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FOREWORD

The Committee to Define Materials Science Experiments for the Space Shuttle/Spacelab is highly indebted to many members of the materials science community for their contributions to this report. Particular thanks are due Professor Franz Rosenberger for his contribution on vapor-solid processes and to Dr. M. C. Weinberg and Dr. G. F. Neilson of Owens-Illinois for their contribution to the area of glass formation in space.

The committee wishes to express its thanks to Dr. Fred J. Kohl, the NASA Program Manager, to Dr. Robert A. Lad and to Mr. John W. Weeton for their guidance and support on this program.

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SUMMARY

A committee of materials scientists whose members have expertise in various facets of the discipline has with the aid of colleague scientists defined a number of experimental areas and specific experiments that would utilize the space environment to further our understanding of materials science. The criteria used for the selection of the experimental areas and individual experiments are that the experiment or area must make a meaningful contribution to the field of materials science and that the space environment is either an absolute requirement for the successful execution of the experiment or that the experiment can be more economically or more conveniently performed in space. The committee was careful to distinguish between materials science experiments in space and space processing.

Among the potentially fertile areas recommended for further exploration were the following:

Nucleation, Undercooling and Glass Formation

Convection Effects in Space Conducted Materials Science Experiments

Experiments Dealing with Surface Tension (Marangoni) Convection

Experiments Dealing with Multiphase Materials

Experiments Dealing with Surface Phenomena

Basic Materials Science Experiments Dealing with Vapor-Solid Processes

Transport Phenomena in Liquids

Materials Science Experiments Involving Float Zone Solidification at Low Gravity

High Temperature Chemistry of Reactive Liquids

In addition to the above listing of fertile areas for space experimentation, experimental areas that did not appear to be fruitful for space experimentation are discussed. Likewise, areas needing further definition are listed. The committee also made recommendations concerning the manner in which materials science experiments are conducted in space and the related studies that should be pursued.

INTRODUCTION

The advent of the Space Shuttle and Spacelab in the early 1980's affords unique opportunities to the materials science community to perform experiments in an environment which cannot be duplicated terrestrially. The present program which was initiated by the Lewis Research Center has as its purpose the definition of meaningful materials science experiments for conduct on the Space Shuttle in the 1980's.

To perform these studies the Contractor, S. H. Gelles Associates, has assembled a group of eminent scientists to accomplish the afore-mentioned program objective. A listing of the committee members, their affiliations and their areas of specialty are presented in Table 1. A number of other scientists contributed to the program in the form of project ideas and background information. Their participation is acknowledged in Appendix A.

Attributes of the Space Environment Pertinent to Materials Science

The major factor in making the environment of an orbiting spacecraft unique is the long periods of weightlessness or lack of net accelerating forces. Acceleration levels on the order of 10^{-5} to 10^{-7} g expected in the Shuttle should minimize gravity induced convection currents and buoyancy effects. The weightless environment would also provide an opportunity to conduct experiments without material containment so that contamination or perhaps heterogeneous nucleation can be avoided.

A restricted low g environment is also available terrestrially at the NASA-Lewis Research Center's drop tower facility, but this environment is limited to 5-10 sec. of low g. A somewhat longer low g time period (~25 sec) is available on KC-135 flights. The Space Processing Applications Rocket (SPAR) program, which is designed to provide opportunities for low-gravity experimentation during the interim period between the Apollo-Soyuz mission (ASTP, 1975) and the Space Shuttle (1980) can provide 4-6 minutes of low gravity (~10^{-5}g). SPAR rocket flight opportunities will occur 2-3 times a year (ref. 1) for the duration of this program.

Levitation devices available terrestrially may also allow some crucible-free materials science experiments to be carried out on Earth. For example, large samples of electrical conductors have been successfully levitated electromagnetically, but with three basic difficulties:

1) Lack of independent control of heating power and levitation force.

2) Disturbance of liquid samples by eddy current forces.

3) Shorting of the levitation coils when in the presence of metallic vapors at high pressures.

Thus, terrestrial levitation appears to be quite feasible for experiments not requiring a quiescent liquid and involving low pressure electrical conductors.

TABLE 1. Members of the Committee to Define Materials
Science Experiments for the Space Shuttle/Spacelab

Member	Affiliation	Specialty Areas
Stanley H. Gelles	Director, S. H. Gelles Associates Columbus, Ohio	Space Experimentation Phase Equilibria Liquid Phase Immiscibles Undercooling Phenomena
Bill C. Giessen	Professor, Northeastern University Boston, Massachusetts	Amorphous Metals (Metallic Glasses) Metastable Phases Phase Equilibria Crystal Chemistry of Alloy Phases
Martin E. Glicksman	Professor, Rensselaer Polytechnic Inst. Troy, New York	Solidification and Crystal Growth Nucleation Undercooling Phenomena Interfacial Phenomena
John L. Margrave	Dean, Rice University Houston, Texas	High Temperature Chemistry Thermodynamics Compound Synthesis Containerless Thermodynamic Measurement
Hershel Markovitz	Professor, Carnegie-Mellon University Pittsburgh, Pennsylvania	Polymer Sciences Rheology
Arthur S. Nowick	Professor, Columbia University New York, New York	Solid State Phenomena Metastable Alloys Ionic Crystals Crystal Defects
John Verhoeven	Professor, Iowa State University Ames, Iowa	Liquid Phase Diffusion Electrotransport Phenomena in Liquid Metals Solidification and Crystal Growth Segregation
August F. Witt	Professor, Massachusetts Institute of Technology Cambridge, Massachusetts	Electronic Materials Surface Chemistry Solidification and Crystal Growth Space Experimentation

For experiments involving non-conductors, terrestrial levitation devices are more limited. For example, current acoustic levitation devices are limited to the levitation of ~4 mm diameter liquid drops of specific gravity 3 to 4. Droplets with smaller diameters composed of higher specific gravity materials can likewise be levitated (ref. 2). However, acoustic levitation devices have the following limitations at present:

1) The requirement of a gas environment.

2) Liquid disturbance from the acoustic energy.

3) Instabilities in long time operation.

The third limitation probably will be overcome in the near future with additional development efforts.

An aerodynamic levitation device is also being developed and used for terrestrial materials science experiments. As presently used, this apparatus has about the same limitations as the acoustic devices (ref. 3).

It may thus be concluded that in the case of non-conductors, terrestrial levitation capabilities limit experiments to those involving relatively small samples, and to those which are not affected by liquid disturbances and a gas environment.

In suggesting materials science experiments for conduct in space, the committee has considered the terrestrial capabilities of levitation equipment. They have, therefore, limited suggested experiments dealing with electrical conductors to those in which a liquid sample will not tolerate a disturbance induced by the levitation or to those situations in which levitation is very difficult (e.g., materials with high vapor pressure). In the case of non-conductors, the space experiments that appear to make sense are those in which either large samples are required, or where liquid disturbances or a gas environment interfere with the experiment.

Another potentially useful aspect of the orbital environment is the reduced ambient pressure. Although the ambient pressure at the normal Shuttle orbiting altitude is approximately 10^{-8} torr, it is much higher in the vicinity of the orbiter due to outgassing. An orbiting molecular shield vacuum facility has been suggested by investigators at NASA-Langley Research Center and Old Dominion University (refs. 4-6). One concept calls for a hemispherical shell behind which vacua on the order of 10^{-13} torr at 300K have been theoretically estimated. This is equivalent to vacua attainable on earth in liquid helium pumped systems (refs. 7,8,9). Thus materials science experiments that require only the vacuum can best be performed terrestrially. The wake shield facility, however, offers the unique combination of high vacuum and weightlessness which may be of advantage in some experiments.

Other properties of the space environment such as the unattenuated source of solar radiation as well as other radiation spectra can be used as a convenience in combination with the unique space feature of weightlessness.

Distinction Between Materials Science
Experiments Conducted In Space and Space Processing

The committee was very careful to distinguish between materials science in space and space processing. The distinction between the two topics can be rather subtle and there is a great tendency for overlap between the two. The committee has distinguished between the two fields in the following way. Space processing makes use of the unique space environment to develop processes that may be used in future space manufacturing operations or which may guide improvements in terrestrial processes and/or products. In contrast, materials science experiments conducted in space take advantage of the unique environment in order to perform experiments which advance the field of materials science and which are either impossible or impractical to conduct on Earth. This definition can be broadened to include the preparation of unique materials in space for subsequent study on Earth. Some materials science experiments have necessarily been conducted as part of the space processing program. Thus it is not surprising that there is some overlap in the activities.

