as physical aging is concerned, the processing of plastics by extrusion, injection molding, etc. may be regarded as a quench. Therefore, the mechanical properties of the glassy plastics are expected to become more brittle

as a function of time. We use an azochromophoric label in the main chain of amorphous polymers in order to provide some insight into the physical aging phenomenon. Analysis of photochemical trans⇌cis isomerization kinetics of such azo labels reveals that kinetics can be characterized by two rate constants. The fast rate is similar to the rate observed in dilute solution, while the slower rate is a hundred times slower. As physical aging proceeds, the fraction (α) which is characterized by the fast rate decreases until it reaches equilibrium. We propose to interpret α to reflect the fraction of free volume above a certain size necessary for the azo label to isomerize, and thus the decrease in α as a function of physical aging means the collapse of free volume of such a size. To the best of our knowledge, this is the first demonstration of the use of molecular labels by which we can estimate a fraction of free volume above a critical size at a given temperature and time of aging. This provides more information about the distribution of free volume and its change with aging.

Sponsors: NSF Polymers Program, Whitaker Health Sciences Fund, Sun Kyong Fibers, Ltd.

Faculty: C. S. P. Sung

Graduate Students: L. Lamarre, K. H. Chung

Publications:

1. C. S. P. Sung, L. Lamarre and K. H. Chung, "Studies of Thermal Transitions and Physical Aging Monitored by Azochromophoric Labels Attached in the Mainchain of Amorphous Polymeric Solids," ACS Polymer Preprints, 22-2, 277 (1981).
2. C. S. P. Sung, L. Lamarre and K. H. Chung, "Use of Azochromophoric Labels as a Molecular Probe of Physical Aging in Amorphous Polymeric Solids," Macromolecules, 14, Nov-Dec (1981).

3. PROCESSING OF THERMOPLASTICS

Cold Forming of Polyvinyl Chloride

Polyvinyl chloride, one of the largest volume plastics, is especially sensitive to heat so melt forming operations require close controls to avoid thermal degradation of the polymer. The situation is exacerbated with formulations intended for higher temperature applications, therefore great benefit would derive from forming methods which could be carried out economically at or near room temperature. The purpose of this research is to identify and explore such methods suitable both for powder and sheet PVC. Considerable success has now been achieved in powder forming of homogeneous PVC samples with promising mechanical properties.

Sponsor: B. F. Goodrich Company
Faculty: F. J. McGarry
Staff: J. F. Mandell
Graduate Student: J. H. Chen

Rapid Solidification of Thermoplastics

The free volume content in glassy thermoplastics depends upon the rate of cooling through the glass transition temperature. It strongly affects certain macroscopic mechanical properties via the process known as aging. Very rapid cooling and solidification of metals has produced amorphous structures with unusual properties. The purpose of the present research is to look for similar effects in glassy polymers containing abnormally large free volume. Some exploratory work with crystalline polymers may be done also. Careful measurements on quenched thin films of polyvinyl-

chloride and polystyrene do show a significant increase in free volume as compared with control specimens.

Sponsor: National Aeronautics and Space Administration
Faculty: F. J. McGarry
Staff: J. F. Mandell
Graduate Students: A. Agrawal, H. Lee

Numerical Modeling of Polymer Melt Processing

Finite element techniques are being developed to model the velocity, stress, and temperature fields which exist during such polymer melt processing operations as extrusion and injection molding. Computer codes have been written and verified for steady and transient nonisothermal flows of Newtonian and shear-thinning fluids in which the effects of viscous heat generation and heat transfer by conduction and convection are incorporated. Research is presently ongoing aimed at extending the models to include chemical reaction and free-surface effects. The ability to model these flows in an economic and accurate manner will be of considerable value in designing processing operations so as to produce polymers of optimal properties and in developing equipment of improved efficiency.

Sponsors: National Aeronatics and Space Administration, Army Materials and Mechanics Research Center, Draper Laboratories, Hysol Corp.
Faculty: D. K. Roylance
Graduate Students: E. Bronaugh, C. Douglas
Publication:

1. D. K. Roylance, "Finite Element Modeling of Nonisothermal Polymer Flows," to appear in ACS Symposium Series, "Computer Applications in Coatings and Plastics."

Processing of Ultrahigh Molecular Weight Polyethylene

The performance of ultrahigh molecular weight polyethylene of total joint replacements depends crucially on how the reacted polymer is processed into the solid implant componant, as processing determines the ultimate molecular weight and defect distribution.

Evaluation of performance depends on accurate total joint simulations and assessments of wear and mechanical and chemical breakdown, and comparisons with clinical retrievals. This is done in several ways with the polymer processing as the independent variable.

Sponsor: NIH
Faculty: R. M. Rose, A. M. Crugnola (University of Lowell)
Staff: G. Arndt, E. Goldfarb, I. M. Puffer
Graduate Student: A. Litsky
Undergraduate Students: A. Casavant, N. Goldberg
Publications:

1. R. M. Rose, A. M. Crugnola, W. R. Cimino, and M. D. Ries, "The In-Vivo Performance of Polyethylene Components of Total Joint Replacements," Proceedings of Implant Retrieval Conference at the National Bureau of Standards, May 1-2, 1980.
2. R. M. Rose, H. J. Nusbaum, H. Schneider, M. Ries, I. Paul, A. Crugnola, S. R. Simon and E. L. Radin, "On the True Wear Rate of Ultrahigh Molecular Weight Polyethylene in the Total Hip Prosthesis," J. of Bone and Joint Surg., Vol. 62-A, No. 4, June, 1980, pp. 537-549.
3. R. M. Rose, A. Crugnola, M. Ries, W. Cimino, I. Paul, A. and E. L. Radin, "On the Origins of High In-Vivo Wear Rates in Polyethylene Components of Total Joint Prosthesis", Clinical Orthopaedics and Related Research, 1979, pp. 277-296.

4. R. M. Rose, H. J. Nusbaum, I. Paul, A. Crugnola, and E. L. Radin, "Wear Mechanisms for Ultrahigh Molecular Weight polyethylene in the Total Hip Prosthesis", J. of Appl. Polymer Sci., Vol. 23, 1979, pp. 777-789.
5. L. E. Lanyon, I. L. Paul, C. T. Rubin, E. L. Thrasher, R. DeLaura, R. M. Rose and E. L. Radin, "In-Vivo Strain Measurements from Bone and Prosthesis Following Total Hip Replacement," J. of Bone and Joint Surg., 63-A, July, 1981, pp. 989-1001.
6. R. M. Rose, M. Ries, I. Paul, A. Crugnola and E. Ellis, "The True Wear Rate of Ultrahigh Molecular Weight Polyethylene in the Total Knee Prosthesis," submitted to J. Bone and Joint Surg., 1981.
7. R. M. Rose, W. R. Cimino, E. Ellis and A. M. Crugnola, Exploratory Investigations on the Structure Dependence of Wear Resistance of Polyethylene," J. of Wear, 1981, in press.
8. R. M. Rose, "Wear Mechanisms and Wear Debris," Bulletin of the Hospital for Joint Diseases, 1980.
9. E. L. Radin, I. L. Paul, R. M. Rose, "Osteoarthrosis as a Final Common Pathway," The Aetiopathogenesis of Osteoarthrosis, G. Nuki, Pitman Publishing Co., Ltd., Kent, England, 1980, pp. 84-89.
10. R. M. Rose, A. M. Crugnola, W. R. Cimino and M. D. Ries, "The In Vivo Performance of Polyethylene Components of Total Joint Replacements," Implant Retrieval: Material and Biological Analysis, NBS Special Publication #601, U.S. Department of Commerce, 1981, pp. 3-28.

Exploratory Research in Nondestructive Testing

This project is aimed at exploring the properties of defects in polymers and polymer-matrix composites as dielectric singularities and at identifying convenient methods of detecting defects in Ti weldments, based on similar approaches.

Sponsor: Office of Naval Research
Faculty: R. M. Rose
Staff: I. M. Puffer
Graduate Student: H. Landis
Undergraduate Student: J. Parse

4. DESIGN TECHNOLOGY OF ADVANCED GRAPHITE/EPOXY COMPOSITES

Design, fabrication, and testing of graphite/epoxy laminates and simple structural components. Evaluation of mechanical properties including strength, fracture, fatigue, stiffness, vibrations, and buckling. Failure mechanisms and damage tolerance of components.

Sponsor: Air Force Materials Laboratory, AFWAL
Faculty: J. W. Mar, J. Dugundji, T. H. H. Pian, E. Crawley
Graduate Students: O. Bauchau, M. Graves, S. Hollowell, D. Jensen, P. Lagace, H. McManus, J. Rogers, M. Wong
Undergraduate Students: About 15 part-time students
Theses:

1. J. C. Rogers, "An Investigation of the Damage Tolerance Characteristics of Graphite/Epoxy Pressure Vessels," M.I.T., Department of Aeronautics and Astronautics, S.M., September 1981.
2. O. A. Bauchau, "Design, Manufacturing and Testing of High Speed Rotating Graphite/Epoxy Shafts," M.I.T., Department of Aeronautics and Astronautics, Sc.D., June 1981.
3. S. J. Hollowell, "Aeroelastic Flutter and Divergence of Graphite/Epoxy Cantilevered Plates with Bending-Torsion Stiffness Coupling," M.I.T., Department of Aeronautics and Astronautics, S.M., January 1981.
4. D. W. Jensen, "NaturalVibration of Cantilever Graphite/Epoxy Plates with Bending-Torsion Coupling," M.I.T., Department of Aeronautics and Astronautics, S.M.,

August, 1981.

5. H. L. N. McManus, "Failure of Modes in a Family of Graphite/Epoxy Laminates", M.I.T., Department of Aeronautics and Astronautics, S.M.,June 1981.

Publications:

1. O. A. Bauchau, "Experimental Measurement of Elastic Shear Modulus of Graphite/Epoxy Tubes," J. of Composite Materials, 15, March 1981, pp. 151-156.
2. J. W. Mar, M. J. Graves and D. P. Maass, "Effect of CompressionCompression Fatigue on Balanced Graphite/Epoxy Laminates with Holes," J. of Aircraft, 18, 9, September 1981, pp. 744-747.
3. P. Bar-Yoseph, T. H. H. Pian, "Calculation of Interlaminar Stress Concentration in Composite Laminates," J. Composite Materials, 15, 1981, pp. 225-239.

5. OTHER RELATED PROJECTS

1. Computational and Experimental Studies of Viscoelastic Flows

   R. A. Brown

   See -- Mathematical and Physical Modelling of Materials Processing, page 238.

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C. CERAMICS PROCESSING RESEARCH

Faculty: H. K. Bowen
R. L. Coble
R. M. Cannon
A. Bleier
B. J. Wuensch

Staff: J. S. Haggerty
R. L. Pober

SUMMARY

A new emphasis on processing of ceramic materials was begun at M.I.T. four years ago with the establishment of the Ceramics Processing Research Laboratory. The recognized purpose of this effort was to develop a processing science base for the ceramics industry. Because of unique institutional problems (at universities, national laboratories and corporations), there has not been a strong base in ceramics processing science as there has been in physical ceramics. Thus, part of the effort at MIT is to form a strong and interactive coalition between MIT, the government agencies, and the ceramics producers and users industries. Sixteen companies have joined the consortium, over 50 companies have made visits to the campus during the past year to discuss research results, and several companies have sent staff members for "internships" in the laboratory.

The research on processing of ceramics is led by 5 faculty members and 1 senior research scientist and involves 4 post-doctoral scientists, 24 graduate students, and 8 under-graduates. Professor Coble continues his innovative research on experiments and models for sintering and microstructure evolution; Professor Cannon has developed models and data for understanding the kinetics of grain boundary motion and of pore coarsening; Professor Wuensch has developed new materials for fuel cells and batteries; Dr. Haggerty has

developed new experimental techniques using lasers for forming fine, monosized powders and for forming stable and metastable structures from liquids, and solar materials research in conjunction with the MIT Energy Laboratory; Professor Bleier, who joined the faculty last year, has begun unique research on colloidal science and ceramics processing; and Professor Bowen has developed research programs on the presintering science necessary for controlled green microstructures. Work is conducted in laboratories in Building 13 and in the Ceramics Processing Research Laboratory located in Building 12. The laboratory and facilities manager of the Ceramics Processing Research Laboratory is Dr. Richard L. Pober.

1. LASER PROCESSING

A facility, consisting of 4 high power CO_2 lasers and peripheral equipment, has been established to conduct directed energy materials processing research. The equipment is being used to conduct processing research in four distinct areas with non-metallic materials. One custom designed, 1300 watt laser is integrated into a unique crystal growth facility. It is being used to produce high purity, high melting point crystals of oxide, carbides, and borides in highly controlled atmospheres. The same apparatus will be used to splat quench various glasses and metastable materials which have been equilibrated in previously inaccessible atmospheres. Another system has been developed to synthesize small diameter, uniform spherical powders of Si, SiC, and Si_3N_4. These powders are used to supply the powder processing research. The third apparatus is being used to investigate a novel laser drive, photo-induced chemical vapor deposition process. A tunable CO_2 laser is being installed to conduct laser induced chemistry research.

Sponsors: Office of Naval Research, Defense Advanced Research Projects Agency, Standard Oil of Indiana, MIT Cabot Fund, National Science Foundation, National Aeronautics and Space Administration, 3M Corporation

Faculty: J. S. Haggerty

Staff: S. C. Danforth, J. Flint

Graduate Students: R. Marra, H. Sawhill, L. Schioler

Undergraduate Students: K. Bleess, M. Gabriel, C. Kerwin, M. Schmair, B. Sheldon, J. Hillman, M. Knittin, G. Beckhart, P. Tiethohl.

Theses:

1. Brenda King, "Crystallization Kinetics in Amorphous Silicon Thin Films," May, 1981.
2. J. Hillman, "Electronic Characterization of Laser CVD Films."

Publications:

1. W. R. Cannon, S.C. Danforth, J. S. Haggerty, R. A. Marra, "Sinterable Ceramic Powders from Laser Driven Reactions, Part I; Process Description and Modeling." Submitted to J. Am. Ceram. Soc.
2. W. R. Cannon, S.C. Danforth, J. S. Haggerty, R. A. Marra "Sinterable Ceramic Powders from Laser Driven Reactions, Part II; Powder Characteristics and Process Variables." Submitted to J. Am. Ceram. Soc.
3. S. C. Danforth, J.S. Haggerty, "Synthesis of Ceramic Powders by Laser Driven Reactions." To be published in Ceramic Engineering and Science proceedings.
4. S. Mizuta, W. R. Cannon, A. Bleier, and J.S. Haggerty, Dispersion and Casting of Silicon Powder Without Deflocculants," submitted to J. Am. Ceram. Soc.
5. J. S. Haggerty, and W. R. Cannon, "Sinterable Powders from Laser Driven Reactions." Chapter in Laser Induced Chemical Processes, Ed., J.I. Steinfield, Plenum Pub. Co., New York, NY (1981).
6. W. R. Cannon, S.C. Danforth, J. H. Flint, J. S. Haggerty,

and R. A. Marra, "Synthesis of Ceramic Powders from Laser Heated Gas Phase Reactants," Proceedings Society for Photo-Optical and Instrumentation Engineers, Vol. 198, Laser Applications in Materials Processing, San Diego, CA 1979.

2. PROCESSING OF CERAMIC POWDERS

The most critical problem, limiting the extensive use of ceramic materials, is that high technology ceramics cannot be reliably and reproducibly manufactured. The focus of our research program is on the physics and chemistry of controlled particulate formation (size, size distribution, dispersion, phase and chemical composition, and shape) and of controlled packing of particles (no particle density gradients). The ceramic systems being studied are: Al_2O_3, $BaTiO_3$, $SrTiO_3$, $BaFe_6O_{19}$, ZnO, Si, SiC, Si_3N_4, SiO_2, TiO_2, TiB_2 and ZrO_2. Powders are made by homogeneous gas phase nucleation (laser driven) or by controlled growth in aqueous and nonaqueous solutions. The colloidal dispersion parameters are being studied and models and techniques are being developed for controlled coagulation of the powders into shapes which are subsequently densified. Low firing temperatures and shorter sintering times are necessary in addition to better control of the microstructure and thus, the physical properties.