Scope of the Program

The field of materials science is very broad. It encompasses the physics and chemistry of a wide range of different types of materials such as metals, ceramics, organic compounds, semiconductors, composites, etc. The broad but still limited expertise afforded by eight committee members made it necessary to concentrate on the areas of specialty represented by the committee members. Successful efforts, however, were also made to broaden the scope of our activities through conversations with colleagues and inputs into our report by non-committee members.

The experimental areas recommended in this report represent a first definition of the topics. It is anticipated that at least some of the ideas will in subsequent efforts be defined in greater detail, and the necessary ground base work to determine their attractiveness as space experiments will be performed. Since this report is not all-inclusive, it is expected that other experimental areas will be recommended by future committees and/or by individual scientists.

In addition to the recommended materials science experiments for space, the present report treats topics that were discussed by the committee and did not appear attractive for conduct in space. Furthermore, some areas which need further analysis to determine their suitability as space experiments are also discussed.

In light of the previous comparison between space processing and materials science in space, it should be emphasized that some of the experiments which may not be acceptable as materials science programs, perhaps because they can be done terrestrially on a small scale (i.e., in a terrestrial levitation device), nevertheless, might be acceptable when conducted on a larger scale as part of a process development effort for the Space Processing Applications Program.

Philosophy of Experiment Selection

The following criteria were used as guidelines for the selection of materials science areas/experiments for conduct in space:

1) The experiment must make a meaningful contribution to the field of materials science.

2) The space environment is either absolutely required for the successful execution of the experiment or it is more economical or appreciably simpler to conduct the experiment in space.

In addition, preference was given to experimental areas that had some relation to present or future technology even though the experiment itself was aimed at acquiring basic understanding in materials science.

Operation of the Committee

The committee operated in two basic modes:

1) Through meetings of the entire committee, and

2) Through homework assignments.

The committee met for a total of four days: July 22, October 15 and 16 and December 15, 1976. The July meeting was spent mainly acquainting members with the Space Transportation System, with the attributes of the space environment, and with the activities of two previous committees, one of which had defined space experiments in combustion (ref. 10) and the other in fluid physics, thermodynamics and heat transfer (ref. 11). However, some time was devoted to the preliminary definition of materials science experiments in space and with the basic philosophy which would guide the operation of the committee.

The second committee meeting was devoted to two days of discussion of ideas that committee members had submitted prior to the meeting. These were discussed in detail, some were accepted, some were rejected, and others were recommended for modification.

The final meeting held in December was devoted to reviewing the modified ideas and guiding philosophy from the previous meetings and in discussing some new ideas.

The final activities of the committee were the review and acceptance of the final report.

Background Studies

The Lewis Research Center has had an active program to define experiments for the Spacelab for the past two years. Two studies similar to the present one have been conducted, one on combustion experiments in space (ref. 9) and one on fluid physics, thermodynamics and heat-transfer experiments (ref. 10). At the present time further in-depth definition and feasibility studies are underway in the above mentioned discipline areas.

For background material, the committee has taken advantage of the literature generated by a number of previous studies in the growing body of information dealing with materials experiments in space. The literature deals with the generation of early ideas in the field by H. Wuenscher and with subsequent experimental efforts in Apollo 16 and 17, aboard Skylab and Apollo-Soyuz and in the current SPAR flights. A bibliography on this related literature is presented at the end of the report.

Discussion of Experimental Areas

Materials science experiments for conduct in space almost invariably involve fluids, either gasses or liquids, since only in this state are there advantages to be gained from the weightless environment.

An attempt has been made to define general categories of materials science involving fluids as a guide so that input in particular areas could be logically categorized and also so that unaddressed areas could be duly noted (See Table 2). There is some duplication among the categories but this is not considered to be a disadvantage. It should be noted, however, that the recommended experiments and experimental areas discussed in the next section are organized in a somewhat different fashion for ease of treatment.

TABLE 2. Materials Science Categories Considered for Possible Space Experimentation

Solidification Phenomena
    Directional Solidification of Eutectics, Monotectics
      and Peritectics
    Undercooling Effects
      Homogeneous and Heterogeneous Nucleation
      Glass Formation (metals and ceramics)
    Effects of Convection
    Stability of Growth Interfaces
      Planar
      Cellular
      Dendritic
    Segregation Phenomena and Distribution Coefficients
    Growth of Single Crystals from the Melt
    Fundamentals of Joining Phenomena

Transport Phenomena in Fluids
    Accurate Measurement of Diffusion Characteristics
    Thermal Conductivity of Liquids
    Soret Effect
    Electrotransport Phenomena
    Thermal Diffusivity

Deposition Studies
    Physical Vapor Deposition
    Chemical Vapor Deposition
    Electrodeposition

Purification and Preparation of Purified Material
    Deposition in Ultra High Vacuum (Distillation)
    Epitaxial Growth
    Crucibless Processing
    Electrotransport
    Zone Refining

Polymeric Materials

Surface Phenomena
    Fluid Motion Resulting from Surface Tension
      Effects
    Equilibrium Configurations and Shapes
    Liquid Phase Sintering
    Infiltration
    Corrosion
    Measurement of Surface Tension

Synthesis of Materials
    Chemical Reactions Without Crucibles

Crystal Growth
    Solution Growth
    Growth from the Melt
    Chemical Vapor Deposition
    Physical Vapor Deposition

Preparation of Composite Materials
    Particulate Composites
    Fiber Reinforced Composites
    Directionally Solidified Materials
    Foams

High Temperature Chemistry and Physics
    Thermal Properties
    Structure of Liquids
    Mechanical Properties
    Electronic Properties
    Chemical Properties

Thermodynamic and Other Physical Properties
    Vapor Pressures
    Calorimetric Studies

Stability of Emulsions
    Systems with Miscibility Gaps
    Totally Immiscible Systems

EXPERIMENTAL AREAS RECOMMENDED

A. NUCLEATION, UNDERCOOLING AND GLASS FORMATION

The space environment offers a unique opportunity to perform experiments in bulk materials without containers and thus provides a possibility of removing a major source of heterogeneous nucleating agents as well as avoiding contamination from the container.

Three groups of related experiments are suggested under this category, "Nucleation and Undercooling Phenomena," "Properties of Supercooled Materials," and "New Oxide Glasses by Containerless Melting".

A.1 NUCLEATION AND UNDERCOOLING PHENOMENA

Background

The understanding of nucleation phenomena is basic to the understanding of glass formation and undercooling phenomena. It is the prevention of prompt nucleation of a crystalline phase which allows undercooling to take place and a glass to be formed. Nucleation almost always occurs on foreign substrates distributed in the melt (heterogeneous nucleation) rather than unassisted within the body itself (homogeneous nucleation). Solidification of crystalline phases at temperatures below the equilibrium solidification temperature often leads to microstructures that are less segregated and which have a fine grain size (refs. 12-15). Such materials have been shown to have improved properties (refs. 12,13,15).

Levitation devices have been used terrestrially to provide for containerless melting of small samples on earth and have shown possibilities of achieving large degrees of undercooling (ref. 15). In spite of some evidence to the contrary (ref. 16), disturbances of the melt by the levitating forces may aid the nucleation process and thus may interfere with the achievement of still larger degrees of undercooling. Undercooling experiments on bulk samples in the absence of convection currents have as yet not been performed.

Significant amounts of undercooling have also been achieved in metallic samples that have been enveloped in a glass slag (refs. 15,17,19). The ability to attain these undercoolings is thought to stem from the non-crystalline nature of the glass slag and its ineffectiveness as a heterogeneous nucleating agent. However, this explanation is not conclusive and is complicated by the observation of a "conditioning" effect (refs. 15,20,21). Cycling the sample through the melting point several times or holding it for a long time at high temperature is usually necessary to achieve a large amount of undercooling. The increase in the degrees of undercooling takes place in a step-wise fashion as the number of solidification and melting cycles increase. It has been hypothesized that this behavior is due to the removal of various heterogeneous nucleating agents which cause nucleation at discrete degrees of undercooling that correspond to the observed plateaus (refs. 15,22). A study of the chemistry and microscopy of the samples after various thermal cycles or thermal treatment can shed light on the effectiveness of various chemical species as heterogeneous nucleating agents. Determining the effect of size, geometry, chemistry

and atomic properties on the potency of a nucleating agent should aid in the development of heterogeneous nucleation theory. This understanding should provice better control in the removal of heterogeneous agents in order to promote undercooling. It should also aid in the selection of materials to be used as innoculants for promotion of fine grain castings.

Objectives

The objectives of experimental work in the area of nucleation and undercooling are as follows:

1) To understand the phenomena involved in heterogeneous nucleation and its effect on undercooling and glass formation.

2) To determine whether the presence of mechanical disturbances or convection currents lead to more effective nucleation.

3) To determine the mechanisms of undercooling improvement due to thermal treatment in the glass-slag envelope technique.

Justification

The following points provide a justification for performing studies dealing with heterogeneous nucleation in relationship to the space program:

1) Research work aimed at understanding heterogeneous nucleation will allow us to take full advantage of the potential for producing unique glasses and improved or unique materials produced by solidification below the equilibrium temperature.

2) The conduct of undercooling experiments in the micro-gravity environment will allow a comparison between heterogeneous nucleation in a containerless and undisturbed melt versus that in a terrestrially levitated melt that has inherent disturbances associated with the levitation device as well as gravity-induced convection currents.

3) The microgravity environment will allow us to learn more about the "conditioning" mechanism. If purification is a factor in this mechanism then concentration gradients should be detectable in the sample processed in space.

Approach

It is envisioned that three studies would be conducted in this area. First of all, a ground based study which would take advantage of the glass-slag technique and the conditioning phenomena would be used to relate the type of heterogeneous nucleating agent (i.e., the chemical species and geometric configuration) associated with the observed degree of undercooling at crystallization. A theoretical analysis would be an integral part of this study.

The second study would involve a space experiment. The undercooling behavior of identical specimens would be investigated in a crucible-free configuration on board Spacelab as well as in a terrestrially levitated condition. Differences in the undercooling behavior will be compared in order to obtain information concerning the effect of melt disturbances on the undercooling process.

Finally, glass-slag experiments will be conducted both in the microgravity environment as well as at 1-g. These experiments should provide us with quantitative data on the conditioning process in terms of the kinetics associated with the development of large degrees of undercooling and the presence of composition gradients in the sample. The latter will provide clues concerning purification processes that might be occuring.

Materials

Materials to be preferred for these experiments are those that have been previously studied with regard to undercooling behavior. Copper-silver alloys are in this category. These alloys have solidification temperatures which are well within the range of space equipment capabilities and yet develop high degrees of undercooling so that a broad range of undercooling behavior is possible.

A.2 PROPERTIES OF SUPERCOOLED MATERIALS

Background

Research on and development of metastable materials, especially metallics, has become a major frontier of current materials science. The following discussion is limited to metals. Alloy types currently under study fall into four categories:

amorphous metals (metallic glasses)

metastable solid solutions

metastable crystalline alloy phases

alloys with equilibrium phases but having altered microstructures

These alloy types have been discussed in review papers (refs. 23-25). The most intensively studied alloys of those listed are amorphous metals, which, beyond their fundamental interest, have entered the realm of industrial applicability because of their unique magnetic, mechanical, or corrosion resistance properties.

Three principal types of preparation technologies are known: vapor deposition (evaporation and sputtering), deposition from solution (electrodeposition or electroless deposition) and supercooling from the liquid (by rapid quenching, e.g., splat cooling or melt-spinning, or by slow supercooling of bulk materials or droplets). Of these methods, only the last (droplet supercooling) (ref. 26) is discussed here. It may be mentioned that a variation of the solution deposition process (electrodeposition in the presence of inert particles) has also been considered for space processing (ref. 27). In this reference whereas no mention was made of forming metastable alloys by this technique, this remains a distinct possibility which might be explored further.

Work on the supercooling of small droplets isolated from each other by oxide or other coatings and suspended in an inert medium is presently in progress (ref. 26). This work is of a great significance as it probes into the properties of alloys under conditions far from equilibrium.

The preparation of highly supercooled melts by cooling small, isolated droplets suspended without container contact can be expected to result in the absence of any sources of heterogeneous nucleation. (For additional comments on the supercooling of liquid droplets, See Section A.3.) The expected low probability of homogeneous nucleation in very small droplets will alloy some alloys to be prepared and studied in a state that is presently unachievable.

Objectives

1) To extend the number of metastable alloys and their ranges of composition with special emphasis on amorphous alloys so as to increase our understanding of these materials.

2) To study the solidification and glass transition during cooling of liquid droplets in the microgravity environment.

3) To determine the specific heat, glass transition or alternately the maximum supercooling temperature and relate these observations to the homogeneous nucleation rate as affected by alloy composition, particle size, melt viscosity and surface tension.

Justification

The experimental technique suggested should produce a wide range of highly supercooled metastable materials which would add to our basic understanding of the theory of metastable alloy formation and could provide materials with interesting magnetic and superconducting properties. Thus the area is not only of intense fundamental interest but also has great technical potential.

The space environment is needed to avoid heterogeneous nucleation, especially in samples requiring long heating and cooling times. Drop tower or KC-135 experiments could be performed with some of the materials where shorter times can be tolerated. Also in some cases terrestrial levitation devices might be used but these have their limitations as described in the Introduction.

Approach

Two principal methods might be utilized. The preferred one is to levitate a charge of particles prepared on the ground, melt them and allow them to solidify at various cooling rates in the micro-g environment. An alternate method would use atomization in the micro-g environment to produce the required melt droplets; these droplets would then be suspended and cooled. Thermal analysis and other possible measurements would be performed on the freezing droplet in situ and the cooled particles would be studied further (probably terrestrially) by x-ray diffraction and other analysis methods.

Preliminary drop tower and KC-135 studies would be needed to delineate the range of experiments to be performed in the Spacelab.

Materials

General categories of materials to be considered: Normal (s-p) metals and alloys, rare earth transition metal alloys, transition metal – normal metal alloys; at a later stage oxides and other inorganic "non-glass forming" solids; "non-glass forming" organic solids.

Specific materials: Sb-Sn W-Ni, Tb-Fe ($GdFe_2$,$TbFe_2$), Nb-Si Nb_3Si) alloys, NaCl, CaF_2, H_2O and dilute aqueous solutions, C_6H_6.

A.3 NEW OXIDE GLASSES BY CONTAINERLESS MELTING

Background

Materials in the amorphous (glassy) state have very different properties from those in crystalline forms, and accordingly, there is much interest in producing a wider range of glasses and studying their properties. For example, optical isotropy is important for refractive optics applications, but most oxides are anisotropic in the crystalline form and only show isotropy as glasses. As discussed in the preceding Section (A.2) on metallic alloys, the advent of the technique of splat cooling (ref. 28) has had a major impact (ref. 29). With ceramics, certain materials (notably those based on silicates, phosphates, and borates) produce glasses very easily, i.e. even under slow cooling rates. On the other hand, a large variety of ceramic materials have never been produced in the glassy state since they crystallize readily (or "devitrify") on cooling from the melt. There is good reason to believe that the range of available properties would be significantly extended if a wider range of glasses could be produced (ref. 30).

Any liquid which is supercooled without the intervention of crystallization can in principle form a glass if the viscosity of the material becomes sufficiently large. What is required is a sufficiently fast cooling rate to avoid hitting the "nose" of the C-shaped T-T-T (time-temperature-transformation) curve, i.e., to avoid nucleation of crystals. To avoid homogeneous nucleation, the minimum cooling rate required depends on thermodynamic and kinetic parameters which are well known from nucleation theory (ref. 31). On the other hand, for most substances heterogeneous nucleation dominates. Such nucleation occurs at interfaces where foreign substances contact the melt. This phenomenon arises in those cases where the surface free energy for crystal nucleus formation is lowered when nucleation takes place on a foreign surface. Inclusions and points of contact with the container also provide such sources for heterogeneous nucleation (ref. 32). The effect of the container can be eliminated, however, by the method of containerless melting in a space environment. If all other inclusions are avoided, nucleation would then only take place homogeneously. Several authors have performed calculations for selected one component and psuedo-one-component (e.g., compound composition) systems and have found that homogeneous nucleation rates are very small (refs. 33-35). Recently, experiments have been carried out using a new technique of laser spin melting to produce small spheres of liquid which are then cooled while falling freely (refs. 36,37). This technique has been successful in producing a number of new glasses in the form of very small spheres, thereby demonstrating that elimination of heterogeneous nucleation due to the container can be significant. However, due to

the prior direct contact between melt and crystalline solid, crystallization nuclei probably still exist in the melt. The method can be used, however, to indicate promising materials for space experiments.

Objective

It is the objective of the suggested research to carry out a series of exploratory experiments on the containerless melting and rapid quenching of small droplets of a wide variety of ceramic materials. Where glasses are successfully obtained, their properties can be studied in detail in experiments on the ground. Such glasses may have optical properties not obtainable with conventional glasses. For example, it is of great interest to obtain materials with a combination of high refractive index, n, and low dispersion, $dn/d\lambda$; where λ is the wave length; these are potentially useful in highly corrected multi-element lenses (ref. 38). Another important application is in the production of better laser glasses. For example, higher CaO contents in Nd^{3+} lasers can mean higher laser efficiency, but when attempts are made to increase the CaO content, crystallization sets in (ref. 39).

If new materials with favorable properties are produced, it may be desirable to incorporate them in a space processing program to produce larger quantities of those materials.