The technological goals of this research are directed towards the use of ceramics as multilayer Si-chip carriers, capacitors, turbine and diesel engine components, permanent magnets, and varistors.

Sponsors: AVX, Corning, Solid State Dielectrics, Union Carbide, Vitramon, Ford, GM-Delco, Hitachi, Tektronix, IBM, EXXON, Department of Energy, ILZRO.

Faculty: A. Bleier, H. K. Bowen and J.S. Haggerty

Staff: R. L. Pober, J. Blendell, S. Mizuta, Y. Suyama, H. Itoh, N. Levoy.

Graduate Students: E. Barringer, C. Huynh, M. Parish, M. Strauss, M. Green, R. Riman, N. Jubb, E. Tormey, R. Garcia, T. Kramer.

Undergraduate Students: N. Levoy

Theses:

1. N. Levoy, "Dispersion, Classification and Sintering of Al_2O_3," B.S., June, 1981.

Publications:

1. E. S. Tormey, et al., "Absorption of Dispersants from Nonaqueous Solutions," Surface and Interfaces in Ceramic and Ceramic-Metal Systems, Eds., J. Pask and A. Evans, Plenum Press, NY, 1981, pp. 121-136.
2. E. Barringer, "Disorder-Order Transition in Monodisperse Titania Sols," M.I.T. Ceramics Processing Research Laboratory, Report #8, December, 1980.

3. MATERIALS FOR SOLAR ENERGY

Materials processing research is being conducted in two solar energy areas. In the first, graded-index of refraction anti-reflection (AR) coatings are being developed on silicate glass by preferentially removing one phase of a phase separated glass. When used on covers of flat plate collectors, these broad band AR coatings increase the extractable heat by 30-50%. The second area involves several materials processing programs for photovoltaic devices. Our analyses indicate that amorphous processes offer the best chance of achieving required cost objectives. Consequently, we have limited our research to this focus. Processes to improve carrier life times in chalcogenide glass semiconductors have been investigated to take

advantage of their low cost and adjustable band gap. Processes to control the nucleation and growth processes in amorphous silicon are being studied to make use of the low cost of amorphous deposition processes and the high efficiency of crystalline Si. The laser CVD deposition process is being developed because of low manufacturing cost and superior properties through better process control.

Sponsors: Department of Energy, SERI, MIT Cabot Fund, 3M Corporation

Faculty: J. S. Haggerty, D. Adler

Staff: S. C. Danforth, T. Gattuso, D. Imeson

Graduate Students: A. Iqbal, M. Meunier, F. Van Gieson

Undergraduate Students: J. Hillman, C. Kerwin, B. King, B. Sheldon, O. Estell

Theses:

1. A. Iqbal, "Determination of Chemistry of Graded-Index, Antireflective Films on Glass," S.M., February 1981.
2. B. King, "Crystallization Kinetics in Amorphous Thin Films," May, 1981.
3. V. Tengzelius, "Development of Antireflective Films on $NO_2/O/CaO/SiO_2$ Glass," January, 1982.
4. F. VanGieson, "Kinetics of Crystallization for Selected Amorphous Silicon Films," January, 1982.

Publications:

1. A. Iqbal, J. S. Haggerty, and S. C. Danforth, "Surface Chemistry of Anti-Reflective Films on Borosilicate Glasses," submitted to the J. Am. Ceram. Soc.
2. J. S. Haggerty, B. Sheldon, and A. G. Emslie, "Exact Computation of the Reflectance of a Surface Layer of Arbitrary Refractive Index Profile and an Approximate Solution of the Inverse Problem," submitted to the J. Opt. Soc. Am.
3. J. E. Ritter, Jr., K. Jakus, K. Buckman, G. Young, nad J. S. Haggerty, "Strength and Fatigue Behavior of a Borosilicate Glass with an Antireflective Surface,"

submitted to Glass Technology.

4. S. C. Danforth, F. VanGieson, I. Kohatsu, and J. S. Haggerty, "Laser Induced Controlled Nucleation and Growth Process for Large Grained Polycrystalline Silicon," American Institute of Physics, Conference Proceedings, Laser and Electron-Beam Solid Interactions and Materials Processing, Ed. Sigmon, Gibbons, Hess, Boston MA. (1980).
5. W. R. Cannon, S. C. Danforth, J. Flint, J. S. Haggerty, and R. A. Marra, "Synthesis of Ceramic Powders from Laser Heated Gas Phase Reactants," Proceedings Society of Photo-Optical and Instrumentation Engineers, Vol. 198, Laser Applications in Materials Processing, San Diego, CA (1979).

4. PROCESSING OF OXIDE POWDERS

A program to examine the application of current colloid-chemical models for single oxides to the processing of technical ceramic powders has been initiated. Its purpose is to extend the models to heterogeneous systems containing multimetallic oxides. Objectives are to prepare model, single and multimetallic oxides, to characterize the materials prepared using crystallographic, chemical, physical, and surface-chemical procedures, and to test recently proposed models of the electrical double layer. The approach consists of evaluating surface reactions and properties, determining intrinsic surface ionization constants, comparing surface and bulk solution chemical equilibria, and comparing computed and experimentally determined specific conductivities for dispersions relevant to high performance ceramics. Results will relate surface ionization reactions and electrical double layer properties to fundamental interactions among solutes, solvents (principally water), and solid particles.

The overall technical goal of this research is to develop predictive capabilities for the processing of real and "model" ceramic oxides.

Sponsor: Department of Energy
Faculty: A. Bleier
Graduate Student: W. C. Hasz
Publications:

1. S. Mizuta, W. R. Cannon, A. Bleier, and J. S. Haggerty, "Wetting and Dispersion of Silicon Powder Without Deflocculants," submitted for publication, Am. Ceram. Soc.
2. A. Bleier, "Role of van der Waals Forces in Determining the Wetting and Dispersion Properties of Silicon Powder," submitted for publication.
3. A. Bleier and R. M. Cannon, "Synthesis and Characterization of Uniform Zirconium Dioxide," to be submitted for publication.

5. SINTERING AND MICROSTRUCTURE EVOLUTION

Most of the important technological developments for processing ceramic materials have resulted from theoretical models of sintering and grain growth coupled with an enormous number of experimental measurements. The efforts at MIT over the past 25 years have been at the frefront of the development of these concepts, and most recently has succeeded in modelling the very complex simultaneous processes which occur during the firing of ceramic greenware.

Because of the extreme sensitivity of ceramic materials to impurities and additives, and because of the difficulties in characterizing fine powders, these theoretical analyses provide guidance to the selection of experimental parameters (T, P, composition, particle size and distribu-tion) for a

critical set of measurements to test the basic theories as well as providing guidance to the ceramic processors. These analyses are also demonstrating the importance of the local distribution of porosity, impurities or dopants, and grain or particle size in determin-ing the densification process and microstructure evolution.

Numerous model materials have been chosen which have widely varying difference in diffusion coefficients, vapor pressures, surface and grain boundary energies, etc. These include: Al_2O_3, ZrO_2, Au, ZnO, Si, SiC, Si_3Ni_4, MgO, LiF, $B9TiO_3$, and $ThO2-ZrO_2$. In each case, fundamental studies are performed which relate the basic thermochemical forces and transport coefficients to the observed evolution of the sintered microstructure.

Some of the particularly exciting recent accomplishments are:

1. analysis of the grain boundary grooving technique as it applies to surface diffusion studies, in particular, the effects of faceting and simultaneous lattice and surface contributions;
2. modelling of sintering kinetics based on virtually mono-dispersed, 1 ·m gold powder;
3. investigation of the complex sintering behavior of ZnO-doped ceramics to determine the nature and extent of the sintering mechanism;
4. partial demonstration of the notion that the Herring scaling laws also apply to nonspherical powder as well; and
5. analysis of the transport processes which occur in the Ni-W system using isothermal creep tests.

Sponsor: Department of Energy

Faculty: R. L. Coble, R. M. Cannon

Graduate Students: J. Dynys, W. Hong, E. Rothman, H. Song, B. Zelinski

Undergraduate Student: A. Roshko

Theses:

1. W. Coblenz, "Physics of Sintering of Silicon," Sc.D., MIT, Department of Materials Science and Engineering, June 1981.
2. A. Roshko, "Grain Coarsening in Doped $BaTiO_3$," S.B., MIT, Department of Materials Science and Engineering, June 1981.

Publications:

1. J. M. Dynys, R. L. Coble, W. S. Coblenz, and R. M. Cannon, "Mechanisms of Atom Transport during Initial Stage Sintering of Al_2O_3," Sintering Processes, Edited by G. C. Kuczynski, Plenum Publishing Corporation, 1980.
2. W. S. Coblenz, J. M. Dynys, R. M. Cannon, and R. L. Coble, "Initial Stage Solid State Sintering Models. A Critical Analysis and Assessment," Sintering Processes, Edited by C. G. Kuczynski, Plenum Publishing Corporation, 1980.

6. SYNTHESIS AND PROPERTIES OF FAST-ION CONDUCTORS

Fast-ion conductors, materials which display ionic electrical conductivities up to six or eight orders of magnitude larger than normal ionic compounds (i.e., up to 5 reciprocal ohm-cm), find important application in fuel cells and battery systems. We are conducting a broad study of such materials, which includes synthesis and power processing of potential new conductors, fabrication of sintered specimens for measurement of electrical properties, growth of single crystals, and precise neutron and x-ray diffraction measurements to provide insight into the mechanisms of the fast-ion conduction process. The materials which are currently the subject of exploratory synthesis and processing are alkali metal conductors of relevance to battery systems. Potential new conductors

include several alkali metal silicates and titanates, and nitrogen-based ceramics. In addition, novel solid-solution series are being prepared with systems which have previously been demonstrated to display fast-ion conduction. Among these are NASICON ($Na_3Zr_2SiPO_{12}$) and LISICON ($Li_{3.5}Zn_{0.25}GeO_4$) related systems. Phases for which single crystals have been synthesized and for which diffraction studies have begun are primarily the prototype cation-disordered Ag and Cu conductors. These are ideal systems for critical examination of models for the distribution and thermal motion of the mobile cations as they constitute a large fraction of the scattering density in these materials. These phases include Cu_2S, CuAgS, Ag_3SI and Ag_2Se.

A variety of processing techniques are employed, depending upon the system of interest. Solid state reaction of component oxides or salts are frequently employed, as are hydrothermal reaction and preparation of gels. The growth of single-crystal materials employs (again depending on the system) hydrothermal techniques, flux growth or vapor transport.

Sponsors: Department of Energy, Lawrence Berkeley Laboratory
Faculty: B.J. Wuensch
Staff: I. Kohatsu, A.-K Ekholm
Graduate Students: C.L. Skarda
Publications:

1. R.J. Cava, F. Reidinger and B.J. Wuensch, "Conductivity Mechanisms in the Superionic Phases of AgI and Ag2S as Determined by Neutron Diffraction," in Fast Ion Transport in Solids: Electrodes and Electrolytes, P. Vashishta, J.N. Mundy and G.K. Shenoy, Eds. Elsevier North Holland, 1979, pp. 217-220.
2. R.J. Cava, F. Reidinger and B.J. Wuensch, "Single-Crystal Neutron Diffraction Study of the Fast-Ion

Conductor -Ag_2S Between 186 and 325°C, J. Solid State Chem., Vol. 31, 1980, pp. 69-80.

N82 27398

D. MATERIALS SYSTEMS ANALYSIS

Faculty: M.B. Bever
J.P. Clark
A.M. Church
J.F. Elliott
M.C. Flemings
N.J. Grant
T.B. King
J. Szekely
M.B. Zimmerman

Staff: G.B. Kenney
S.M. Mathur

SUMMARY

Recognizing the need to better understand the societal, economic, and policy tradeoffs associated with materials processing and utilization, the Materials Systems Analysis Group was established within the Department of Materials Science and Engineering in 1975. The principal purpose of the materials systems effort is to provide the materials engineer with the systems analysis required to formulate sound materials processing, utilization, and resource development policies and strategies for private industry and government.

The interdisciplinary research on materials systems analysis involves the collective efforts of 9 faculty members, 2 research staff members, 9 graduate students, and 1 undergraduate from the Departments of Materials Science and Engineering, Sloan School of Management, and Centers for Materials Processing and Policy Alternatives. Prof. Clark continues to expand his innovative materials system simulation and modeling research program which includes assessments of materials substitution dynamics, public policy implications, and materials process economics. This effort includes several collaborative programs with

materials engineers, economists, and policy analysts. Prof. Bever coordinates an ongoing program concerned with the technical and socioeconomic issues of materials recycling, input-output analysis, and technological change and productivity. The major thrust areas in materials systems research are outlined below.

1. MODELING OF MATERIALS SUPPLY, DEMAND, AND PRICES

Imbalances in the supply and demand of basic materials has periodically led to short term shortages and gluts which have sometimes resulted in substantial fluctuations in prices. Although an efficient free market system can be expected to balance supply and demand in the long run, there is a need to anticipate the conditions that lead to these short term fluctuations to facilitate more efficient planning at the level of the nation, industry, and firm. We have been developing detailed engineering and economic models of materials industries for these purposes. The models are usually built from the supply side from an engineering process analysis basis and then transformed to cost and supply functions, which are estimations of the relationship between output and price. The demand models are usually estimated by statistical analyses as a first approximation and then modified with engineering judgment. Thus far we have or are in the process of applying variations of this approach to the following industries: iron and steel (carbon steel, alloy steel, stainless steel and foundry products), aluminum, copper, manganese nodules, magnesium, and cobalt.

Sponsors: U.S. Office of Surface Mining, U.S. Bureau of Mines, National Science Foundation

Faculty: M. B. Bever, J. P. Clark, J. F. Elliott, M. C. Flemings, N. J. Grant, T. B. King, J. Szekely

Staff: G. B. Kenney, S. M. Mathur

Graduate Students: P. Baverstam, M. Cummings, F. Field, P. Foley, S. Kometani, J. Newman, D. Richards, D. Wadekar, R. Upaa

Publications:

1. F. E. Katrak, T. B. King and J. P. Clark, "Analysis of Supply of and Demand for Stainless Steel in the United States," Materials and Society, 4, No. 4, p. 427, 1980.
2. F. E. Katrak and J. P. Clark, "An Analysis of the Determinants of Stainless Steel Pricing and Imports in the United States: Part I - Pricing," Materials and Society, 4, No. 4, p. 437, 1980.
3. J. P. Clark and F. E. Katrak, "An Analysis of the Determinants of Stainless Steel Pricing and Imports in the United States: Part II - Imports," Materials and Society, 4, No. 4, p. 447, 1980.
4. J. P. Clark, N. J. Grant, and T.B. King, "The Potential for Utilization of Manganese Derived from Deepsea Nodules," Natural Resources Forum, 5, p. 249, 1981.
5. J. P. Clark and G. B. Kenney, "The Dynamics of Intermaterial Competition in the Automotive Industry, Part I: A Framework for Analysing the Dynamics of Intermaterial Competition," Materials and Society, 5, No. 2, 1981.
6. G. B. Kenney and J. P. Clark, "The Dynamics of Intermaterial Competition in the Automotive Industry, Part II: A Case Study of the Demand for Magnesium," Materials and Society, 5, No. 2, 1981.
7. P. Foley and J. Clark, "U.S. Copper Supply - An Economic/Engineering Analysis of Cost-Supply Relationships," Resources Policy, 7 No. 3, p. 171, 1981
8. B. J. Reddy and J. P. Clark, "Effects of Deepsea Mining on International Markets for Copper, Nickel, Cobalt, and Manganese," in Deepsea Mining, J. T. Kildow, ed., M.I.T. Press, 1980.

2. PUBLIC POLICY

Public policy as enunciated by federal, state, and local regulations shapes corporate policies which determine processing strategies and resource development, or the lack thereof. Consequently, public policy is an important endogenous variable and/or tool to the materials systems analyst. One specific study evaluates the effect of public regulations on the U.S. copper industry by developing a methodology for assessing the costs and benefits of regulations.

Sponsor: National Science Foundation

Faculty: J. P. Clark, M. B. Zimmerman, A. M. Church (University of New Mexico)

Graduate Student: P. Foley

Publication:

1. A. M. Church, P. T. Foley, H. B. Zimmerman, and J. P. Clark, "The Effects of Taxation of the U.S. Coal and Copper Industries," Materials and Society, 5, No. 1, p. 81, 1981.

3. RECYCLING

Research on the technological and socioeconomic aspects of materials recycling was continued. The research was concerned with resource recovery from waste, the recovery of metal scrap, the recycling of automotive materials, and the recycling of chromium.

In the area of resource recovery, an undergraduate student worked in the laboratories of the Raytheon Company, Research Division under the supervision of Dr. Ernst F. Schloemann as part of the Undergraduate Research Opportunities Program. This work contributed to the redesign and testing of an eddy

current separator with the objective of increasing its capacity. Work planned for the next phase will involve the magnetic separation of light and heavy scrap recovered from municipal solid waste and the separation of aluminum from shredded polyester bottles.

The analysis of technical, economic, and institutional aspects of the recovery of resources from waste was continued. This analysis was carried out in support of a study by a panel on the "Recovery of Energy and Materials from Solid Waste" of the Building Research Advisory Board of the National Research Council.

As a continuation of earlier research on the disposal of discarded automobiles, detailed planning was carried out for a study on the "Impact of Materials Substitution on Energy Conservation, Environmental Goals and Resources Recycling: A Case Study of Recyclability in the Automotive Industry." This study will be conducted as part of the research program of the American Society of Mechanical Engineers with funding from the National Science Foundation.

As an extension of the work on recyling, the strategies of conservation of materials efficient utilization, substitution, recyeling and research and development were reviewed. An analysis made previously for the Congressional Research Service was updated for publication.

Sponsors: Raytheon Company; National Science Foundation (through American Society of Mechanical Engineers)
Faculty: M. B. Bever
Undergraduate: D. G. Facinelli
Publications:

1. M. B. Bever, "The Potential for Reduction of Import Dependency: Efficient Materials Utilization, Substitution, Recyling, and Research and Development,"

Congressional Seminar, in Emerging Issues in Science and Technology, Congressional Research Service, U. S. Government Printing Office, Washington, 1980, pp. 88-100.

2. D. G. Facinelli, "The Development of Non-Ferrous Metal Separators Using Permanent Magnets and Their Application to Municipal Solid Waste," S.B. Thesis.
3. E. Schloemann and D. Facinelli, "High-Capacity Nonferrous Metal Separator Using Permanent Magnets," Proc. 2nd International Symposium on Materials and Energy from Refuse, Antwerp, Belgium, October 1981 (to be published).

4. APPLICATIONS OF INPUT-OUTPUT ANALYSIS

The production and consumption of twenty-six basic minerals has been analyzed within the framework of input-output models at the Institute of Economic Analysis, New York University, under the direction of Professor Wassily Leontief. In research carried out in collaboration with Ms. Sylvia Nasar, the recycling of six metals was analyzed for three scenarios. This analysis will be continued with revised data and expanded to include environmental and energy aspects.

A study of the recycling of chromium by input-output analysis will be completed. It will be complemented by an investigation of structural aspects of the recovery of secondary chromium and its use by industry.

As a continuation of the work mentioned in the foregoing, planning was completed for a project on "Evaluating the Impact of Prospective Changes in Materials Use: An Input-Output Approach." This project will be conducted at New York University and will be sponsored by the Bureau of Mines.

Sponsor: Bureau of Mines (at New York University)
Faculty: M. B. Bever
Publication:

1. S. Nasar-O'Brien and M. B. Bever, "Applications of Input-Output Analysis to Investigations of Metals Recycling," Proceedings, Council of Economics, AIME, 1981, pp. 27-40.

5. MATERIALS, TECHNOLOGICAL CHANGE AND PRODUCTIVITY

The relations of materials and productivity are of critical importance for economic performance and long-term resource availability. These relations are greatly affected by technological change. An investigation of materials, technological change, and productivity was undertaken in collaboration with Ms. Sylvia Nasar. Results were presented at the 3rd Conference on Productivity at Rutgers University, April 23, 1981. The research is continuing.

Faculty: M. B. Bever
Publication:

1. M. B. Bever and S. Nasar, "Materials, Technological Change and Productivity," (accepted for publication).

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E. WELDING RESEARCH

Faculty: T. W. Eagar
D. E. Hardt
J. H. Lang
K. Masubuchi
H. M. Paynter
J. Szekely
K. Terai (Visiting)
W. C. Unkel

Staff: C. Allemand
A. Block-Bolten
A. Imakita
(Visiting)
G. Oreper
B. Russell
A. Zona

SUMMARY

Although continuously present for many decades, the welding effort at MIT has expanded rapidly in the past five years. Presently, this constitutes the largest academic program in welding in the United States. It is led primarily by Professors Masubuchi and Eagar who study Welding Fabrication and Welding Processes, respectively. A number of other faculty are actively involved in many ways, creating an interdisciplinary effort centered in the Departments of Ocean Engineering, Mechanical Engineering, Materials Science and Engineering, Electrical Engineering, and Materials Processing Center.

Personnel include eight faculty, four research scientists and engineers, two technical staff members, twenty-one graduate students, and three undergraduate students. A selection of the ongoing research is presented below.

1. WELDING FABRICATION

The research effort during the period from October 1, 1980 through September 30, 1981 centered around the following projects:

- Residual Stresses and Distortion in Structural Weldments in High-Strength Steels
- Improvement of Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes)
- Development of Fully Automated and Integrated ("Instamatic") Welding Systems for Marine Applications
- Further Advancement of Welding Technology
- Research on Metal Working by High-Power Laser.

Further details of the research activities are described in the following pages. The Kawasaki Heavy Industries Research Fund also provided financial assistance in conducting research on welding fabrication.

The final report of a proposal entitled "Development of Joining and Cutting Techniques for Deep-Sea Applications" was issued from the M.I.T. Sea Grant Office in June 1981 as MITSG 81-2. The objective of the research program from July 1976 through June 1980 was to (1) generate basic information pertinent to joining and cutting techniques for deepsea applications and (2) to develop some prototype tools suitable for underwater joining and cutting for deep-sea applications.

Residual Stresses and Distortion in Structural Weldments in High Strength Steels

The objective of the original three-year research program, which started on December 1, 1977, was to analytically and experimentally study residual stresses and distortion in structural weldments in high-strength steels, especially HY-130 steels. The program included the following tasks:

Task 1: Research on thick butt welds

Task 2: Research on girth welds of cylindrical shells

The program has been extended for another year to cover the following additional tasks:

Task 3: Development of information on weldments in bronze

Task 4: Research on thermal stress relieving of weldments

Task 5: Development of improved computer programs.

Most of the efforts under Tasks 1 and 2 were completed before November 1980 and the results were included in the first and second technical progress reports issued in November 1979 and November 1980, respectively. The remainder of Tasks 1 and 2, primarily the completion of two Ph.D. theses, were completed by May 1981. Task 3 was also completed by June 1981. These results and results of the work under Tasks 4 and 5, which will be completed by November 1981, will be included in the third technical progress report which we plan to issue in November 1981. However, we may not be able to complete all the intended efforts by November 30, 1981. Those efforts which are likely to be unfinished include (1) experiments under Task 4 and (2) manuals of some two-dimensional finite element programs for analyzing transient thermal stresses and residual stresses in weldments. We are asking the sponsor for an extension of six months; therefore, the entire research program will be completed by May 30, 1982. We plan to issue a final report at the conclusion of the program.

Sponsor: Office of Naval Research

Faculty: K. Masubuchi

Staff: A. Imakita (Visiting), A. J. Zona

Graduate Students: J. Agapakis, E. Goncalves, R. S. McCord, V. J. Papazoglou

Research Report:

1. V. J. Papazoglou and K. Masubuchi, Second Technical Progress Report on "Study of Residual Stresses and Distortion in Structural Weldments in High-Strength Steels," Office of Naval Research, Contract No. N00015-75-0469, November 1980.

Theses:

1. E. Goncalves, "Fracture Analysis of Welded Structures".
2. R. S. McCord, "An Investigation of Strain, Distortion, and Heat Distribution During Welding of Nickel-Aluminum Bronze".
3. V. J. Papazoglou, "Analytical Techniques for Determining Temperatures, Thermal Strains, and Residual Stresses During Welding".

Publications:

1. V. J. Papazoglou and K. Masubuchi, "Analytical Methods for Determining Temperatures, Thermal Strains, and Residual Stresses Due to Welding," a paper presented at the 1981 Annual Meeting of the American Welding Society, Cleveland, Ohio, April 6-9, 1981.
2. K. Masubuchi, "Welding Stresses," presented at the 28th Sagamore Army Materials Research Conference, Residual Stress and Stress Relaxation, Lake Placid, New York, July 13-17, 1981.

Improvement of Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes)

The overall objective of this three-year research program which started on June 15, 1979, is to improve the reliability of welding by developing "smart" welding machines. A smart welding machine is equipped with sensors, artificial intelligence, and actuators with the goal of reducing welding errors by one or two orders of magnitude. Although the concepts and techniques which will be developed in this

program will have more general applications to welding, this research program is focused specifically on welding of pipes.

Sponsor: Department of Energy

Faculty: D. E. Hardt, K. Masubuchi, H. M. Paynter, and W. C. Unkel

Graduate Students: J. Converti, Y. Dror, S. Liang, J. Moore, M. Zacksenhouse

Research Report:

1. Third Progress Report on "Improvement of Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes),", to the Department of Energy under Contract No. DE-AC02-79ER10474.A000, June 1981.

Theses:

1. Y. Dror, "Calculations and Measurement of Weld Puddle Geometry in Gas Tungsten Arc Welding".
2. J. Converti, "Plasma-Jets in Arc Welding".

Development of Fully Automated and Integrated ("Instamatic") Welding Systems for Marine Applications

The objective of this two year research program which started in July 1980 is to develop fully automated and integrated welding systems, which may be called "instamatic" welding systems for various marine applications. These systems which will be developed through careful engineering will be able to perform certain prescribed welding jobs by a person with no welding skill. In many cases welding will be performed in a completely enclosed system so that no spark and very little fume will be generated from the welding systems.

Sponsors: National Sea Grant Office, National Atmospheric and Oceanic Administration, Department of Commerce.

Faculty: K. Masubuchi
Staff: A. J. Zona
Graduate Students: H. L. Gustin and D. W. Schloerb
Publications:

1. K. Masubuchi, "Underwater Factors Affecting Welding Metallurgy," a paper presented at the Seminar on Underwater Welding of Offshore Platforms and Pipelines by the American Welding Society, New Orleans, LA, November 5-6, 1980.
2. K. Masubuchi, "Review of Underwater Welding Technology," Oceans '81 - Proceedings of a Conference held in Boston, MA, September 16-18, 1981, pp. 649-651.

Further Advancement of Welding Technology

This three-year research program, which started in October 1980, covers the following three subjects:

1. Automation of welding processes
2. Computer applications to welding
3. Improvement of reliability of welded structures.

Sponsors: A group of industrial sponsors including Hitachi, Ltd., Hitachi Shipbuilding and Engineering Co., Ishikawajima-Harima Heavy Industries, Kawasaki Heavy Industries, Kubota Ltd., Kobe Steel Works, Mitsubishi Heavy Industries, Mitsui Engineering and Shipbuilding Co., Nippon Kokan Kaisha, Nippon Steel Corp., Osaka Transformer Co., Sumitomo Heavy Industries, and Tokyo Shibaura Electric Co.
Faculty: K. Masubuchi and K. Terai (Visiting)
Staff: A. Imakita (Visiting) and A. J. Zona
Graduate Students: J. Agapakis, E. Goncalves, and V. J. Papazoglou
Publications:

1. K. Masubuchi, "New Directions in Welding Reserach and

Development," a special lecture given at the International Conference on Welding Research in the 1980's, Osaka, Japan, October 27, 1980.

2. A. Imakita, V. J. Papazoglou, and K. Masubuchi, "Annotated Bibliography on Numerical Analysis of Stresses, Strains, and Other Effects Due to Welding," Document X-996-81 presented at the 1981 Annual Assembly of Commission X of International Institute of Welding, Oporto, Portugal, September 8-11, 1981.

Research on Metal Working by High-Power Laser

This research program includes the following tasks:

Task 1: Study on applications of high-power laser for metal working.

Task 2: Experiments on characteristics of high-power lasers.

Sponsor: Japan Welding Engineering Society

Faculty: K. Masubuchi and K. Terai (Visiting)

Staff: A. Imakita (Visiting)

2. WELDING PROCESSES (T.W. EAGER)

The major thrusts of the new program include:

- Fluxes
- Sensors for automation (see Materials Processing Research Base Abstract)
- Heat and fluid flow
- Mechanical properties of weldments.

The majority of the research is concerned with arc welding although studies of resistance spot welding and laser welding are underway. These topics are described in greater detail below.

Flux Development

Flux shielded welding processes account for the largest quantity of welded products; yet our understanding of the flux chemistry and slag-metal reactions remains poor. Reactions involving manganese, silicon, chromium, and oxygen are being studied in fused and bonded submerged arc fluxes. A thermodynamic analysis of the slag-metal equilibrium has been developed and tested with remarkable success.

Investigation of active fluxes and flux-cored electrodes is planned. Studies of halide fluxes for use with titanium have shown a number of advantages. Submerged arc welding, gas metal arc, and electroslag welding of titanium are all being studied.

Sponsors: National Science Foundation, Office of Naval Research
Faculty: T. W. Eagar
Staff: A. Block-Bolten, B. Russell
Graduate Students: S. K. Fan, U. Mitra, D. Ries
Undergraduate Students: T. Lynch, R. Schoder
Publications:

1. C. S. Chai and T. W. Eagar, "Slag-Metal Equilibrium During Submerged Arc Welding," Met. Trans., 12B, 1981, p. 539.
2. C. S. Chai and T. W. Eagar, "Slag Metal Reactions in Binary CaF_2-Metal Oxide Welding Fluxes," accepted by the Welding J.
3. C. S. Chai and T. W. Eagar, "Prediction of Weld Metal Composition During Flux Shielded Welding," to be published in the Proceedings of the ASM Conference on Welding Consumables and Process Developments, Peoria, IL, September 1981.

Heat and Fluid Flow

A number of investigators have provided heat flow models for welding involving a moving point source of heat. While this approximation works well away from the source, it produces erroneous predictions near the weld pool. A comprehensive model allowing for a more realistic distributed heat source is being developed. Both theory and experiment show that the size of the weld pool and the HAZ can vary by a factor of two or more for equivalent heat inputs.

Studies of fluid flow in the welding arc plasma and the molten weld pool are underway. The bulk of this work is theoretical. Somer experimental studies of the effects of convection on the size and shape of the weld pool are underway.

A comprehensive model of heat and fluid flow in electroslag welding has been completed and tested experimentally. This study indicates that there is little opportunity to vary the size of the heat affected zone by altering the welding process parameters.

The mechanism of heat transfer during laser welding of aluminum is being studied by measurements of reflectivity and plasma formation as functions of surface preparation and alloy content. Initial results indicate differences of a factor of 20 in the initial heat transfer rate depending on the particular alloy and surface preparation.

Sponsors: Department of Energy, Office of Naval Research
Faculty: T. W. Eagar, J. Szekely
Staff: C. Allemand, A. Block-Bolten, G. Oreper
Graduate Students: M. Lin, N. S. Tsai
Undergraduate Student: G. Dunn
Theses:
1. N. A. Dudziak, "Spectrographic Measurement of Metal

Vapor Concentration in a Welding Arc," S.B., June 1981.