These studies can also be directed toward a better fundamental understanding of the factors which control homogeneous nucleation and glass formation, by elimination of the relatively complex situation of container-induced heterogeneous nucleation.

Justification

As already made clear, the reason for using a space environment for this project is to make possible disturbance-free levitation melting. There are other methods to accomplish this objective, but electromagentic levitation is suitable only for materials with an appreciable conductivity, while other methods are limited as previously delineated. The most plausible ground based method is acoustic levitation, but this offers the possibility that the agitation produced may assist crystal nucleation. Thus, space experimentation is at least required to help establish whether or not the effect of agitation may be serious.

Approach

A group of selected materials, both pure compound and binary mixtures, will be used. In each case, a small sintered piece of pre-melted and solidified samples is to be subjected to high temperature and melted into a spherical globule. A pre-treatment in vacuum will usually be required, in order to eliminate volatile constituents which can form bubbles in the melt. This pre-treatment can probably best be done on Earth. The final heating should take the material far enough above the melting point to destroy all residual crystalline nuclei. Heating may be accomplished by laser, focused solar radiation, or electron bombardment. (Preliminary ground base work must be carried out to determine which method is most convenient for the purpose.) An oxidizing atmosphere will often be required. Where thermodynamic data are available, suitable oxygen partial pressures can be estimated.

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After melting, the sample must be cooled rapidly. In many cases radiation cooling will be sufficient. Since the materials are transparent, radiation will occur from the bulk of the sample and temperature gradients within the sample will be relatively uniform, thus reducing the possibility of fracture during cooling. A typical figure for the required cooling rate for many oxides is ~1 K/sec (ref. 40); rates two or three orders of magnitude higher than this should be readily attainable by the method described.

Materials

Initial experiments should concentrate on simple systems, notably high purity compounds, to see to what extent glass formation is possible. Materials such as HfO_2, ZrO_2, Nb_2O_5 and TiO_2 are all of interest, in part because they offer the possibility for producing glasses having a particularly high index of refraction (ref. 41). Once the pure materials have been explored, the study can be broadened using additions intended both to enhance glass formation and to widen the range of attainable properties.

Materials which are of interest for laser applications are particularly worth exploring. In the case of Nd^{3+} glass lasers it is believed (ref. 39) that a higher CaO content serves to increase the efficiency of the laser, but crystallization is a problem with higher CaO content. Also, glasses of higher Nd^{3+} content, which are attainable only by suppressing nucleation, may lead to better laser action.

B. EXPERIMENTS DEALING WITH SURFACE TENSION DRIVEN (MARANGONI) CONVECTION

INTRODUCTION

One of the most attractive features of space processing for materials science experiments is the absence of gravity and the resulting possibility of eliminating convection effects. However, one must be careful in assuming that a 10^{-4} to 10^{-6} g-level will entirely eliminate convection. For example, Ostrach (ref. 42) and Grodzka, et al. (ref. 43) have pointed out that convection may be caused by surface tension gradients {Marangoni convection (ref.44)}, volume changes produced by phase changes, and g-gitter in the spacecraft. Even natural convection due to density differences in a liquid may not be completely eliminated in the micro-g environment.

A number of experiments have been suggested to study convection phenomena which are little influenced by gravity and which would therefore be dominant when gravity induced convection currents are essentially eliminated at low-g. Marangoni convection is a prime example and is one of the areas of extreme interest.

Other experiments have been suggested in which the near elimination of convection effected by the micro-g environment would help sort out the effects of convection currents from other mechanisms influencing such processes as dendrite solidification, electrotransport or the Soret effect.

Marangoni convection arises when gradients in surface tension are produced by gradients in either temperature or composition (refs. 42-44). Gradients in both temperature and composition are inherently present in alloy solidification experiments; composition gradients are inherently present in measurements of chemical diffusion coefficients in liquids; temperature gradients and composition gradients are inherently present in measurements of Soret coefficients in liquid alloys. Consequently, it is clear that Marangoni convection may be an important factor in several types of materials science experiments. However, in many of these experiments the liquid boundaries are in contact with a solid container and the no-slip hydrodynamic condition at this interface is expected to dominate. As a result, one only expects Marangoni convection at liquid-liquid or liquid-vapor surfaces, which are generally termed, free surfaces; an example of the latter would be the free surface of the molten zone in a floating zone experiment. This case was the subject of a very recent theoretical analysis (ref. 45) from which it was concluded that Marangoni-type convection is virtually unavoidable for liquid-solid phase transformations (crystal growth) of the industrially most important electronic materials. This publication suggests further that surface tension gradients constitute a larger driving force for convection than density gradients. While the validity of the conclusions is questioned by some of the scientific community the arguments on both sides remain largely conjectural because of lack of required basic data.

Marangoni convection may be strongly surpressed and perhaps even eliminated at the free surface of a floating zone by the presence of an oxide film or a solute which tends to segregate either at the surface or away from it. This latter case has been treated theoretically (refs. 46,47) and Earth-based experiments (refs. 47,49) have shown that theroetical predictions of the reduction of Marangoni convection by surfactants is observed. It is apparent, therefore, that the extent of Marangoni convection will be strongly dependent upon liquid surface conditions.

Experiments done to date are somewhat confusing. The drop tower experiments of Ostrach (ref. 42) as well as the Benard experiments of Grodzka and Bannister (ref. 50) aboard Apollo have found Marangoni convection to occur in very low g conditions as predicted theoretically in systems possessing free surfaces. However, the interpretation of experiments carried out in closed containers is not as clear.

An interesting complication involving the liquid/container boundaries arises in systems employing closed containers. In many of the experiments conducted in space it was found that the liquid displayed a strong tendency to pull away from the container walls, apparently due to surface tension forces. In the experiments of Witt, et al. (ref. 51), the liquid pulled away from the wall at all points except for a few ridges which maintained contact. Therefore, one suspects that the liquid surface should have been essentially a free interface subject to Marangoni convection. Bourgeois and Spradley (ref. 52) have analyzed Witt's experiment and predict Marangoni convection several orders of magnitude higher than observed. The ridges of contact would reduce convection but it seems unlikely that this effect could account for the large difference between theory and experiment. A similar disparity was found (ref. 52) in the analysis of Walters' (ref. 53) experiment on Skylab where the liquid surface did not

touch the container. Hence, it is apparent that in these experiments (refs. 51,53) which were both done on InSb, the convection, if present, is much smaller than predicted. A possible explanation for this conflict is that an undetected oxide layer was present on the liquid surface.

In the solidification experiments of Yue and Voltmer (ref. 54) on Ga doped Ge alloys in graphite containers, both macro- and microsegregation effects are reported which suggest the presence of convection during the phase transformation. This is puzzling because: (a) The molten alloy appeared to maintain good contact with the graphite container, except at the end of the molten zone (which was well displaced from the initial solid-liquid interface) and (b) the experiment of Witt, et al., (ref. 51) on InSb performed under very similar conditions, appeared more likely to have a free surface, and yet exhibited no significant convection. Perhaps the molten Ge alloy was maintained completely free of oxide in the graphite container and the surface tension force was able to prevent any significant contact with the graphite container thereby allowing Marangoni flow in the Ge experiments. Convection in the InSb experiments may have been inhibited by an oxide film as suggested above.

In the recent Apollo-Soyuz flight, Gatos and Witt (ref. 55) have also carried out experiments involving the solidification of Ga-doped Ge which, upon analysis, showed the presence of compositional variations. The observed segregation irregularities could, however, be attributed to a deficient thermal configuration in the multi-purpose furnace which resulted in pronounced variations of the growth interface morphology. The observed microsegregation effects cannot therefore be taken as evidence for the presence of convective melt flow.

In addition to the solidification studies described above, two space experiments have been carried out on diffusion in liquid metals. The first experiment by Ukanwa (ref. 56) was done on self diffusion in liquid Zn contained in graphite tubes. These experiments were done under a temperature gradient of 45 C/cm so that a significant driving force for potential Marangoni flow was present. Interpretation of these experiments is complicated because of the unknown effects of melting and solidification upon liquid movement. Analysis of centerline diffusion profiles shows good reproducibility and good agreement with experiments done on Earth in capillary geometries where convection is thought to be absent. Comparison to identical Earth bound experiments shows a dramatic reduction in convection for the Skylab experiments. Unfortunately, the Skylab experiments show radial concentration variations as high as 20 to 25% thus indicating that some small amount of convection was present in these experiments. It is not certain, however, if this convection may have been caused by fluid flow induced by melting and freezing.