2. C. A. Huntington, "The Reflectivity of a CO_2 Laser Beam by Aluminum," S.B , June 1981.

Mechanical Properties of Weldments

Factors influencing the fracture toughness of HY80 weld metal are being studied through investigation of high heat input variations with commercial submerged arc fluxes, and the effect of nitrogen on strain aging of the weld metal. In the former, the effects of flux composition and welding process parameters on inclusion composition, size, and distribution as well as phase transformation behavior is of interest. In the latter project, the effect of weld metal composition on the state of nitrogen is being studied with concern for the effects of residual stresses and thermal cycles in multi-pass welds. Internal friction is being used to follow the combination of nitrogen in submerged arc and gas metal arc welds.

The effects of weld repair on the fatigue properties of cast titanium have been studied. It is concluded that weld repair is not detrimental but that the final surface finishing technique should be chosen with care. In particular, chemical milling of the final part is inferior to either mechanical polishing or peening of the surface.

Sponsors: Office of Naval Research, General Dynamics Corporation, U.S. Army Materials and Mechanics Research Center

Faculty: T. W. Eagar

Graduate Students: O. Boydas, B. Wilson, G. Hunter

Thesis:

1. G. B. Hunter, "Processing Effects on the High Cycle Fatigue Life of Weld Repaired Cast Ti-6Al-4V Parts," S.M., June 1981.

3. EXPLORATORY RESEARCH ON NONDESTRUCTIVE TESTING

This project has two goals:

(a) the exploration of the dielectric singularities associated with defects in polymer-matrix composites in order to ascertain the degree of detectability and differentiation of the various defect types.

(b) exploration of the electrical properties of titanium weldments to ascertain the feasibility of electromagnetic or electrical NDE as a method of monitoring interstitial gas content.

Sponsor: Office of Naval Research
Faculty: R. M. Rose
Staff: I. M. Puffer
Undergraduate Student: J. Parse

4. OTHER RELATED PROJECTS

1. Electromagnetically Driven Flows in Materials Processing
   J. Szekely
   See -- Mathematical and Physical Modelling of Materials Processing, page 234

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F. SOLIDIFICATION PROCESSING

Faculty: T. W. Eagar
M. C. Flemings
J. F. Elliott
D. K. Roylance
D. R. Sadoway
J. Szekely

Staff: P. Charreyron
Z. Hu
G. Kenney
M. Simpson
Y. Shiohara
M. Yerebakan

SUMMARY

The Solidification Processing activities underway include the studies of Professor Flemings on behavior of semi-solid metals, purification and strengthening by fractional melting, continuous casting, control of ingot surface quality, and metal-matrix composites. Professor Elliott continues his work on formation of deoxidation products in steels. These studies are summarized below.

In addition, there are ongoing studies by many faculty members on rapid solidification. There are studies on crystal growth being conducted by Professors Witt and Gatos. In addition, there are studies on experimental and mathematical modeling of solidification processes. These studies are summarized in separate parts of Section IV of this report.

1. DEFORMATION BEHAVIOR OF SEMI-SOLID METALS

This ongoing program is concerned with the fundamental rheological behavior of semi-solid metals. Past work has been on non-dendritic "Rheocast" metals, current work is primarily on dendritic solids and on metal powders which are liquid phase sintered under pressure. Engineering applications are to better understand liquid phase sintering phenomena, and

to develop improved forming materials and purification methods for materials which are partly liquid.

Sponsor: Army Research Office, Department of Energy
Faculty: M. C. Flemings
Staff: P. Charreyron
Graduate Student: D. Pinsky
Publications:

1. V. Laxmanan and M. C. Flemings, "Deformation of Semi-Solid Sn-15 Pct Pb Alloy," Met. Trans., Vol. 11A, No. 12, December 1980, pp. 1927 - 1937.
2. T. Matsumiya and M. C. Flemings, "Modeling of Continuous Strip Production by Rheocasting," Met. Trans., Vol. 12B, No. 1, March 1981, pp. 17-31.
3. M. Suery and M.C. Flemings, "Deformation Behavior of Semi-Solid Alloys," accepted for publication, Met. Trans.

2. STRENGTHENING OF METALS BY FRACTIONAL MELTING

Ultra-high strength alloys are produced by partially melting alloy ingots and "squeezing" out interdendritic residual liquid, thereby drastically lowering impurity levels and residual second phases. Properties in wrought material produced by these ingots are equivalent to, or better than, the best properties obtained in ingots of equivalent alloys produced by other means, including consolidation of rapidly solidified powders. Work currently is on 7000 series aluminum alloys. Mechanical properties obtained are in excess of 90,000 psi yield strength, 100,000 psi tensile strength, and 10% elongation. The process has been scaled up to 1.5 lb. ingots of aluminum, and plans are underway to extend the research to superalloys.

Sponsor: U.S. Army Armament Research and Development Command.
Faculty: M. C. Flemings
Staff: Z. Hu
Graduate Students: M. Gungor, T. Piness
Publication:

1. F. E. Goodwin, P. Davami, M. C. Flemings, "Strengthening of Wrought Aluminum Alloys by Fractional Melting," Met. Trans. A., Vol. 11A, Nov. 1980, pp. 1777-87.

3. SURFACE QUALITY OF STEEL INGOTS

This is an experimental modeling study of factors affecting ingot surface quality in steel ingots and continuous castings. Work has been on low melting point alloys in molds which have one transparent face and on steel solidifed around "dipped" bars. High speed photography has been used to record wave motion and meniscus behavior during filling, which is subsequently compared with surface and subsurface structures obtained. Wave motion and metal-mold heat transfer coefficients have an important effect. The dampening effect of a steady D.C. magnetic field on convection alters the surface wave motion significantly, greatly improves surface quality, and enhances columnar grain growth.

Sponsor: American Iron and Steel Institute
Faculty: M. C. Flemings
Graduate Students: M. Neff, D. Stemple
Publication:

1. D. K. Stemple, E. N. Zulueta, and M. C. Flemings, "Effect of Wave Motion on Chill-Cast Surfaces," submitted Met. Trans. B.

4. SECONDARY FORMATION OF DEOXIDATION PRODUCTS IN STEELS

A study is underway of the influence of the principal parameters of solidification, temperature gradient and rate of movement of the solidification front on the composition and morphology of oxides and oxysulfides that may form in steels after ladle deoxidation. The Fe-Si-O, Fe-Si-Mn-O, and Fe-Si-Mn-O-S systems are being investigated.

Sponsor: American Iron and Steel Institute
Faculty: J. F. Elliott
Graduate Student: D.-C. Hu

5. METAL MATRIX COMPOSITES

Metal matrix composites, consisting of a light metal matrix and high strength ceramic fibers, show promise for engineering applications where high modulus, high temperature strength, or high fatigue strength are required. Emphasis of this program is on fundamental aspects of setting and interface reactions in infiltration processes.

Sponsor: U.S. Army Armament Command
Faculty: M. C. Flemings
Graduate Student: D. Pinsky

6. OTHER RELATED PROJECTS

Solidification, in the generic sense, permeates much of the ongoing materials processing research. The following sections involve a variety of aspects of solidification processes:

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G. MATHEMATICAL AND PHYSICAL MODELLING OF MATERIALS PROCESSING

Faculty:		Staff:	
	R. A. Brown		P. Brewer
	T. W. Eagar		G. Chang
	M. C. Flemings		M. Choudhary
	R. M. Latanision		N. El-Kaddah
	D. K. Roylance		I. Gabbalah
	D. R. Sadoway		J. McKelliget
	J. Szekely		G. Oreper

SUMMARY

Professor Szekely's major area of research is mathematical and physical modelling of metals processing with major efforts underway on (1) turbulence, (2) electromagnetically driven flow, and (3) gas-solid reactions. Professor Roylance continues his work on numerical modelling of polymer melt processes. Professor Sadoway is modelling electroprocessing and Professor Flemings has modelling studies underway on electroslag casting and continuous casting.

1. MATHEMATICAL AND PHYSICAL MODELLING OF METALS PROCESSING OPERATIONS

Turbulence Phenomena in Metals Processing

There are many practical metals processing systems, where molten metal or slag phases undergo turbulent recirculating flow and where the characteristics of this flow play a major role in determining the overall process kinetics. The purpose of the research is to obtain an improved fundamental understanding of the nature of these flows and then to apply this understanding to the solution of practical problems.

This work involves mathematical modelling, viz the solution of the turbulent Navier-Stokes equations, physical model experiments, viz the use of laser anemometry to characterize the turbulence parameters and the flow fields in water model systems, and plate scale experiments to verify the models. The actual problems currently tackled include the erosion of blast furnace hearths, mixing and desulfurization kinetics in ladle metallurgical operations, AOD steelmaking, hot metal desulfurization, and dust removal from gases.

Sponsors: National Science Foundation, primary sponsor; fellowship support from the Brazilian Government, the People's Republic of China, and Nippon Steel Corporation

Faculty: J. Szekely

Staff: G. Chang, N. El-Kaddah

Graduate Students: L. Britto, R. Figueira, T. Kang, K. Shirable

Electromagnetically Driven Flows in Materials Processing

Electromagnetically driven flows play an important role in many metals processing operations, such as Electro-slag Refining, Electro-slag and Arc Welding, Electric Arc Steelmaking, Induction Stirring, and the like. The purpose of this program is to develop a quantitative representation of the electromagnetically driven fluid flow phenomena in these systems.

The current work includes the modelling of ESR systems concerning pool profiles and temperature profiles. The theoretical predictions have been found to be in excellent agreement with measurements obtained both in the laboratory and on industrial scale installations.

Work is also in progress on the modelling of Electro-slag and Arc Welding operations; the emphasis is to relate the role played by the principal operating parameters in determining the structure and the properties of the welds produced. Here again, the theoretical predictions were found to be in good agreement with the measurements. The research concerning the modelling of electric arc furnaces is aimed at representing the plasma region formed between the electrodes, with the ultimate objective of defining the optimum arc length for a given set of operating conditions.

Electromagnetically driven flows also play an important role in the work aimed at modelling grain refining in space processing applications. Here the specimens are positioned by electro-magnetic forces, which may also induce motion. The purpose of the work is to define the fluid motion resulting from the positioning forces, both during the flight and in the land based experiments. This understanding of the fluid flow field should be helpful in the development of grain refining modules.

Sponsor: National Science Foundation
Faculty: J. Szekely
Staff: M. Choudhary, J. McKelliget, G. Oreper
Graduate Student: A. Murthy

Gas-Solid Reactions

In terms of tonnages handled, the reduction of iron oxides and the gasification of coke in the iron blast furnace are perhaps the two most important metallurgical applications of gas-solid reaction systems.

The work which is being carried out is largely experimental,

aimed at developing an improved understanding, how the solid structure and the mode of preparation affects the rate at which coke particles react with CO_2/CO gases under conditions which are representative of the iron blast furnace.

Parallel with this investigation the rate of iron oxide reduction is also being studied, so that a composite picture may be developed of the coupled gas - solid reaction system, namely iron oxide reduction - coke gasification that controls the performance of the iron blast furnace.

Sponsor: NATO - through Fellowship support
Faculty: J. Szekely
Staff: I. Gabbalah

The Modelling of Rapid Solidification Processes

This program of research involves the development of mathematical models of rapid solidification processes, with the objective of relating the processing conditions to the cooling rates that may be realized in given applications.

Recent work includes the modelling of splat cooling, using the piston and anvil technique, and the operating of the twin roll quenching technique.

In this latter work, allowance has been made for two dimensional fluid flow, heat flow, and plastic deformation and the governing equations were solved numerically. The theoretical predictions were compared with measurements and it was found that for this system there is only a very limited range of the process variables over which stable operation may be maintained.

Sponsor: Mexican Government (through Fellowship support)
Faculty: J. Szekely
Staff: N. El-Kaddah
Student: M. Guttierez

Electroslag Casting

This program is a mathematical and experimental model of the electroslag casting process, including study of thermal behavior, macrosegregation, and internal stresses.

Sponsor: National Science Foundation
Faculty: M. C. Flemings
Staff: M. Simpson, M. Yerebakan
Graduate Student: A. Jain

2. THE ROLE OF COPPER IONS AND OTHER CATHODIC DEPOLARIZERS IN THE CORROSION OF ALUMINUM IN SEAWATER

Four materials -- titanium, plastics, stainless steel, and aluminum alloys -- are considered as candidates for the construction of heat exchangers in ocean thermal energy conversion (OTEC) systems. Of these, aluminum alloys appear attractive as the material of construction of heat exchanger tubes. Certain components (intake screens, etc.). however, must be made from materials which resist fouling such as alloys of copper. Copper ions, on the other hand, are likely to accelerate the localized corrosion of aluminum alloys. In this program, the mechanism by which copper ions affect pit initiation on aluminum alloys in seawater is being pursued with a view toward corrosion control under service conditions. Likewise, the effect of bacterial fouling on this process will also be

studied. A scanning potential microprobe has been constructed for use in this work. This research to date has shown that the oxide films formed on aluminum in seawater are different from those formed in laboratory saline solutions, the most significant difference being the presence of substantial Mg concentration on the surface exposed to seawater. We have, during the past year, computer modeled the speciation of complex solutions and the adsorption of ions on aluminum surfaces in seawater. This program is part of the MIT/WHOI Joint Program in Materials Science and Ocean Engineering.

Sponsor: MIT Sea Grant
Faculty: R. M. Latanision
Staff: P. Brewer (WHOI)
Graduate Student: S. W. Smith

3. COMPUTATIONAL AND EXPERIMENTAL STUDIES OF VISCOELASTIC FLOWS

The ability to quantitatively predict the flow of viscoelastic fluids for describing the flow of polymeric solutions used in coating operations and in the design of dies for casting thermoplastics and thermosets is the long term goal of this project. Our research is aimed ultimately at developing numerical methods for calculating the flow of viscoelastic fluids in such complicated geometries and at careful experimental measurements of velocities in these flows. These combined approaches will give us the ability to test constitutive equations for these flows.

All present numerical methods fail when elastic effects are comparable to or greater than viscous effects. We have tracked this failure to inadequacies in the numerical schemes

for approximating the elastic portion of the stress, which may have steep gradients near corners and contractions in the flow. These steep gradients have been demonstrated for finite element based calculations with contravariant convected Maxwell and second-order fluid models. Improvements to the finite element method that will allow accurate approximation of these stress fields are being developed.

Sponsor: MIT Sloan Fund, Union Carbide

Faculty: R. A. Brown and R. C. Armstrong

Graduate Students: A. Beris, M. Kim-E, P.-W. Yeh, M. A. Mendelson

Thesis:

1. M.A. Mendelson, "On the Numerical Solution of Viscoelastic Flow," M.S. thesis.

Publications:

1. M.A. Mendelson, P.-W. Yeh, R.A. Brown, and R.C. Armstrong, "Approximation Error in Finite Element Calculation of Viscoelastic Fluid Flows," J. Non-Newtonian Fluid Mech., in press (1981).
2. H.M. Ettouney and R.A. Brown, "Effect of Heat Transfer on Melt/Solid Interface Shape and Solute Segregation in Edge-Defined Film-Fed Growth: Finite Element Analysis," J. Crystal Growth, submitted.
3. C.J. Chang and R.A. Brown, "Effect of Steady Buoyancy-Driven Convection on Melt-Solid Interface Shape and Radial Solute Segregation in Vertical Bridgman Growth," J. Crystal Growth, submitted.
4. G. Harriott and R.A. Brown, "The Fluid Mechanics of a Differentially Rotated Captive Drop," J. Fluid Mech., submitted.
5. Y. Yamaguchi, C.J. Chang and R.A. Brown, "Axisymmetric Buoyancy-Driven Convection in a Vertical Cylinder Heated from Below," J. Fluid Mech. to be submitted.