The second experiment was carried out by Reed aboard Apollo-Soyuz (ref. 57). These experiments involved diffusing small amounts of Au into Pb contained in steel containers. The materials were melted and solidified from the same and alternate ends to test for effects on fluid motion. Again, a radial concentration profile was found thus indicating a small amount of convection. In these experiments there is evidence that this convection was not caused by the melting and solidification process and it has been postulated (ref. 58) that the convection in spite of the solid container results from

Marangoni flow. It should be noted that in both of these diffusion studies the liquid metal had pulled away from the corners at the ends of the diffusion column so that at these points a free surface would definitely be present and could produce local convection due to surface tension gradients.

While convective melt instabilities are common to many liquid-solid phase transformations conducted on Earth, their origin is generally not attributed to surface tension gradients but to unavoidable destabilizing density gradients (ref. 59). In fact, the basic assumption that gravity controlled destabilizing density gradients are responsible for unavoidable convective melt flows during solidification led to the first crystal growth experiments on Skylab and ASTP (refs. 51,53,60). These experiments were performed with the expectation that if convective melt instability could be suppressed, then otherwise unavoidable defect formation and compositional fluctuations in the resulting solids would be eliminated. The results of these experiments, which were conducted under considerable constraints, must in the light of the previous discussions be considered inconclusive and to some extent controversial.

B.1 EXPERIMENTS DESIGNED TO ELIMINATE CONVECTION AT LOW-G

Objective

It is clear from the above discussion that convection due to Marangoni flow and volume changes upon solidification will be present under some conditions in space experiments. The conditions which produce this convection are at present not well defined. Two factors may play a critical role in Marangoni convection: (1) The condition of the liquid surface, i.e., whether or not a solid film is present such as an oxide (even a monolayer). (2) The degree of contact at the liquid/container interface. This contact may be significantly reduced by the action of surface tension upon the liquid in near zero-g.

The objective of the proposed experiments is to determine the experimental conditions which are required to insure the elimination of convection in materials science experiments which are inherently subject to temperature and/or composition gradients, e.g., solidification, diffusion, Soret effect.

Justification

One of the major advantages of the space environment is the greatly reduced gravitational force with the potential for eliminating convection from several processes utilized in materials science and materials processing. However, initial experiments have demonstrated that simply doing experiments in space does not guarantee the absence of convection. Consequently, experiments must be done to pinpoint the causes of convection in the low gravity environment and to allow design of space experiments which are free from convection.

It is apparent that such experimental convection studies may overlap to some degree the work recommended in the area of fluid physics (ref. 11). However, convection studies should also be done in the materials sciences area, so that they may be directed at particular processes of interest, for example, crystallization from the melt. The fluid physics studies will be done on

transparent liquids of relatively high Prandtl number at relatively low temperatures and such studies will be very useful model systems for understanding the nature of surface tension driven convection. However, it will still be necessary to see if such model systems can be extrapolated to the high temperature, non-transparent, low Prandtl number liquids of interest in much of the field of materials science. Hence, it seems most appropriate that convection studies should be carried out in the materials science area, in close communication and perhaps even in collaboration with the group or groups doing the fundamental studies in fluid physics.

Approach

There are several experimental techniques which could be used. In the non-transparent liquids which are of primary interest here one can detect convection by its effects upon heat flow or mass flow. In materials science concern is focused on control of composition, and it seems appropriate to conduct experiments which detect convection by means of its effect upon mass flow. In addition, such experiments are as sensitive or perhaps more sensitive than experiments which detect convection by its influence on heat flow.

Two types of experiments suggest themselves, liquid diffusion experiments and unidirectional solidification experiments. The solidification experiments have some advantages for the present study: (1) The process directly produces a solid so that one does not need to be concerned with the effect of freezing upon the prior solute distribution in the liquid. (2) In addition to possible Marangoni convection, liquid flow due to the volume change upon solidification is also inherent to the process and could be evaluated. Hence, it is suggested that solidification experiments be employed in this study.

The experimental design would be aimed at determining the effect of several experimental variables upon liquid convection. The variables which would be studied are: (1) The contact at the solid-container interface. This contact could be varied by applying a small hydrostatic pressure to the liquid by a technique as simple as spring loading the liquid. (2) The atmosphere around the liquid. This could be changed from reducing to oxidizing, to determine effects of surface oxide layers. (3) Other significant variables such as, (a) container material, (b) temperature gradients, (c) sample diameter, and (d) shape of solid-liquid interface.

The technique for determining the presence and extent of convection would involve measuring the longitudinal and radial composition of the solidified sample. Analysis of the initial transient region and steady-state regions would detect the presence of convection (ref. 61). Provisions should also be made to allow the experiment to be terminated by quenching the liquid. Analysis of the composition profile in the quenched liquid (refs. 61,62) would provide an additional means of evaluating convection and would provide a check on the initial transient measurements.

Materials

It is suggested that experiments be done on both semiconducting materials and metallic materials because of the difference in their respective

volume changes upon solidification and because of the importance of both types of materials. The semiconducting materials especially lend themselves to very sensitive chemical analysis using resistivity techniques; in addition the clever technique of Witt, et al. (ref. 51), may be used to detect microfluctuations in interface movement. Radioisotope techniques (refs. 61,62) have also proved to be very senstitive for measuring composition profiles and should be used in both the metal and semiconductor studies.

General Comments

In evaluating solidification experiments accomplished to date in the space program it is clear that part of the difficulty in evaluating the results stems from the restricted experimental technique imposed on the experimenters. In future experiments very careful consideration should be given to design of the experiments so that (a) solidification rate may be held constant and measured accurately, (b) temperature gradient may be held constant and accurately measured, (c) heat flow may be adequately controlled at the solid-liquid interface to allow control of the solid-liquid interface shape, (d) start-up conditions can be controlled to insure that the initial melt-back procedure does not alter the solute profile, and (e) provisions can be employed to terminate the experiment by quenching the liquid, thereby preserving the solute profile in the liquid near the solid-liquid interface where the quench produced unidirectional solidification.

B.2 THE INFLUENCE OF SURFACE TENSION DRIVEN CONVECTION ON SEGREGATION DURING SOLIDIFICATION UNDER REDUCED GRAVITY CONDITIONS

Objectives

The primary objectives of the suggested research are: (1) the determination of the effects of surface tension driven convection on segregation, growth behavior and defect formation during solidification; (2) the compilation of basic scientific data required for the establishment of a comprehensive quantitative understanding of Marangoni-type convection flows; (3) the provision of input for the optimization of materials processing technology on Earth.

Justification

As detailed in Section B.1, the origin of unavoidable convection melt flows in solidification systems involving free surfaces is the subject of great scientific interest and controversy. Moreover, the determination of the origin of convection melt flow is of paramount importance for the solid state device industry since the specific source of convection dictates which approaches should be taken to eliminate or reduce its effect and to optimize our currently deficient processing technology.

The primary driving forces for convection in solidification systems are provided by density gradients and surface tension gradients. In view of the present unavailability of experimental data ($d\gamma/dT$, $d\gamma/dc$, dT/dx where γ is the surface energy, c the solute concentration, T the temperature and x a space coordinate), it is impossible at this time to use and test the validity of the existing theoretical framework for the determination of the dominating driving force for convection on Earth. Moreover, it is experimentally

impossible to suppress one of the driving forces on Earth in systems having free surfaces and thus to investigate experimentally surface tension driven convection in solidification systems unambiguously. However, experiments conducted under reduced gravity conditions will provide data which will allow us to reach unambiguous conclusions concerning the dominating forces responsible for convection flow associated with solidification. (Since density driven convection is gravity dependent whereas surface tension driven convection is not, the inherent characteristics of surface tension induced convection can thus be determined without interference.) The long duration flights of the Space Shuttle will allow for variations in solidification speeds and will also make possible an investigation of slow time dependent convection. This is not feasible on the shorter duration SPAR flights.

The study of surface tension driven convection in solidification systems must be considered as fundamental for the assessment of the potential of space processing. If, as suggested from theoretical consideration, Marangoni-type flows may indeed assume a turbulent nature in solidification systems with free surfaces, the potential of space processing will be significantly limited, and specifically the exploration of containerless and float-zone processing must be re-examined. Accordingly, the results of the proposed study should provide basic input to the design of solidification configurations by which the use of the reduced gravity environment can be optimized.

Approach

In the first phase of the suggested study the existing theoretical framework for surface tension driven convection would be subjected to an exhaustive analysis to determine its applicability to conditions prevailing during liquid-solid phase transformation, and inadequacies in the theory would be corrected. Previously conducted low gravity solidification experiments would be evaluated for identifiable surface tension-driven convection effects. On the basis of these preliminary studies specific systems would be identified for experimentation in the reduced gravity environment.

In the second phase of the study basic data such as γ, $d\gamma/dT$, $d\gamma/dc$ would be determined for selected pure and dilute binary or multicomponent systems. In addition, experimental approaches for the study of surface tension driven convection in space would be developed. These would be concerned with the development of techniques which will permit the precise determination of temperature and compositional gradients in the vicinity of the solid-liquid interface. Moreover, procedures must be developed which permit the direct or indirect quantitative analysis of time-independent and time-dependent convective flows in the bulk and on the surface of the system to be investigated. Finally, optimized solidification configurations for low gravity experimentation must be developed and tested to the extent possible on Earth and, if required, in short duration rocket flights.

The exact experiments to be carried out in Spacelab must evolve from the ground-based research and should be exhaustively analyzed by a panel of experts prior to execution.

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Criteria for systems selection include: scientific and technological revelence; availability of required characterization techniques (or the possibility of the development of such); stability; availability in the required purity or with appropriate compositional control; amenability of systems to exhaustive experimental analysis. On the basis of these requirements, and for the purpose of obtaining broad and meaningful data, it is suggested that at least one low Prandtl number fluid semiconductor system and one high Prandtl number fluid transparent system be selected.

C. EXPERIMENTS DEALING WITH SOLIDIFICATION AND CRYSTAL GROWTH IN THE NEAR-ABSENCE OF NATURAL CONVECTION CURRENTS

INTRODUCTION

The ability to eliminate natural convection in space laboratory experiments affords a potentially powerful experimental tool for studies of solidificaion which are affected by convection. However, it is important to realize that it is also possible to completely eliminate convection in solidification experiments done at 1-g if proper experimental design is observed. It is possible to classify natural convection into two categories, threshold and thresholdless convection. By a simple analysis of the Stokes-Navier equations (ref. 63) one may show that if a horizontal density gradient appears in a liquid due either to a horizontal temperature or composition gradient a finite convective velocity will appear, and this is termed thresholdless convection. If, however, horizontal density gradients are zero, and one produces a destabilizing vertical density gradient (top denser than bottom) a finite convective velocity will not appear until some critical value of density gradient is exceeded, and this type of convection is termed threshold convection. The critical density gradients have been calculated from hydrodynamic theory for several simple geometries. For example, in a long vertical tube of liquid heated from below, convection is predicted to begin when the verical temperature gradient exceeds the critical value,

$$G_{CR} = - \frac{68.0 \nu K}{g \alpha r^4}$$

where ν is kinematic viscosity, K is the thermal diffusivity, g the gravitational constant, α the thermal expansion coefficient and r the tube radius. Hence, convection may be eliminated from Earthbound experiments by insuring the absence of horizontal temperature and composition gradients and by insuring that vertical temperature and composition gradients are either stabilizing or, if destabilizing, are less than certain critical values. Liquid diffusion experiments are routinely carried out on Earth without convection by following the above guidelines. Vertical tubes are used with stabilizing vertical temperature and composition gradients. Since threshold convection is a strong function of tube diameter and since horizontal concentration gradients are minimized in small diameter tubes, these experiments generally employ tube diameters of 1 to 2 mm or less.

In a similar manner, convection may be eliminated from solidification experiments by using small diameter vertical geometries with the hotter liquid above the solid and with the composition gradient such as to reduce the density

in the vertical directions. Several such experiments (refs. 62,64,65) have been carried out in recent years. However, because of the inherent nature of solidification in binary or higher order systems there are some experiments in which the conditions for zero convection at 1-g can simply not be assured.

Plane Front Conditions

When the solid-liquid interface is planar, two interesting examples arise.

(1) In a binary system with the distribution coefficient less than 1 the solute concentration will decrease going up into the liquid. For the case of solute lighter than solvent, this then produces a destabilizing density gradient due to the concentration profile. One might expect that stability would be maintained by a large positive temperature gradient but calculations (ref. 63) and experiments (ref. 66) show that only a small concentration gradient is required to override the stabilizing influence of a positive temperature gradient. One could in this case solidify downward to make the concentration gradient stabilizing, but then the temperature gradient becomes destabilizing. One must then operate with the temperature gradient below the critical value but there are two problems with this. (1) Theoretical critical values are not known for the case of superposed temperature and composition gradients and (2) in many experiments large gradients are required to maintain the solid-liquid interface planar. Hence, it is unlikely that convection can be eliminated from Earth-bound solidification experiments in systems where the solute decreases the liquid density.

(2) Elimination of convection requires the solid-liquid interface to be horizontal. The surface tension balance at the trijunction of liquid-wall/liquid-solid/solid-wall will invariably cause the liquid-solid interface to meet the wall at an angle other than 90°. Hence, the interface cannot be horizontal near the wall and this in turn will produce horizontal concentration gradients which may produce thresholdless convection. Such convection can be kept to a negligible level using small diameter containers, on the order of 1 to 2 mm. However, experiments requiring larger diameters may inherently produce convection in Earth-bound experiments for this reason and because of the inherent difficulty of maintaining planar isotherms and isoconcentrates in large systems.

Dendritic Conditions

When the interface becomes dendritic, as is the case in virtually all alloy castings, it becomes impossible to force concentration and temperature gradients to lie only in the vertical direction. This is due to the inherent three dimensional character of the surface profile of dendrites. Hence, dendritic solidification is a process in which one cannot assuredly eliminate convection in Earth-Bound experiments.

Specific Experiments

Based on the above ideas, experiments are suggested which could not be carried out on earth in the total absence of convection, but may be carried out in space with zero convection if convection induced by surface tension gradients and volume changes can be effectively eliminated. (See Section B.1)

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C.1   PLANE FRONT SOLIDIFICATION AT OFF-EUTECTIC COMPOSITIONS

Background

The question arises as to whether the micro-g environment would be beneficial to directional solidification of eutectic alloys. First, it should be emphasized that convection free experiments can be conducted on Earth by employing small diameter vertical tubes. In addition, the solute fields which occur at the eutectic front extend into the liquid phase on the order of the lamellar spacing, around 10 μm at the most. Even with rather severe liquid mixing, convection free boundary layers of 50 to 60 μm are present in the liquid at the solidifying interface. Hence, convection can have very little direct effect upon the solute redistribution occuring in the liquid at the eutectic interface. There are, however, two other possible effects which should be considered. The first concerns the possibility of improving the perfection of the lamellar structure. There is fairly good evidence (ref. 67), that the fault density of lamellar structures may be improved by eliminating temperature oscillations which inhibit the uniform advance of the solid-liquid interface. This is basically a heat transfer problem and one could argue that microtemperature oscillations may more effectively be eliminated in micro-g. This follows because even with small diameter vertical tubes, where the heat is restricted to flow unidirectionally in the vertical direction at the solid-liquid interface and convection may be eliminated in Earth-bound experiments, it is necessary to have lateral heat transfer where the heat is introduced above the interface. This causes convection in the upper part of the system which could produce temperature oscillations on a small scale even at the solid-liquid interface. However, by use of very low temperature gradients, proper heat transfer design, and a magnetic field at the location of heat input it seems quite possible that one could do as well at 1-g as in space for considerable less cost. In addition, recent experiments with capillary sized samples (ref. 68) have shown that fault dendrites may be considerably reduced by simply utilizing capillary containers. Since the capillary dimension is quite small, it seems very likely that such systems could be designed convection free, even at one-g, and thereby afford the same advantage as micro-g. It thus seems improbable that space processing by directional solidification of eutectics at on-eutectic composition will offer any advantage over Earth experiments, except where larger diameter samples are required or where chemical interactions with the capillary material is a problem.

The second effect concerns the solidification of off-eutectic alloys. It is only possible to eliminate convection from experiments done on Earth at alloy compositions on one side of the eutectic composition. For example, in the Pb-Sn system no convection is produced on the high tin side of the eutectic, but quite severe convection has been shown to occur (ref. 66) at compositions just slightly on the high lead side. Moreover, in off-eutectic alloys a long range solute build-up may be present, and convection has a larger effect than in the eutectic alloys. Hence, the microgravity environment of space offers an opportunity to study the effects of material and growth parameters on the segregation, structure, and properties of these alloys without the presence of convection.

Objective

The objective of this study is to demonstrate that off-eutectic studies may be conducted in space on either side of the eutectic composition without convection.

Justification

Plane front solidification at off-eutectic compositions offers a potentially important technique for varying the volume fraction of the constituent phases in directionally solidified composites. It would be useful to demonstrate that convection can be eliminated in space conducted experiments at compositions on both sides of the eutectic. In addition to its scientific interest it would then be clear that space processing has the potential to increase the volume fraction of second phase of a eutectic composite in a system where solute convection prohibits such processing on Earth.