4. OTHER RELATED PROJECTS

1. Numerical Modelling of Polymer Melt Processing
   D. K. Roylance
   See -- Effect of Processing on Polymer/Composite Structures and Properties, page 193.

2. Modelling of Materials Supply, Demand, and Price
   J. P. Clark
   See -- Materials Systems Analysis, page 211.

3. Heat and Fluid Flow (in Welding Processes)
   T. W. Eagar
   See -- Welding Research, page 225.

4. Surface Quality of Steel Ingots
   M. C. Flemings
   See -- Solidification Processing, page 230.

5. Studies of Zinc Electrorefining
   D. R. Sadoway
   See -- Electroprocessing Research, page 242.

6. Transport Phenomena in Improved Electrochemical Cell Designs for the Production of Magnesium
   D. R. Sadoway
   See -- Electroprocessing Research, page 243.

7. Fluid Flow in Crystal Growth
   R. A. Brown
   See -- Semiconductor Processing, page 258.

N82 27402

H. ELECTROPROCESSING RESEARCH

Faculty: D. R. Sadoway Staff: J. Flint

SUMMARY

It is generally true that electrodeposited metal is of better quality than the thermal reduction product. However, for many metals, notably the refractory metals, hydrometallurgical routes are closed because the decomposition potentials exceed that for hydrogen evolution and the metallic ions undergo redox reactions with the solvent. However, when these metals are deposited from high temperature non-aqueous electrolytes, the solid electrodeposites are powdery and/or dendritic. The challenge is to make coherent solid metal.

Research in electroprocessing at MIT under the direction of Prof. D. R. Sadoway is concerned with the study of the fluid dynamics of the electroreduction process to determine how it may be modified to improve the quality of the deposit. A variety of experimental techniques, some uncommon to electroprocessing, is being used in this research. These include laser Schlieren photography, laser Doppler velocimetry, and frequency spectrum analysis. The work is sponsored both by government and industry. The specific projects involve fluid flow studies of zinc plating in aqueous and molten salt electrolytes (NASA), cell design studies for magnesium chlorides electrolysis (DOE), digital signal analysis of manganese electrodeposition in molten chlorides (NSF), and electroplating of molybdenum from low melting salts (Dow Chemical). This last project is particularly significant as it represents endorsement by industry of the electroprocessing effort and stands alone at MIT as a project involved in the primary processing of

refractory metal. Looking to the future, one sees growth in the use of refractory metals as materials of construction in engineering. Their electrodeposition from molten salt electrolytes could weigh heavily in the extraction metallurgy of refractory metals.

There is another emerging area of interest which will have a bearing on electroprocessing research in the Materials Processing Center. The problem of producing coherent metal deposits of high surface quality is one faced by electronic device manufacturers. According to industry sources, very little work is being done in the universities on this problem. For example, copper plating of multilayer circuit board interconnects from sulfate baths would fall into this category. It is expected that research activity will grow in this area almost exclusively through industrial support.

1. STUDIES OF ZINC ELECTROREFINING

To understand better the electrodeposition process, fluid flow patterns in the electrolyte are being followed by laser Schlieren photography in order to determine how mass transport affects the morphology of the metal deposit. Zinc is being studied as it is electrorefined both in aqueous electrolytes and in transparent molten salt electrolytes. Process variables such as current density and composition of the electrolyte are adjusted to change the morphology of the electrodeposit and, thus, to permit the study of the nature of electrolyte flow in relation to the quality of the electrodeposit.

Sponsor: National Aeronautics and Space Administration
Faculty: D. R. Sadoway
Graduate Student: A. Abdelmassih
Undergraduate Student: P. T. Rogers

Theses:

1. A. Abdelmassih, "Fluid Flow Sutdies of Zinc Electrolysis in Acid Chloride Solutions," due January, 1982.
2. P. T. Rogers, "A Laser Schlieren Study of Electrolyte Flow Patterns During the Electrorefining of Zinc from ZnC_{12}-LiClKCl Melts," S.B., June 1982.

2. TRANSPORT PHENOMENA IN IMPROVED ELECTROCHEMICAL CELL DESIGNS FOR THE PRODUCTION OF MAGNESIUM

Increased use of magnesium as a structural material in transportation vehicles will significantly reduce fuel consumption. At present the restricted use of magnesium by the automotive industry is as much the result of inadequate capacity as price. To learn how transport phenomena in molten salt electrolysis cells affect magnesium production rates the effects of (a) forced convection of the electrolyte, (b) electrode configuration: vertical vs. horizontal; monopolar vs. bipolar, and (c) applied electromagnetic field will be studied. With the use of transparent laboratory magnesium electrolysis cells, not only will cell operating characteristics be measured, but the electrolysis process itself will be observed visually. The result of this work will serve to guide future developments in high yield cell designs.

Sponsor: Department of Energy
Faculty: D. R. Sadoway
Graduate Student: S. Dokras

3. HIGH PURITY MANGANESE BY FUSED CHLORIDE ELECTROLYSIS

Electrochemical cells have among the lowest metal production rates of any metallurgical reactor. Molten salt

electrolysis cells are particularly poor in this regard owing to their primitive designs for the most part. To determine whether digital signal analysis by fast Fourier transform of the cell voltage during operation can serve as the basis of diagnosis instrumentation for optimization and automation of electrolytic metal productin processes the electrodeposition of manganese from molten alkali chlorides is being studied.

Sponsor: National Science Foundation
Faculty: D. R. Sadoway
Staff: J. Flint

4. ELECTRODEPOSITION OF MOLYBDENUM FROM LOW MELTING SALTS

High purity molybdenum is a very desirable material due to its strength to weight ratio and corrosion resistance (particularly with respecc to molten metals). Electrodeposition of molybdenum is attractive because with this process come the prospects of plating a refractory metal coating onto less costly base metal.

Sponsor: Dow Chemical
Faculty: D. R. Sadoway

N82 27403

I. SEMICONDUCTOR PROCESSING

Faculty: R. C. Armstrong
R. A. Brown
P. K. Houpt
T. B. King
W. M. Rohsenow
A. F. Witt

Staff: E. D. Bourret
T. Carlberg
J. R. Carruthers
K. Crouch
J. Fan
C. J. Herman
Z.-J. Xing
Q.-M. Zhou

SUMMARY

The primary thrust of the semiconductor processing group is directed (1) at advancing the theoretical basis for bulk growth of elemental and compound semiconductors in single crystal form and (2) at developing new experimental approaches by which semiconductor matrices with significantly improved crystalline and chemical perfection can be obtained. This effort, which evolved primarily with NASA and Air Force support, has recently been strengthened through DARPA which made it possible to acquire all instrumentation required to engage in a meaningful and comprehensive study of most advanced approaches to silicon crystal growth. The research base, moreover, could be enlarged through an industrial grant (Mobil), generous donations of instrumentation for both crystal growth and characterization by industry (T.I., BTL, Western Electric, and Semicon) and through industrial collaboration in sponsored research (H.P.). Implementation of the projected research expansion, directed toward the capability of growth of 4" diameter silicon crystals, has now been made possible through the allocation of additional laboratory space which is currently being modified to meet requirements. To broaden the theoretical and experimental research potential of the group, both intra- and interdepartmental programs were established

which involve the areas of process metallurgy Professor King), heat transfer (Professor Rohsenow), mass transfer Professor Brown) and systems control (Professor Houpt). Through NASA sponsorship, a cooperative research effort with the French Atomic Energy Commission (C.E.N. Grenoble) on solutal convection in melt growth systems could be expanded.

1. ANALYSIS OF CRYSTAL GROWTH AND SEGREGATION IN VERTICAL BRIDGMAN CONFIGURATION

Crystal growth and segregation in vertical seeded Bridgman configuration was experimentally studied using Ge-Ga as a test system. Using coded interface demarcation (CID) and spreading resistance measurements, it was possible to determine in post-growth analyses the shape and location of the solidification isotherm within the hot-zone as a function of time and to establish quantitatively the axial and radial segregation behavior.

It is found that, depending on the axial thermal gradient in the growing crystal, the microscopic rate of growth does not reach a steady state value and deviates from the mechanical lowering rate by up to and in excess of ±50%. Upon arrest of ampoule lowering, thermal (and chemical) equilibration for periods ranging from 5 minutes to 120 minutes resulted in all instances in a relocation of the solidification isotherm (crystal-melt interface).

Quantitative composition analyses based on spreading resistance measurements indicate that radial segregation increases with continuing growth, but is significantly less than predicted by the Corriell-Sekerka theory.

Anomalous, quantitatively reproducible segregation behavior is observed for gallium in germanium. Contrary to normal

segregation theories, it is found that for growth rates of less than 1 μm/s, the concentration of Ga in Ge increases with decreasing rates of growth. There is evidence that an inverse relationship for the interface distribution coefficient dependence on the growth rate exists. The presently reported results are used as a basis for the design of a Bridgman system in which two-dimensional heat flow is established about the crystal-melt interface.

Sponsor: National Aeronautics & Space Administration
Faculty: A.F. Witt
Staff: J.R. Carruthers
Graduate Student: C. Wang
Publication:

1. C. Wang, J.R. Carruthers and A.F. Witt, "Analysis of Crystal Growth and Segregation in Vertical Bridgman Configuration," Proc. of the ICVGE-5/ACCG-5, Coronado, CA, July 19-24, 1981.

2. THE EFFECT OF DIRECT CURRENT ON CRYSTAL GROWTH FROM THE MELT: InSb

Passage of direct current across a crystal-melt interface has been shown to affect the growth rate and segregation on a microscale. In this study, pulses of direct current with predetermined amplitude/time characteristics were passed across the liquid/solid interface during Czochralski pulling of doped InSb crystals for the purpose of producing spatially uniform alternating regions of high and low impurity concentration. [Such a "superlattice" is expected to function as a matrix for a tunable spin flip Raman laser (SERL) to operate in the far infrared region.] The influence of temperature control and crucible design on current-induced layer characteristics was quantitatively investigated through the use of simultaneous interface demarcation during

current pulsing. The experimental results were compared to a theoretical analysis utilizing a finite-difference numerical solution to the time-dependent energy transport equations and found to be in quantitative agreement. A theoretical transient segregation analysis was performed using experimental microscopic growth rate data in conjunction with the numerical solution of the time-dependent mass transport equation calculated by J. Favier. The results are found to be in qualitative agreement for long duration (20s) pulses. It is shown that the application of direct current pulses during crystal growth from the melt provides a means for the in situ measurement of the Peltier coefficient of a solid semiconductor in contact with its own melt.

Sponsor: National Aeronautics & Space Administration
Faculty: A. F. Witt
Graduate Student: M. Wargo

3. THEORETICAL APPROACH TO THE DESIGN OF A VERTICAL BRIDGMAN GROWTH CONFIGURATION

Heat transfer in a vertical Bridgman crystal growth system is analyzed with the intent of achieving optimized axial and radial temperature gradients in the vicinity of the growth interface through controllable experimental variables. The Bridgman system considered is composed of a hot and cold heat pipe separated by a region called the gradient zone in which the growth interface is located. The gradient zone comprises elements which prevent the establishment of satisfactory thermal gradients near the interface. A one-dimensional heat transfer model that neglects radial temperature gradients in the charge has been developed for the determination of the axial temperature distribution. Effects of charge motion, thermal coupling to the heat pipes, charge length, gradient zone length, latent heat,

conductivity change at the interface, crucible conductivity, and thickness could thus be demonstrated. Thermal coupling to the furnace (expressed by the non-dimensional Biot parameter, Bi), gradient zone length and conductivity change were shown to be parameters which strongly affect the axial gradient in the liquid at the interface. The origins of radial temperature gradients in the gradient zone has been considered in an extension of the one-dimensional model. It could be shown that Bi, as well as the temperature difference between the furnace and charge, in the gradient zone have a pronounced effect on radial temperature gradients. Strategies aimed at reducing critical radial gradients were developed and provide the basis for further analysis and systems design.

Sponsor: National Aeronautics & Space Administration
Faculty: W. M. Rohsenow, A. F. Witt
Graduate Student: T. Jasinski
Publications:

1. T. Jasinsi, W.M. Rohsenow, A.F. Witt, "Vertical Bridgman Type Crystal Growth: A Heat Transfer Analysis. Part I: Axial Temperature Distribution According to One-Dimensional Models," submitted to J. of Crystal Growth.
2. T. Jasinski, W.M. Rohsenow, A.F. Witt, "Vertical Bridgman Type Crystal Growth: A Heat Transfer Analysis, Part II: Radial Temperature Distribution According to Two-Dimensional Models," submitted to J. of Crystal Growth.

4. THEORETICAL ANALYSIS OF DIRECTIONAL MELT-BACK

A theoretical analysis of directional back-melting, which constitutes the initial step in all seeded crystal growth experiments, has been conducted for binary systems. It is

found that the achievenent of steady state conditions is strongly influenced by the magnitude of the liquidus-solidus separation; while steady state is readily reached in "doped" semiconductor systems, it cannot be reached in systems with large liquidus-solidus separation such as $Hg_{0.8}Cd_{0.2}Te$, for example. The analysis reveals, as a major complication in seeded vertical Bridgman growth, that upon initiation of growth the crystal-melt interface is not, as generally assumed, at the liquidus temperature, but at a temperature which is significantly lower than predicted from equilibrium phase diagrams. The equilibration process, following back-melting, has been investigated for the case where the seed-melt system prior to back-melting is not at equilibrium composition ($CS = C_L/k_o$). In this case, the behavior of a given system after arrest of back-melting is strongly affected by the respective values of the initial solid and liquid composition; the result will be spontaneous solidification, melting, or equilibration by solid and liquid state diffusion prior to controlled regrowth. The primary theoretical conclusions of this analysis are currently subject of experimental verification.

Sponsor: National Aeronautics & Space Administration
Faculty: A. F. Witt
Staff: E. D. Bourret
Publication:

1. E. D. Bourret and A. F. Witt, "Theoretical Analysis of Directional Melting," Proc. of the ICVGE-5/ACCG-5, Coronado, CA, July 19-24, 1981.

5. DYNAMIC OXYGEN EQUILIBRIUM IN SILICON MELTS DURING CRYSTAL GROWTH BY THE CZOCHRALSKI TECHNIQUE

A model for the dynamic oxygen level in silicon melts during Czochralski growth was established on the basis of balanced

oxygen fluxes through the melt. The theory predicts first order effects in good agreement with experimental results and accounts well for both absolute oxygen concentration and its axial variation in grown crystals. Basic approximations in the model limit its usefulness for a detailed analysis of second order effects. On the basis of this model it is proposed that axially uniform oxygen incorporation into growing crystals can be achieved by compensating the continuously increasing surface ratio (A_s/A_c) through controlled immersion of auxiliary quartz surfaces or alternately through a controlled decrease in δ_c, the diffusion boundary layer thickness, at the crucible melt interface.

Sponsor: Defense Advanced Research Projects Agency
Faculty: T. B. King, A. F. Witt
Staff: T. Carlberg
Publication:

1. T. Carlberg, T. B. King and A. F. Witt, "Dynamic Oxygen Equilibrium in Silicon Melts During Crystal Growth by the Czochralski Technique," J. of the Elec. Soc., 129 (1) 189 (1982).

6. DYNAMICS OF OXYGEN INCORPORATION DURING CZOCHRALSKI SILICON GROWTH

The incorporation and distribution of oxygen during conventional Czochralski silicon growth has been studied in commercial crystals and was compared with a theoretical model recently developed. The comparison allows conclusions concerning the transport of oxygen from the crucible into the melt. It was found that the flux of dissolved oxygen into the melt is diffusion controlled with both melt flow and melt temperature affecting the dissolution rate.

The behavior of oxygen in silicon was examined by several experimental techniques; infrared spectroscopy was used to measure interstitial oxygen, spreading resistance to measure electrically active oxygen, and chemical etching to reveal crystallographic defects related to oxygen. The findings of all three techniques indicate non-uniform dissolved oxygen and precipitate distribution attributable to the crystal growth process and to automatic growth control functions.

Sponsor: Defense Advanced Research Projects Agency
Faculty: A. F. Witt
Graduate Student: D. Bliss
Publication:

1. D. F. Bliss, "Dynamics of Oxygen Incorporation During Czochralski Silicon Growth," S.M. Thesis, Department of Materials Science & Engineering, June, 1981.

7. AUTOMATIC DETERMINATION OF PID PARAMETERS FOR TEMPERATURE CONTROL IN CRYSTAL GROWTH SYSTEMS

The most common means of temperature control in crystal growing systems uses a thermocouple for temperature feedback and a standard proportional plus integral plus derivative (PID) series compensator. Owing to the length of the time constants in these systems, manual online tuning procedures tend to be tedious, time consuming, unrepeatable and unreliable. An effort was made to develop an off-line computer-aided procedure for choosing acceptable PID controller parameters.

The process of choosing the controller parameters can be divided into the following six steps. (1) Quantify system performance: In this case, acceptable performance is defined in terms of the thermocouple response to step changes in commanded temperature. The requirements are zero

steady state error, no overshoot and settling time between one-tenth and one-half that of the uncontrolled plant. (2) Formulate a plant model: A simple first-order lag was used to relate thermocouple output to power amplifier input. Thus, $(dx/dt) = x/T + (Ku)/T$, where x = thermocouple output (volts), u = power amplifier input (volts), K = plant DC gain (volts/volt) and T = plant time constant (secs). (3) Design the controller: Since we are restricted to the PID control structure, the controller output (i.e. power amplifier input) is given by $u = -G_1(x-x_r) - G_2 \int_0^t (x-x_r)dt - G_3(d/dt)(x-x_r)$ where x_r is the reference signal to be tracked and G_1-G_3 are constant gains to be determined. The simplest approach is to use a PI compensator: choose the compensator zero to cancel the plant pole; choose the compensator gain such that the DC loop gain is equal to the desired closed loop pole. Therefore, $G_1 = 10/K$, $G_2 = 10/KT$ and $G_3 = 0$. (4) Formulate a discrete time plant model: The following difference equation can be written: $x(nP+P) = Ax(nP) + Bu(nP)$, where $A = \exp(-P/T)$, $B = K(1-A)$, n = number of the sampling interval and P = duration of sampling interval (secs). (5) Evaluate the plant parameters: A computer with appropriate A/D conversion hardware is used to monitor input (u) and output (x) as arbitrary excitations are manually applied to the system. A least squares estimate for A and B is then found by simple linear regression. (6) Evaluate PID controller gains: Solving the difference equation and substituting in G_1 and G_2 yields $G_1 = (10/B)(1-A)$ and $G_2 = (-G_1 \ln A)/P$. A digital simulation of the proposed closed loop system was implemented. A computer code was written to perform the linear regression parameter identification from stored data.

Sponsor: National Aeronautics & Space Administration
Faculty: P. K. Houpt, A. F. Witt
Graduate Student: G. Goodman

8. APPLICATION OF SOFT MOLD TOTAL LIQUID ENCAPSULATION TO GROWTH OF CdTe BY THE VERTICAL BRIDGMAN TECHNIQUE

An analysis of reported work on growth of CdTe suggests that the failure to achieve adequate crystalline perfection is largely related to deficient heat flow control (unfavorable and changing growth interface morphology), heterogeneous nucleation at crucible walls, stresses induced by the confinement, and to inadequate control over stoichiometry. A growth system is currently being developed in which the crystal-melt interface morphology can be changed in a controlled manner from concave through planar to convex by making use of two coaxially aligned heat pipes separated by a "graded" heat guide zone. Preliminary studies indicate that complications arising from solid confinement materials can be avoided through the use of soft-mold, total liquid encapsulation with B_2O_3. This approach is based on the use of three coaxial cylinders consisting of BN (ampoule), B_2O_3 and porous high purity graphite surrounding the cast CdTe charge. The ampoule system is configured so as to provide for isolation of the liquid encapsulated crystal from the confining graphite and BN cylinder prior to solidification of the encapsulant.

Sponsor: Defense Advanced Research Projects Agency
Faculty: A. F. Witt

9. LEC GROWTH AND CHARACTERIZATION OF InP

With the cooperation of the Electronic Materials Group at the Lincoln Laboratories, a comprehensive study of synthesis and LEC growth of InP was initiated at AFCRL. In initial growth experiments, four out of four undoped charges yielded multiple-twinned to polycrystalline crystals. After establishing rigorous cleaning procedures, revising the

out-baking process, replacing a conventional susceptor with a susceptor of UHP Poco graphite and using B_2O_3 of higher purity, nine out of eleven charges yielded untwinned single crystals. The defect density achieved with the modified growth procedure in which the thermal configuration remained unaltered was in the low 10^3 range. Attempts to establish a meaningful relationship between the charge carrier mobilities of InP ingots and those of crystals grown by the LEC method were unsuccessful until quite recently when, with the modified growth procedure, it was found that a correlation does exist. Details of this correlation are currently under investigation. During this study it was found that Hall mobilities determined on the same samples in two laboratories yielded noticeably different values. A study of the causes for the differences has been initiated.

The primary thrust of this investigation is aimed at the effects of solid solution hardening and the influence of liquid encapsulation on growth and segregation. A complementary study of the specific effects of liquid B_2O_3 encapsulation is carried out on campus.

Sponsor: Air Force - Rome Air Development Center
Faculty: A. F. Witt
Staff: J. Fan
Graduate Student: B. Ahern

10. EFFECTS OF LIQUID ENCAPSULATION ON CRYSTAL GROWTH AND SEGREGATION DURING CZOCHRALSKI PULLING

The purpose of the present study was to determine the effects of liquid encapsulants on the segregation and growth behavior in Czochralski configurations. For this purpose, Ge-Ga was selected as a test system since it permits growth with and without liquid encapsulation and thus an

unambiguous analysis of the effects of encapsulants on the thermal melt characteristics and on the growth and segregation behavior. The melt characterization was conducted with an assembly of stationary and rotating thermocouples; the growth and segregation behavior was studied making use of coded growth interface demarcation and spreading measurements.

Preliminary results obtained indicate the establishment of enhanced turbulent melt convection as a result of B_2O_3 encapsulation. It is also observed that under constant thermal boundary conditions microsegregation in the central facet growth region changes from growth rate controlled to boundary layer controlled with use of B_2O_3 as liquid encapsulant. A detailed study of the observed pronounced differences in growth and segregation behavior with and without liquid B_2O_3 is in progress.

Sponsor: Air Force - Rome Air Development Center
Faculty: A. F. Witt
Staff: Q.-M Zhou
Publication:

1. Q.-M. Zhou and A. F. Witt, "Effects of Liquid Encapsulation on Crystal Growth and Segregation During Czochralski Pulling," Proc. of the ICVGE-5/ACCG-5, Coronado, CA, July 1924, 1981.

11. EFFECTS OF CONICAL INFRARED REFLECTORS ON CRYSTAL GROWTH AND SEGREGATION DURING CZOCHRALSKI PULLING

In an effort to establish optimized crystal growth conditions for InP it was found that the heat transfer conditions across the crystal-melt interface and in the lower part of the crystal largely control the growth behavior, segregation, and crystal perfection. Controllability of

heat transfer in the critical regions is studied through the use of conical IR reflectors installed coaxially about growing crystals. To avoid complications associated with high pressure growth conditions, Ga-doped Ge is used as a model system.

It is found that with the installation of the reflector, thermal asymmetry effects on growth become immeasurable and that the microscopic rate of growth becomes constant at all parts of the crystal-melt interface. Segregation studies indicate that the effective segregation coefficient during growth with a reflector increases significantly, which suggests a reduction in convective melt flow and a corresponding increase in the diffusion boundary layer thickness. Associated with the increase in the diffusion boundary layer thickness is an increased sensitivity of segregation to variations in bulk convective flow. Related to it, pronounced variations in dopant incorporation (segregation) are observed under conditions of constant microscopic rate of growth. These composition variations remain in all instances confined to the central facet growth region; peripheral off-facet regions exhibit uniform composition during all phases of growth.

It is found that the use of IR reflectors decreases the sensitivity of the system to growth interface breakdown associated with constitutional supercooling. All crystals grown with IR reflectors were dislocation-free (EPD < 100/cm^2) while for growth without reflectors the dislocation density ranged from 300 to 2000/cm^2. Detailed studies of the cause and effect relationships for growth with reflectors are in progress.

Sponsor: Air Force - Rome Air Development Center
Faculty: A. F. Witt
Staff: Z.-J. Xing

12. PREPARATION OF ORIENTED GaAs BICRYSTAL LAYERS BY VAPOR-PHASE EPITAXY USING LATERAL OVERGROWTH

A novel technique that utilizes vapor-phase epitaxy to grow bicrystal semiconductor layers with predetermined rotation axis, misorientation angle, and grain boundary plane was developed. The geometrical structure of the grain boundary in each layer is therefore completely specified. The technique has been demonstrated by using the AsC_{13}-GaAs-H_2 method to grow a series of GaAs bicrystals, each containing a [110] tilt boundary formed by a grain with a (111)B boundary plane and a grain rotated from (111)B by a selected misorientation angle. The results of initial electrical measurements indicate that the height of the potential barrier associated with each grain boundary varies systematically with the misorientation angle.

Sponsor: Air Force - Rome Air Development Center; Solar Energy Research Institute

Faculty: A. F. Witt

Staff: J. Fan

Graduate Student: J. Salerno

Publication:

1. J. P. Salerno, R. W. McClelland, P. Vohl, J.C.C. Fan, W. Macropoulos, C. O. Bozler and A. F. Witt, "Preparation of Oriented GaAs Bicrystal Layers by Vapor-Phase Epitaxy Using Lateral Overgrowth," Proceedings of Annual Materials Research Society Meeting, Boston, MA, Nov. 16-19, 1981.

13. FLUID FLOW IN CRYSTAL GROWTH

This research program is a comprehensive theoretical and computational study ultimately directed towards a fundamental understanding of the interactions of heat, mass, and

momentum transport in crystal growth from the melt. Emphasis has been placed on the floating zone, vertical Bridgman, Edge-Defined Film-Fed Growth processes, and on the microscale instabilities in directional solidification.

In each research project, a combination of analytical modelling and computer-aided calculation is being used to develop qualitative understanding of the relevant physics and quantitative models of the selected crystal growth processes. To do this, state-of-the-art numerical methods have been developed for handling solidification problems. Five research projects are currently underway; each is described in detail in Chapter 3, Project B1 of this report.

Sponsors: National Aeronautics and Space Administration, Mitsubishi Chemical Industries Ltd., Mobil Foundation, National Science Foundation

Faculty: R. A. Brown

Graduate Students: C. J. Chang, H. M. Ettouney, G. M. Harriott, L. H. Ungar, and Y. Yamaguchi

Publications:

1. C. J. Chang and R. A. Brown, "Finite Element Calculation of Buoyancy-Driven Convection Near a Melt/Solid Phase Boundary," to appear in Proceedings of the Second National Symposium on Numerical Methods in Heat Transfer, Hemisphere Press (1981).
2. L. H. Ungar and R. A. Brown, "The Dependence of the Shape and Stability of Captive Rotating Drops on Multiple Parameters," Philos. Trans. R. Soc. Lond., in press (1981).
3. H. M. Ettouney and R. A. Brown, "Finite Element Methods for Steady Solidification Problems," J. Comp. Physics, submitted.

N82 27404

J. ELECTRONIC MATERIALS RESEARCH

Faculty: H. C. Gatos
J. Lagowski (Senior Research Associate)

Staff: P. Becla
S. Isozumi
M. Kaminska
Y. Nanishi
K. Wada
X.-F. Yang

SUMMARY

The research program of the group is focused on semiconductor materials and aimed at the establishment of quantitative relationships underlying Crystal Growth Parameters - Materials Properties - Electronic Characteristics - Device Applications. The overall program evolves about the following main thrust areas: (1) Crystal Growth - novel approaches to engineering of semiconductor materials; (2) Investigation of materials properties and electronic characteristics on a macro- and microscale; (3) Surface properties and surface interactions with the bulk and ambients; (4) Electronic properties controlling device applications and device performance.

1. BRIDGMAN-TYPE APPARATUS FOR THE STUDY OF GROWTH-PROPERTY RELATIONSHIPS: GaAs

In a high precision Bridgman-type apparatus the investigation of relationships between crystal growth parameters and the properties of GaAs crystals was continued. Key features of the system are a heat pipe for arsenic vapor pressure control and seeding without the presence of a viewing window. Pertinent growth parameters, such as arsenic source temperature, thermal gradients in the growing

crystal and in the melt, and the macroscopic growth velocity can be independently controlled. During operation, thermal stability better than 0.02°C is realized; thermal gradients can be varied up to 30°C/cm in the crystal region and up to 20°C/cm in the melt region; the macroscopic growth velocity can be varied from 50 μm/hr to 6.0 cm/hr. The density of dislocations was found to depend critically on As partial pressure and essentially dislocation-free crystals were repeatedly grown under As pressure precisely controlled at 617°C. The free carrier concentration varied with As pressure variations. This variation in free carrier concentration was found to be associated with variations in the compensation ratio rather than with standard segregation phenomena.

Sponsor: National Aeronautics and Space Administration
Faculty: H. C. Gatos, J. Lagowski
Staff: Y. Nanishi
Graduate Student: J. Parsey
Publication:

1. J.M. Parsey, Y. Nanishi, J. Lagowski and H.C. Gatos, "Bridgman-Type Apparatus for the Study of Growth-Property Relationships: Arsenic Vapor Pressure-GaAs Property Relationship," accepted by J. Electrochem. Soc.

2. OXYGEN-INDUCED LEVELS IN GaAs

Utilizing our high precision Bridgman-type apparatus, the effects of oxygen (added in the form of Ga_2O_3 in the melt) on the characteristics of bulk GaAs single crystals were investigated. It was found that oxygen induced or enhanced electron traps, particularly the level at 0.82 eV below the conduction band; it also decreased the carrier concentration, the minority carrier diffusion length and suppressed the 1.2 eV luminescence band. All these effects

were shown to be indirectly induced by oxygen through the reduction of the Si concentration. SIMS analysis was extensively used in this study.

Sponsors: National Aeronautics and Space Administration, National Science Foundation

Faculty: H. C. Gatos, J. Lagowski

Staff: M. Kaminska, K. Wada

Graduate Student: J. Parsey

Publication:

1. M. Kaminska, J. Lagowski, J.M. Parsey, K. Wada, and H.C. Gatos, "Oxygen-Induced Levels in GaAs," presented at 1981 Symposium on GaAs and Related Compounds, Tokyo, Japan, 1981.

3. ORIGIN OF THE 0.82 eV ELECTRON TRAP IN GaAs AND ITS ANNIHILATION BY SHALLOW DONORS

The concentration of the major electron trap (0.82 eV below the conduction band) in GaAs (Bridgman-grown) was found to increase with increasing As pressure during growth. It was further found that (for a given As pressure) the concentration of this trap decreased with increasing concentration of shallow donor dopants (Si, Se and Te). Donor concentrations above a threshold of about 10^{17} cm^{-3} led to the rapid elimination of the trap. On the basis of these findings the 0.82 eV trap was attributed to the antisite defect AsGa formed during the postgrowth cooling of the crystals.

Sponsors: National Aeronautics and Space Administration, National Science Foundation

Faculty: H. C. Gatos, J. Lagowski

Staff: M. Kaminska, K. Wada

Graduate Student: J. Parsey

Publications:

1. J.M. Parsey, Y. Nanishi, J. Lagowski and H.C. Gatos, "Electron Trap-Free Low Dislocation Melt-Grown GaAs," J. Electrochem. Soc. 128, 936 (1981).
2. J. Lagowski, H.C. Gatos, J.M. Parsey, K. Wada, M. Kaminska and W. Walukiewicz, "Origin of the 0.82 eV Electron Trap in GaAs and Its Annihilation by Shallow Donors," accepted by Appl. Phys. Lett.