Approach

Directional solidification of off-eutectic alloys would be carried out with carefully controlled heat flow conditions to ensure planar solid-liquid interfaces, controlled growth rates and temperature gradients. Studies of the macrosegregation profile would then establish whether or not the space environment was effective in eliminating convection at compositions where convection is present in Earth-bound experiments.

Materials

It is suggested that initial experiments be carried out on simple binary alloys such as Pb-Sn and Al-Cu which have been well studied on earth. It would then be desirable to extend the experiments to ternary alloys such as the nickel base superalloys which are of some commercial interest.

C.2   THE EFFECTS OF REDUCED GRAVITY ON PLANE FRONT SOLIDIFICATION INVOLVING SEGREGATION

Background

The field of solidification and single crystal growth in particular is characterized by a wide gap between theory and experiment, and crystal growth technology, the basis for most of the materials used in the solid state electronics industry, relies heavily on empirical procedures. This situation must be considered as highly undesirable. Accordingly, control of composition and perfection is inadequate for most systems, and a wide range of materials remains inaccessable for device fabrication.

The lack of a quantitative framework for solidification can be attributed largely (1) to gravity induced perturbations associated with solidification and (2) to our inadequate knowledge of basic materials parameters. Consequently, with the availability of a low gravity environment through the NASA program, some basic crystal growth experiments were performed with the intent of exploring the potential of materials processing in space (refs. 51,54,69). The reported results indicate a multitude of unpredicted and as yet unexplained basic phenomena not previously observed. Some of the experiments performed appear to confirm diffusion controlled growth and segregation (compositional homogenity) and thus the absence of convection melt flow (ref. 51), whereas in contrast others seem to provide evidence for the existence of limited convection melt flow (ref.54). The latest comprehensive analysis of the ASTP experiments (ref. 70) involving solidification of gallium-doped germanium indicates, however, that the longitudinal and radial compositional variations reported earlier are not convection induced but rather reflect variations in growth conditions induced by the thermal configuration of the multipurpose furnace used.

A comparison of these results with the established theory of segregation under diffusion conditions is found inconclusive for several reasons: the theory was developed for the unrealistic condition of a step function in growth rate (from zero to a finite constant value); furthermore, the accuracy of published diffusion constants is insufficient, and generally accepted values of the equilibrium distribution coefficients have been found to be erroneous.

The preliminary crystal growth experiments in space have, in spite of serious experimental limitations, unambiguously established the great value of a reduced gravity environment for the quantitative study of solidification; they have revealed deficiencies in the existing theoretical framework and have provided evidence that basic, as yet unavailable, material constants may be obtained from solidification experiments under reduced gravity.

Objectives

The primary objective of crystal growth experiments in space is the establishment of a quantitative theoretical framework for growth and segregation which is consistent with experimental results. Other objectives are to acquire a better understanding of the important phenomena of dopant segregation in the radial direction and along growth facets, and to provide measurements of needed basic material parameters, including distribution coefficients and diffusion constants of high temperature melts.

Justification

Our inability to produce materials on Earth with theoretically uniform composition and with crystalline perfection is undisputed. In addition, there is little argument that a wide gap between solidification theory and experiment exists at least as far as electronic materials are concerned. Both deficiencies can be related to gravity induced perturbations during solidification and to our inadequate knowledge of basic materials parameters. Crystal growth experiments under reduced gravity can be instrumental in removing the connotation of "art" from this activity, by providing a sounder scientific base. As a consequence, it should be possible to optimize our terrestrial processing technology, which in turn should enable us to produce better materials and to make new materials available for device fabrication.

The suggested space experiments will not only further our understanding of solidification but will also establish a scientific basis for the assessment of the true potential of the low gravity environment for space processing.

Whereas the preliminary results of experiments conducted in space are ambiguous – and completely convection-free conditions are not predicted by theory for the low gravity environment – it has already been established that valuable scientific information not obtainable from Earth can be obtained from solidification experiments in space. Thus, for example, deficiencies in our basic solidification theory may have been revealed through experiments in space and the possibility of deficiencies in the established fluid dynamic theory which predicts residual convection in space cannot be ruled out a priori.

Approach

The design of meaningful experiments in space must be preceded by an exhaustive ground-based analysis of all growth and segregation experiments thus far conducted in a reduced gravity environment. As a second phase, growth systems suitable for the low-gravity environment must be selected. This phase must be coordinated with the development of experimental approaches for the quantitative in situ characterization and monitoring of growth processes. In addition, adequate (more sensitive) materials characterization techniques must be developed to permit exhaustive analysis of space experiments. In parallel with these activities, effort must be made to advance the existing theoretical framework by interpreting and incorporating the findings of earlier experiments conducted in space.

In order to optimize the experimental activities in space it is mandatory that the specific experiments not be prematurely defined but that they evolve logically from the conclusions drawn during the ground-based research and development phase. Moreover, the solidification experiments should be coordinated as closely as possible with other related experiments conducted on Spacelab. All experiments ultimately suggested should be studied by a small group of experts in solidification prior to their execution.

Materials

In order to achieve a maximum of unambiguous information, it is mandatory that the solidification systems which are studied are: (a) the "purest", (b) the most easily characterized systems in which details of phenomena taking place during the phase transformation are extractable through "post mortem" analysis. These requirements appear to be best met by semiconductors.

C.3   DENDRITIC GROWTH IN CONGRUENTLY MELTING SYSTEMS

Background

In most instances, the solidification of metallic materials occurs by the growth of dendritic crystals. The dendritic or branched crystal morphology is now recognized as a direct result of two opposing tendencies: (a) the so-called "point-effect" in diffusion, wherein sharply pointed slender shapes tend to reject heat and matter most efficiently into an adjacent 3-dimensional diffusion field and (b) the relaxation (blunting) of sharply pointed bodies under the influence of surface tension, which raises the chemical potential of regions with large curvatures relative to regions with small curvatures. Thus, diffusion-limited phase changes often display overall transformation kinetics which is a compromise between achieving efficient diffusion and achieving a low surface-to-volume ratio.

The control and understanding of dendritic growth is considered important because the dendritic process is responsible for the origin of chemical inhomogenities (microsegregation) and other internal defects in castings, ingots, and weldments. More subtle effects introduced by dendritic growth include crystallographic texturing of solidified materials, non-equilibrium phases, reduced corrosion resistance, and sub-optimal mechanical strength and toughness.

Theoretical studies of dendritic growth (refs. 71-78) have concentrated on the steady-state development of a one-component dendrite growing in a pure melt. This is the simplest form of dendritic growth, insofar as the sole diffusant is heat, and only on-axis behavior is considered. Only recently, in fact were the first detailed comparisons made between theoretical predictions and experiments (refs. 79,80). The major factor inhibiting earlier quantitative comparison of theory with experiment is that the theoretical expression for the axial dendritic growth rate, V, of even a pure material requires knowledge of five materials constants. Specifically, it can be shown (ref. 78) that

$$V = \beta G \Delta \theta^n, \tag{1}$$

where β and n are theoretically derived constants independent of the material properties; G is a lumped material parameter defined as $G = \alpha \Delta S\, L/C\gamma$, where α is the thermal diffusivity, ΔS is the entropy of fusion per unit volume, L is the molar heat of transformation, C is the molar specific heat, and γ is the solid-liquid surface tension; $\Delta \theta$ is the ordinary supercooling, ΔT, normalized to L/C, and consequently is a dimensionless variable having values between 0 and 1. Thus it was not until systems were studied sufficiently well to obtain G accurately that Equation (1) could be tested on a rigorous basis. To date, only two systems exist for which G is known to within about 10%: water/ice (ref. 80), and succinonitrile (ref. 79).

The major findings so far indicate that the theoretically predicted value of n = 2.6 is correct, but that β is much smaller (by a factor of about 1/3 to 1/7) than theory predicts. Hence, it appears that the dendritic growth process behaves almost cubically (n = 2.6) for supercoolings $\Delta \theta > 0.1$, which in the systems tested correspond to thermal supercoolings $\Delta T > 1°C$.

Objective

Ideally, one would like to test equation (1) at smaller supercoolings where the dendrites are both larger in size scale and grow more slowly. The size-scale of a dendrite is related to the diffusion distance, α/V, which as indicated by equation (1) should increase rapidly with decreasing supercooling. Experiments in near zero-g would permit additional measurements in the supercooling regime 0.1 to 1C, where careful morphological observations of the tip geometry (radius of curvature) and branch formation could be made.

Justification

The difficulty encountered under terrestrial conditions in performing dendritic growth experiments at small supercoolings is that gravitationally driven thermal convection enters (and confuses) the heat transfer situation. More specifically, the diffusion process is a nearly cubic function of supercooling whereas convection is essentially a linear function; consequently, on Earth diffusion dominates at large ΔT, and convection dominates at small ΔT. A clear manifestation of this effect is that the axial growth rate of a dendrite becomes a function of its orientation with respect to gravity at small supercoolings.