4. ELECTROEPITAXIAL GROWTH OF BULK GaAs

In Czochralski-type apparatus bulk GaAs growth (single crystals with a thickness of the order of millimeters) was successfully carried out electroepitaxially at 900°C (isothermal liquid phase epitaxy initiated and sustained by passing current through the substrate-solution interface) at growth rates more than an order of magnitude greater than those obtained in thermal liquid phase epitaxy. Preliminary characterization of these crystals showed that their properties (crystalline perfection, carrier mobility, and carrier lifetime) are comparable to those of thin epitaxial layers. This is the first time that "bulk" single crystals of GaAs have been grown from solutions more than 300°C below the melting point of GaAs.

Sponsor: National Aeronautics and Space Administration
Faculty: H. C. Gatos, J. Lagowski
Graduate Students: C. Boucher, C. Wong

5. SELECTIVE EPITAXIAL GROWTH OF GaAs BY LIQUID PHASE ELECTROEPITAXY

Selective epitaxial growth of GaAs windows (patterns) on SiO_2-masked (100) substrates was achieved by liquid phase

electroepitaxy (LPEE). Prior to growth, wells (of the desired depth) were formed in the window areas by selective current-controlled dissolution. Overgrowth on the SiO_2 layer was prevented by arresting epitaxial growth at the SiO_2 layer height. Since both selective dissolution and growth rates are proportional to the current density, the depth of the wells and the thickness of the epitaxial layers can be precisely controlled by controlling the current density and process time. Another distinct advantage of the present approach is that, following the formation of the wells, electroepitaxial growth is initiated by simply reversing the polarity of the current passing through the substrate solution interface. Best results regarding the geometry of the wells and uniformity of the epitaxial layers were achieved at relatively low current densities (less than about 15 A/cm^2).

Sponsor: National Aeronautics and Space Administration
Faculty: H. C. Gatos, J. Lagowski
Staff: X.-F. Yang
Graduate Student: C. Wong
Publications:

1. X.-F. Yang, L. Hwang and H.C. Gatos, "Selective Epitaxial Growth of GaAs by Liquid Phase Epitaxy," accepted by J. Electrochem. Soc.
2. J. Lagowski, H.C. Gatos, J.M. Parsey, K. Wada, M. Kaminska and W. Walukiewicz, "Origin of the 0.82 eV Electron Trap in GaAs and Its Annihilation by Shallow Donors," accepted by Appl. Phys. Lett.

6. "IN SITU" MONITORING THE LPE GROWTH

The in situ continuous monitoring of the LPE growth rate and growth thickness of GaAs was achieved in an electroepitaxial growth configuration where the substrate back contact was

eliminated by positioning the substrate between two segments of GaAs solutions. Monitoring is based on the measurement of the total resistance of the substrate and the growing layer. Quantitative analysis indicated that this approach enables the determination of an LPE layer thickness as low as 0.1 μm.

The in situ measurements of growth kinetics is uniquely suited for the study of growth-property relationships.

Sponsors: National Aeronautics and Space Administration, National Science Foundation
Faculty: H. C. Gatos, J. Lagowski
Staff: S. Isozumi
Graduate Student: A. Okamoto

7. ELECTROEPITAXIAL GROWTH OF InP

High quality InP layers were grown electroepitaxially from In-P solutions. The growth rate of these layers was found to be proportional to the current density. Growth rates greater by more than one order of magnitude than in thermal LPE were achieved. These results indicate that the growth of "bulk" InP crystals of epitaxial quality is possible.

Sponsor: National Aeronautics and Space Administration
Faculty: H. C. Gatos, J. Lagowski
Staff: X.-F. Yang

8. ENHANCEMENT OF INTERFACE STABILITY IN LIQUID PHASE ELECTROEPITAXY

The thermodynamic as well as the dynamic constitutional supercooling criteria were derived for liquid phase

electroepitaxy (LPEE) taking into account the Peltier effect and electromigation, which control the growth interface temperature and the mass transport in the solution, respectively. It was shown that solute transport by electromigration enhances significantly the interface stability during growth. Thus, this treatment explains the experimentally attained stable electroepitaxial growth with velocities as high as 25 μm/min. Furthermore, it defines the geometry of the LPEE configuration and the growth parameters (current density and polarity, temperature and substrate characteristics) which lead to the optimization of surface morphology.

Sponsors: DARPA, National Aeronautics and Space Administration

Faculty: H. C. Gatos, J. Lagowski

Graduate Student: A. Okamoto

Publication:

1. A. Okamoto, J. Lagowski and H.C. Gatos, "Enhancement of Interface Stability in Liquid Phase Electroepitaxy," accepted by J. Appl. Phys.

9. ISOTHERMAL GROWTH OF HgCdTe

$Hg_{1-x}Cd_xTe$, n-type, layers with low carrier concentration and high carrier mobilities (approaching theoretical values) were obtained, for the first time, in the "as-grown state," i.e., without the standard post-growth annealing in Hg-rich atmosphere. This achievement was the result of the discovery that in isothermal growth, $Hg_{1-x}Cd_xTe$ layers of a given composition and optimum electronic properties can be grown only from a source of a well-defined composition and at well-defined temperature. Such layers also exhibit mirror-like surface morphology, and their composition is highly uniform radially and axially (to a depth up to about 15 μm).

Sponsor: DARPA

Faculty: H. C. Gatos, J. Lagowski

Staff: P. Beela

Graduate Student: H. Ruda

Publication:

1. P. Beela, J. Lagowski, H.C. Gatos and H. Ruda, "A Modified Approach to Isothermal Growth of Ultra-High Quality HgCdTe for Infrared Applications," J. Electrochem. Soc. 128, 1171 (1981).

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K. METALS PROCESSING

Faculty: J. L. Bostock
J. P. Clark
J. F. Elliott
M. C. Flemings
R. Kaplow
T. B. King
R. M. Latanision
M. L. A. MacVicar
R. M. N. Pelloux
T. A. Ring
R. M. Rose
D. R. Sadoway
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Staff: R. G. Ballinger
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S. F. Cogan
C. W. Finn
I. Gabbalah
R. Gelinas
G. B. Kenney
I. V. Klumpar
I. M. Puffer
P. Stohr
P. Tedrow
M. A. Weiss

SUMMARY

The metals processing effort is directed towards improvement of performance and usefulness of materials through modification and control of shape and internal structure. This includes the efforts of Professor King to analyze the interaction of reactive gases, introduced into a plasma arc, with iron alloys. Professors Flemings, Clark, Sadoway, Szekely, and Dr. Kenney have completed an assessment of the technology of magnesium production. The study of fast fluidized bed reactors is being continued by Professor Elliott. Aspects of separation processes are being investigated by Professor Ring. Also included in this section is Professor Rose's program to develop high-field superconducting composites for use in large magnetic fusion devices. Professors MacVicar and Bostock are concerned with the processing, structure, and property relationships of superconducting materials and with the substitution of precious metals in standard electrical contact and connector applications. Professor Pelloux is investigating the influence of

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processing procedures on the structure of zircaloy and nickel-base alloys with a goal of improving mechanical properties and performance. Professor Kaplow's investigation of the potential of Metal-Insulator-Semiconductor junctions as photovoltaic devices is also reported. All of these research activities are presented in more detail below.

Additional materials processing activities reported in other sections are cross-referenced at the end of this section.

1. KINETICS OF INTERACTION OF ARC PLASMAS WITH LIQUID METALS

When a transferred plasma arc is used to melt metals, the gas used to support the arc is normally argon. Gases such as nitrogen are dissociated in the arc and the atomic species is, generally, much more reactive than the molecular species. It has been shown in this work that, when nitrogen is added to the plasma gas, it dissolves extremely rapidly in liquid rion and the amount of dissolved nitrogen reaches a steady-state solubility well above the value for equilibrium with molecular nitrogen. The steady state solubility increases as the percentage of the nitrogen in the gas increases, up to about 30% N_2, when a maximum value is reached. The value is also increased markedly by increasing the oxygen content of the iron. A quantitative theory of the solution process has been established. Studies have also been carried out on iron-chromium, iron-nickel, and iron-manganese alloys. When hydrogen is also added to the plasma gas, the rate of nitrogen solution and the value of the steady-state solubility are markedly reduced. Hydrogen has also been shown to accelerate the rate of desorption of nitrogen.

Work is continuing using hydrogen to deoxidize and decarburize.

Sponsor: National Science Foundation
Faculty: T. B. King
Graduate Student: J. Katz

2. PRIMARY PRODUCTION OF MAGNESIUM

Magnesium, with a density less than two thirds that of aluminum, is an important domestically available light weight material which offers substantial potential energy savings to the transportation sector. The magnesium program was initiated in 1976 to consider the energy efficiency and economic viability of expanded magnesium production and use in the automotive sector. An international conference was also convened at MIT in 1977 to consider the production and use of magnesium, the most energy efficient automotive material with respect to net life cycle energy use. Work has recently been completed on a technical and economic assessment of current and proposed magnesium primary production technologies as a basis for future programming in process research and development.

Sponsor: Department of Energy
Faculty: J. P. Clark, M. C. Flemings, D. R. Sadoway, J. Szekely
Staff: G. B. Kenney
Publications:

1. Report from the International Conference on Energy Conservation in the Production and Utilization of Magnesium, edited by Merton C. Flemings, et al., Conference held at MIT, Cambridge, MA., May 1977.
2. G. B. Kenney and J. P. Clark, "Magnesium: Energy Panacea?", American Metals Market - Minor Metals Section, August 18, 1977.
3. G. B. Kenney and J. P. Clark, "An Analysis of Pricing in the Domestic Magnesium Industry," Proceedings of the Council of Economics of the IME, March 1978.

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4. G. B. Kenney, An Analysis of the Energy Efficiency and Economic Viability of Expanded Magnesium Utilization, Garland Publishing Series of "Outstanding Dissertations Bearing on Energy," 1979.
5. M. C. Flemings and G. B. Kenney, "Materials Research for the Fuel Efficient Automobile," Report to the Transportation Systems Center, U.S. Department of Transportation, October 1979.
6. M. C. Flemings and G. B. Kenney, "Materials Substitution and Development for the Light Weight, Energy Efficient Automobile," Report to the Office of Technology Assessment, Congress of the United States, February 1980.
7. G. B. Kenney, D. R. Sadoway and M. C. Flemings, "An Assessment of the Potential for Magnesium Penetration of the U.S. Automotive Industry," Proceedings of the 37th International Magnesium Association.
8. J. P. Clark and G. B. Kenney, "The Dynamics of International Competition in the Automotive Industry. Part I: A Framework for Analyzing the Dynamics of Intermaterial Competition," Materials and Society, Vol. 5, No.4, pp. 383-389, (1981).
9. G. B. Kenney and J. P. Clark, "The Dynamics of Intermaterial Competition in the Automotive Industry. Part II: A Case Study of the Demand for Magnesium" Materials and Society, Vol. 5, No. 4, pp. 391-406, (1981).
10. M. C. Flemings, et al, "An Assessment of Magnesium Primary Production Technology," Final Report to U.S. Department of Energy, Contract Number EX-76-A-01-2295, February 1, 1981.

3. FLOW OF GASES AND SOLIDS IN A FAST FLUIDIZED BED REACTOR

The fast fluidized bed reactor shows promise of being an important type of reactor in the non-fuels minerals

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industry. An experiental 8 inch diameter, 30 foot high, stainless steel reactor is in operation. Currently study is in progress of the nature of flow of gases and solids in the reactor as influenced by the principal operating parameters, air flow and solids loading.

Sponsors: Bureau of Mines, Department of the Interior (Program in the Mining and Minerals Resources Research Institute of MIT)
Faculty: J. F. Elliott
Staff: C. W. Finn
Graduate Students: V. Velina, C. Ribaudo

4. SEPARATION PROCESSES

Beneficiation of Oil Shale

A large fraction of the energy used in retorting oil shale to produce crude oil is wasted on the mineral component. These decomposed minerals are easily dissolved in water and thus create environmental problems in disposal. Beneficiation is the physical separation of ground oil shale into two parts, one rich in kerogen and the other rich in minerals. The kerogen rich part becomes the retort feed and the chemically unaltered mineral component is discarded. Methods of beneficiation which are being considered include: froth flotation, electrostatic separation, and density separation.

Sponsor: Department of Energy
Faculty: T. A. Ring, C. R. Peterson
Staff: M. A. Weiss, I. V. Klumpar
Undergraduate Students: M. Lamey, F. Michaud

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Selective Flotation of Ultrafine Mineral Particles

Selective froth flotation is inefficient when the mineral particles are of micron size. Selective froth flotation of a two component mixture of micron sized mineral particles is being studied. Each type of mineral particle is generated in such a way as to give spherical particles of a narrow size distribution. Two processes occur simultaneously in selective flotation of micro sized particles. They are coagulation and bubble collection. The kinetics of both of these processes are being studied individually and in total to provide a detailed understanding of the flotation process. Photon correlation is being used to study coagulation kinetics while collection kinetics are being monitored by chemical analysis of the froth.

Sponsor: Unsupported
Faculty: T. A. Ring
Graduate Student: B. Novich

5. FABRICATION OF ADVANCED MULTIFILAMENTARY SUPERCONDUCTING COMPOSITES

The goal of this project is the development of high-field superconducting composites for use in large magnetic fusion devices. The requisite properties are:

10^5 amps/cm^2 current density at 15 T magnetic field at 4.2^{0}K; and

strain tolerance of at least 2% without significant degradation of superconducting properties.

Recently we demonstrated that microfilamentary composites, i.e. multi-filamentary composites with submicron filament sizes, are the best candidate materials. We have since concentrated on the processing problems associated with the external diffusion method for bronze matrix Nb_3Sn-based composites. These include:

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1. Kirkendall porosity,
2. Residual stresses,
3. Dewetting and Rayleigh coalescence of molten external tin layers,
4. Diffusion kinetics in multifilamentary materials.

Sponsor: Department of Energy

Faculty: R. M. Rose

Staff: S. F. Cogan, I. M. Puffer

Graduate Students: J. D. Klein, S-J. Kwon

Undergraduate Students: L. Granick, P. Goldwhite

Publications:

1. S.F. Cogan, D.S. Holmes, J.D. KLlein, and R.M. Rose, "Multifilamentary Nb_3Sn by an Improved External Diffusion Method," Proceedings of ICMC Conference, Brookhaven National Laboratories, NY (May 1980).
2. J. D. Klein, S.F. Cogan, G. Warshaw, N. Dudziak and R.M. Rose, "Properties of Microfilamentary Superconducting Composites Produced by a Modified External Diffusion Method," IEEE Trans. on Mag., Vol. MAG-17, No. 1, pp. 378-379 (January 1981).
3. J. D. Klein, G. Warshaw, N. Dudziak and R.M. Rose, "On the Suppression of Kirkendall Porosity in Multifilamentary Superconducting Composites," IEEE Trans. on Mag., Vol. MAG-17, No. 1, pp. 380-382 (January 1981).
4. J. D. Klein, S.F. Cogan, S. Kwon and R.M. Rose, "Manufacture of Multifilamentary Nb_3Sn Superconductor by the External Diffusion Method: Tin Coalescence and Diffusion," to be presented at the 9th Symposium on Engineering Problems of Fusion Research, Chicago Illinois, October 26-29, 1981.

6. SUPERCONDUCTING AND ELECTRICAL MATERIALS

Relationship of Materials Processing to Superconducting and Mechanical Properties

In most of the high T_c:H_{c_2} intermetallic compounds the micromechanisms by which the alloys become hard are such as to severely restrict dislocation substructure motion thereby limiting the possible plastic flow of the materials and cause these alloys to be very brittle. However, the specific effects of internal defects and microstructure on the mode of fracture and degradation mechanisms of superconducing properties are unknown. A microstructural characterization of the physical properties of C15 and A15 superconductors is underway. Both Laves phase and comparison A15 alloys are now under test.

An analytical data base consisting of the mechanical properties of as-grown single crystals with artificially induced defects, arc cast materials, and of various composite wire configurations is being developed specifically for ZrV_2 (C15) and for Nb_3Sn (A15). Evaluations of surface fracture and hardness numbers in pure and arc cast ZrV_2 have been already obtained. A four-point bending jig for determining the stress-strain relations in single crystal and selected polycrystalline specimens over the range of room temperature to 4.2K has been designed and constructed which permits elastic modulus and breaking stress determinations. Methods for producing very small specimens with geometrical integrity are being developed.

Role of Structural Perfection and Texture in Refractory Superconductors

Among the binary cubic Laves phase (C15) compounds, ZrV_2, HfV_2, and their pseudobinary alloys, $Hf_xZr_{1-x}V2$ have the

highest superconducting transition temperatures. In addition, many of these materials undergo low temperature lattice transformations to lower lattice symmetry.

Using a traveling heater solvent zone technique, we have grown, with great difficulty, relatively large single crystals (2 mm - 7 mm) of ZrV_2, several extremely pure large-grained polycrystalline rods, and a few polycrystalline rods containing approximately 1% by volume Zr inclusions. Preliminary investigations of the resistivity, the low temperature structural transformation properties (by neutron scattering and ultrasonics), and the critical field and superconducting transition temperature of these samples showed that the properties of ZrV_2 are extremely stress sensitive and that for all samples there appears to be an electronically driven transformation at about 100K which is independent of the existence of the structural phase transformation. The lattice transformation of twinned single crystals to the rhombohedral structure at 96K is accompanied by the onset of an incommensurate charge density wave which becomes commensurate when the lattice transformation is completed. Although there is considerable diffuse scattering in the "perfect" single crystal in the same temperature range, no charge density wave or structural transformation has been observed. Inductive (super-conducting) critical field measurements are underway on single crystal samples to determine if twinned and untwinned samples have different $H_{C_2}(0)$. If so, an attempt will be made to correlate the difference to Fermi characters.

The absolutely highest T_c values of any materials are realized in the A15 class of alloys. The chief difficulties generally encountered in their fabrication all appear to relate to the development of a high degree of order and/or stoichiometry in the A15 phase. The resolution of questions concerning the exact nature of these materials is important

both practically, in terms of understanding the relationship of microstructure to their high T_c superconductivity. A variety of approaches is being used in this laboratory to characterize various A15's of interest (Nb_3Sn, Nb_3Ge, Nb_3Au). These include studies of the morphology of growth of sputtered and diffusion-reacted A15 films and their surface oxides, investigations of epitaxial growth mechanisms and texturing in bulk materials, fabrication of single crystal and or single phase materials, considerations of the thermodynamic predictions of order-disorder kinetics and phase field stability, and evaluations of composition.

We have found that the electrical (superconducting), physical, and mechanical properties of Nb_3Sn diffusion layers fabricated on single crystal and polycrystalline Nb substrates exhibit behaviors deriving from substrate orientation and texturing, respectively. Notably, when the preferred orientation of the A15 layer is significantly A15-(111), the properties of the Nb_3Sn layer are undesirably degraded in all respects. We have recently found that annealing treatments of niobium foil starting stock dramatically affect the physical properties of the final Nb_3Sn layer and its phase composition. A systematic investigation of the effects of Nb treatments and surface conditions is underway.

Electron-beam Imaging Via Thin Film Cryogenic Devices

By incorporating a cryogenic-dewar stage into a scanning electron microscope, a two-dimensional image of the non-equilibrium responses of a superconductor to electron beam irradiation can be observed. Irradiation of a current-carrying "weak link" film with an electron beam causes a change in the resistive voltage of the link; this change in voltage, as a function of the spatial position of the beam

spot, can be used to modulate the brightness of the microscope's CRT tube in much the same way as the emission of secondary electrons is used to produce conventional SEM pictures. However, the non-equilibrium response of superconductors is not confined to resistive voltage changes but is a complex mixture of interchanges between Cooper pairs and quasi-particle populations (accompanied by emission or absorption of phonons). Past research using a variety of other detecting techniques has not sharply delineated the microscopic mechanisms underlying the non-equilibrium responses. This is especially true near the critical temperature for decay of the superconducting state. Using this new two-dimensional imaging technique to examine a variety of sample configurations (including "weak links" and superconducting tunnel junctions), we expect to obtain new information concerning relaxation mechanisms in superconductors. A detailed investigation of the internal structures (or, the physical disposition) of metal films based on this mechanism also appears possible. Design and construction of a second-generation low temperature stage for insertion into an SEM is well underway. Electron irradiation effects on tunnel junction characteristics are the first experimental step. Planning and design of the experiments to be undertaken with the SEM stage are almost complete.

Deformation Effects in Electronic Behaviors of Cryogenic Diodes

In utilizing materials for practical devices considerable deformation results from ordinary processing techniques. The superconductivity of such materials also undergoes (sometimes dramatic) changes. Since Nb is the highest T_c element and the host matrix for the highest known T_c materials, it is particularly important to establish the connection between its microstructure and its superconducting parameters.

Recently an acid-etch oxidizing technique has been developed for fabricating superconducting tunnel junction barriers on severely plastically-deformed (up to a true strain of 3.9) bulk Nb. The electron-coupled phonon spectra determined from the superconducting tunneling data shows two clear trends: those having a character similar to undeformed bulk Nb but predicting an increase of T_c over the bulk value; and those with distinctly different characters, predicting the decreased T_c of comparably deformed material. The effects of surface etching inherent in the barrier formation technique with regards to those results is still to be determined. The electron-phonon coupling parameter and effective Coulomb pseudopotential derived from the tunneling data indicate that a threshold of mechanical deformation exists: on one side of it, λ and μ^* do not agree with conventional theory, while on the other side of it, conventional theory is suitable for the results obtained. These data, and results on amorphous Nb films investigated by Stanford University and Bell Labs, suggest the possibility of a non-BCS mechanism.

Since much of the tunneling we observe for the Nb-based A15 substrates is very reminiscent of data from tunneling into highly deformed Nb surfaces and since very low effective tunneling T_c's indicate a damaged surface layer on the A15 films, we have begun exploring specific configurations which can be reliably used to extract the energy gap information about superconductors. These include proximity effect junctions and point contact microbridge configurations.

Precious Metals Elimination Initiative

An investigation is underway to determine the feasibility and desirability of mounting a collaborative MIT-Industrial consortium effort to pursue mutually desirable avenues of

research with the objective of reducing or eliminating the use of precious metals in standard electrical contact and connector applications. Activities which duplicate lines of inquiry currently being pursued within industrial laboratories or which have been found unproductive in the past would have low priority in comparison to activities relating to more exotic, longer range, innovative approaches, e.g., intercalated graphite, integrated composites, surface treatments, preferred orientation processing, etc. The immediate task is to evaluate the degree of industry interest in such an effort and to identify industry candidates ready to develop a mutually desirable research agenda and format.

Sponsors: Department of Energy, West German Science Foundation, National Science Foundation, Honeywell Co., Inc.

Faculty: J. Bostock, M.L.A. MacVicar

Staff: A. Callegari, R. Gelinas, P. Stohr, P. Tedrow

Graduate Students: S. Chen, Y. Epps, L. Salamanca-Riba

Undergraduate Students: K. Allen, S. Arney, J. Bellingham, Z. Bern, A. Cohen, J. Izatt, R. Jaimes, D. Kieda, E. Leiser, K. Sidikman

Publications:

1. M.L.A. MacVicar and J. Bostock, "Influences on Electron-Coupled Phonon Spectra α^2F Obtained From Tunneling Data Deconvolutions," Physics of Transition Metals II-Univ. of Leeds, England, 8/80, p. 527.
2. M.L.A. MacVicar, K.R. Milkove, W.N. Cheung and J. Bostock, "Tunelling Characteristics as a Diagnostic of Superconducting Electrode Disposition," 158th Electrochemical Society Meeting, Hollywood, Florida, 10/80. Invited paper.
3. M.L.A. MacVicar, J.F. DeBroux, V. Diadiuk and J. Bostock, "Effects of Nb Substrate Orientation on Nb_3Sn Diffusion Layer Properties," 158th Electrochemical

Society Meeting, Hollywood, Florida, 10/80. Invited paper.

4. M.L.A. MacVicar and J. Bostock, "α^2F from Tunelling: Considerations and Influences." To be published.
5. M.L.A. MacVicar and P.C. Wyatt, "Carburetor," The World Book Encyclopedia, 1982 Edition; Invited author.
6. M.L.A. MacVicar and P.C. Wyatt, "Brakes," The World Book Encyclopedia, 1982 Edition; Invited author.
7. M.L.A. MacVicar, Encyclopedia of Materials Science and Engineering, subject editor and overview author for superconductivity, Pergamon Press Ltd. Encyclopedia to be published (1982).
8. P.L. Stohr, "High Resolution Imaging of Magnetic Structures and Inhomogeneities of a Superconductor Using Scanning Electron Microscopy," 16th International Conference on Low Temperature Physics, Los Angeles, California, 8/81; proceedings published in Physica, 107B, 1981, pp. 441.

7. PROCESSING/PROPERTY RELATIONSHIPS IN ZIRCALOY AND NICKEL-BASE ALLOYS

Environmentally Induced Cracking Under Cyclic Loading of Nickel-Base Alloys Used in Light Water Reactors - Modification of Aging

This program is oriented toward study of the intergranular fracture of Inconel 600 under cyclic loading and electrochemical control in PWR environments. During the past year particular emphasis has been placed on the synergistic effects of thermal treatment and cathodic polarization on the fatigue crack growth behavior of Inconel 600 at ambient temperatures and pressures. The essence of this work is that aging treatments of longer duration than those typically used in the industry at present lead to both desen-

sitization (i.e., an increase in the Cr concentration in the grain boundary proximity following an initial sensitizing thermal treatment) and phosphorus desorption from the grain boundaries, the consequence of which is reduced susceptibility to intergranular cracking at cathodic potentials.

Sponsor: Electric Power Research Institute
Faculty: R.M. Latanision, R.M.N. Pelloux
Staff: R.G. Bellinger
Graduate Student: W. Moshier

Crystallographic Texture Control in Zircaloy Tubes

Mechanical properties, stress corrosion cracking resistance, and irradiation creep resistance of zircaloy cladding tubes can all be improved by taking advantage of crystallographic texture effects. The fundamental objective of this program is to conduct a systematic investigation of the manufacturing parameters which control the formation of crystallographic textures in Zircaloy-2 and -4 tubing. Precise control of texture development during tube production must be based on: (1) close observation and detailed analysis of the process, and (2) a thorough understanding of the deformation behavior of the material. In order to accomplish these tasks, samples of Zircaloy from intermediate stages in the tube rocking process are being analyzed dimensionally, microstructurally, and crystallographically. In addition, mechanical tests simulating the deformations incurred during tube production are being performed with similar analyses. The texture sharpening and rotation during the intermediate recrystallization steps is also being evaluated. A computer model based on the micromechanics of deformation in Zircaloy is used to simulate the tube rocking process and to predict the resulting crystallographic textures. The main goal of this

research program is to achieve process control in the formation of crystallographic textures.

Sponsor: Exxon Nuclear Company, Inc.
Faculty: R. M. Pelloux
Graduate Student: J. Shewbridge

8. PHOTOVOLTAIC DEVICES

Summary

Metal-Insulator-Semiconductor (MIS) junctions show promise for low cost production of efficient photovoltaic cells and other devices. An MIS junction consists of a insulator-metal sandwich in which the energy barrier height depends on the relative work functions of the metal and the semiconductor and is strongly affected by the properties of the interfacial layer.

Metal-Insulator-Semiconductor Solar Cells (MISSC) are being fabricated using p-type silicon (boron doped, 0.5-10Ω-cm resistivity, (100) and (111) orientations) and a low work function metal (Al, Co, Hf, Mn, Y). The wafer is first chemically cleaned and 0.5 μm thick Al film is evaporated on the back surface. This back contact is then heat-treated in a vacuum better than 2×10^{-5} torr to 400-500°C to form an alloyed ohmic contact. When the equilibrium temperature has been reached, ultrapure dry oxygen is introduced in the chamber to grow a thin oxide on the front surface (10-15 Å thick). This oxidation is performed after obtaining well-defined starting surface conditions, e.g. a chemical cleaning procedure has been developed to give reproducibly a 6 Å thick ultrathin native-silicon oxide. Our first diodes were fabricated using aluminum as a contacting metal. Device fabrication is completed by evaporating a copper film

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on both sides to lower contact resistance and to attach gold wires with silver epoxy. A 694 mv barrier height for a completed device has been determined from I-V and C-V electrical measurements.

MISSC behavior and performance will be optimized in terms of silicon resistivity and orientation, silicon oxide thickness and growth conditions, and metal work function. Surface studies performed on silicon before and after oxidation (Auger, XPS) will be correlated with device characteristics and performance.

Faculty: R. Kaplow*
Graduate Student: M. Baddi
Undergraduate Students: A. Kress, Z. Smith, V. Walters

*We regret the death of a highly valued member of our faculty, Professor Roy Kaplow.

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L. TECHNOLOGY TRANSFER AND INTERNATIONAL DEVELOPMENT: MATERIALS AND MANUFACTURING TECHNOLOGY

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SUMMARY

The Center for Policy Alternatives (CPA) under the directorship of J. Herbert Hollomon has conducted, over the past eight years, a series of policy-oriented studies on technological development in several relatively advanced developing countries. These have been directed by Dr. Nagaraja Rao, Senior Research Associate at CPA. Priority sectors defined in terms of technological sophistication, capital intensity, value added, and export potential have been studied in the cases of Brazil, Venezuela, Israel, and Korea. These projects have been supported directly by the countries themselves or through loans and grants made to them by international agencies such as the World Bank and the U.S. Agency for International Development. Research teams include graduate students from M.I.T. Schools of Engineering and Management, and senior researchers from the countries sponsoring the study.

Although the objectives of these studies are generally to develop technological policy alternatives for the sponsoring country, much emphasis is placed on understanding the dynamics of the sectors through structured interviews with a large sample of firms in the leading manufacturing and materials processing sectors.

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Technological Status and Development of Portuguese Industry

This is a study at the Center for Policy Alternatives by the National Laboratory for Engineering and Industrial Technology (LNETI) of Portugal and partially financed by the Government of Portugal through a project loan from the World Bank.

The objective of the study is to assess the present status of technology in the major industrial sectors of Portugal and examine alternative approaches to the upgrading of technology in industry and to strengthen the relationship of industry and public research and development institutes, and promote better utilization of standardization, engineering, and quality control services. The Portuguese Government is actively promoting industrial development through a variety of incentive programs to enable industry to become competitive with those of the members of the European Economic Community, which Portugal hopes to join in the mid-eighties.

Plans for the improvement of product and process technology in a sample of one hundred Portuguese firms are assessed through structured interviews with entrepreneurs. Literature studies are conducted and expert opinions are sought on the potentials for diversification of Portuguese manufacturing and industries based on locally available mineral, agricultural, and ocean resources. These economic and technical assessments will form the basis for LNETI to develop a mid-term technology development plan and to identify projects for funding by the Government or international financial agencies.

Sponsor: Laboratorio Nacional de Engenharia e Tecnologia Industrial - LNETI

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Publications:

1. K. Nagaraja Rao, R. F. Baddour and C. T. Hill, The Changing World Chemical Industry and the Need for New Strategies, "Strategic Aspects of Chemical Industry Development in the Rapidly Industrializing Nations," 2nd World Congress of Chemical Engineering, IX Interamerican Congress of Chemical Engineering, Montreal, October 1981.
2. C. Rodrigues, "Report from Abroad," Policy Choices, CPA/MIT, Fall, 1981.