Approach

Performance of these experiments would require temperature control of better than 1% to permit velocity measurements to 3%. Thus at the smallest supercoolings, 1 millidegree control is needed. A serious limitation in these measurements is that the thermal diffusion distance must not become excessively large, because excessively long relaxation times and inconveniently large system volumes would result. Data from this experiment could be used to check the heat transfer theory through the Peclet number, $VR/2\alpha$, where R is the radius of curvature at the dendrite tip. In addition, the dependence of R on $\Delta\theta$, and the relationship of convection-free branch spacing to R, V and $\Delta\theta$ could be investigated.

Materials

As explained above, unless full characterization of the material is available, detailed verification of the growth model will be limited. At present, only water/ice and succinonitrile are sufficiently well characterized to warrant their immediate study. Semiconductors and pure metals are other candidate materials which for this study primarily lack accurate solid-liquid surface tension measurements. Oxides and low melting point anhydrous salts are ideal for observation of the growth morphology, but they again are often poorly characterized with respect to solid-liquid surface tension. Materials which have relatively large entropies of fusion ($\Delta S/R > 2$, where R is the gas constant) also tend to form growth facets which modify the dendritic morphology. Dendritic growth theory, in its present form, cannot account for faceted growth morphologies, so quantitative comparison would be limited for such systems.

C.4 DENDRITIC GROWTH AND MACROSEGREGATION IN ALLOY SYSTEMS

Background

Although no refined theories of alloy dendrites exist, several interesting areas of investigation are possible. Solute rejection at a moving solid-liquid interface results in a coupling of the temperature and concentration fields of the dendritic crystal. At present, it is unclear how solutes influence the growth speed, although experience shows that solutal dendrites have finer, more delicately branched structures than do thermal dendrites. Presumably, this difference arises because of the reduced diffusion distance for slowly diffusing solutes versus rapidly diffusing heat flux.

Solutes also complicate the solidification process because of gravity-driven convection arising from density gradients in the melt. This form of convection may have profound effects on the solidified structure. For example, the phenomenon of "freckling" in superalloy ingots has been shown to be a result of unstable fluid jets penetrating and fragmenting the dendritic zone during solidification (ref. 81). Studies by Hunt and his co-workers have shown that solutal convection is a major factor in determining basic microstructural parameters of the as-cast structure, such as the primary dendrite spacing (refs. 82,83). Dendritic spacings in freezing ammonium chloride solutions varied by a factor of ten depending upon whether growth was

parallel or antiparallel to gravity. The effect was qualitatively discussed in terms of how the gravity-induced flow aided solute diffusion and either increased or decreased the lateral segregation depending on the relative directions of the convective flow and the dendritic velocity. A recent study by Okamoto, et al. shows similar effects on the primary spacing in unidirectionally solidified cyclohexanol (ref. 84).

The ability to carry out such experiments under reduced gravity permits direct probing of the convection mechanism by de-coupling the diffusive transport from the convective transport. Comparison of resultant solidification structures would yield post mortem evidence for the influence of gravity.

Objectives

There are two major objectives to a suggested study of alloy dendrite growth and macrosegregation: 1) To determine if convective flow at dendrite tips plays a significant role in alloy dendrites growing into a positive temperature gradient; 2) To determine the role of temperature gradient and solute gradient induced convection upon macrosegregation in alloys solidifying with dendritic interfaces.

Justification

The work of Burden and Hunt (ref. 85) and Tassa and Hunt (ref. 86) has shown that agreement between experiment and theory becomes poor in studies on dendrite growth into a positive gradient as the concentration is further removed from the eutectic composition. It is felt that this effect results from increasing convection due to the corresponding longer dendrites. Experiments conducted in space could be used to determine whether convection is the cause of this discrepancy between theory and experiment. As previously shown it is not possible to design Earth-based dendritic growth experiments in which density gradient convection is zero.

Cast alloys virtually always solidify with dendritic interfaces. Macrosegregation (segregation along the length or diameter of the casting) has been studied fairly extensively in the past two decades. Theory and experiment (refs. 87-89) have shown fairly conclusively that under conditions where the dendritic length is changing, macrosegregation will occur due to flow produced by the volume change on freezing. When the dendrite array moves with a steady state length no macrosegregation occurs. If, however, there is a convective interchange of liquid in the dendrite array region with liquid ahead of the growing dendrite array, then one would expect a significant alteration of the macrosegregation. Theoretical treatments of this case are yet forthcoming. However, experimental studies indicate that in some cases the effect is large (refs. 90, 91) and in other cases it is not (ref. 92). Zero-g experiments would be extremely useful in clarifying this situation because, as mentioned above, density induced convection cannot be eliminated from Earth-based experiments.

Approach

For the study on dendritic growth into a positive temperature gradient, experiments on dendrite tip temperatures and eutectic interface

temperatures would be carried out in ground-based and space-based environments.
Comparison of experimental results with theory as a function of alloy composition and acceleration level would then be made to determine the role of convection in dendrite growth. Initial experiments should be done on well characterized systems such as Pb-Sn and Al-Cu. The experiments should be extended to several systems having a wide range of material properties to establish a correlation which would allow one to predict conditions where convection becomes a significant factor.

For the macrosegregation studies comparative experiments on the ground and in space could be performed on the systems investigated in refs. 90-92, Sn-Pb, Sn-Ga, Al-Ag and Al-Mg. Evaluation of macrosegregation would then permit an analysis of the relative importance of different variables such as thermal expansion and solute expansion coefficients, and the direction of solute gradients versus temperature and density gradients. The space experiments would serve as a reference to establish macrosegregation in the absence of density induced convection but including volume induced convection.

D. EXPERIMENTS ON MULTIPHASE MATERIALS

INTRODUCTION

The reduction of convection currents and buoyancy forces in the micro-gravity environment minimizes the rates at which second phase materials such as solid or liquid particles or gas bubbles segregate in a matrix fluid and the rate at which agglomeration occurs. We have suggested two areas of experimentation in this category, "Experiments on Liquid Phase Immiscible and Monotectic Materials" and "Solidification of Foams and Dispersions". Other related areas such as the movement of bubbles or droplets in a temperature gradient and the interaction of bubbles, particles and droplets with solidification fronts are desirable areas to investigate. However, no experiments along these specific areas have been detailed by the committee. Some low gravity investigations on bubble motion and particle pushing at solid-liquid interfaces are currently being conducted on SPAR flights (refs. 93,94).

D.1 EXPERIMENTS ON LIQUID PHASE IMMISCIBLE AND MONOTECTIC MATERIALS

Background

Liquid phase immiscible materials are of current commercial importance as electrical contact materials and bearing materials and have potential application as superconductors, catalysts, superplastic materials and magnetic materials among others (ref. 95).

Since the microstructure and thus the properties of these materials are very sensitive to the thermal history in the two-phase liquid field, and since the size and space distributions of the liquid droplets are expected to be greatly affected by gravitational forces, these systems are excellent candidates for space studies. In addition, the solidification process should play an important role in determining the structure and properties of these materials.

In terms of overall space experimentation on materials, there has been a fair effort already devoted to experimental work on this class of materials (refs. 95-101). Most of the experiments have been exploratory in nature and were performed under a variety of circumstances; in Apollo Missions (ref. 96), in Skylab (refs. 97-99), on KC-135 flights (ref. 99) and the MSFC drop tower (ref. 99), on the Apollo-Soyuz Mission (ref. 101) and on a SPAR flight (ref. 100).

There has been relatively little effort devoted to understanding the evolution of microstructure in these materials and the effect of gravity on this evolution. The theoretical work conducted thus far predicts that the material prepared in the microgravity environment should have a more uniform and finer microstructure than comparable material prepared at 1-g (ref. 100). This is due to the near absence of droplet collisions caused by gravity driven Stokes migration or by convection currents. In addition, it may be possible to produce spinodal structures (refs. 102,103) in the liquid which may be of value in that state or which may be retained after solidification. Experimental results thus far indicate that unexpected fluid flow mechanisms are producing unanticipated structures (ref. 100).

In the limited amount of work conducted on directional solidification of monotectic materials (refs. 104-108), it has been shown that coupled growth producing filamentary composite structures is possible in some of these systems. Structural banding (due to perturbations in growth conditions) and gross segregation in off-monotectic compositions (due to buoyancy effects) have been noted and should be avoidable in the microgravity environment (refs. 105,106). The perturbations are undoubtedly caused by convection currents induced by thermal or compositional gradients. As in the case of eutectics, convection currents can be largely eliminated from materials of exact monotectic composition by directional solidification in an upward direction if L_2* has a higher specific gravity than the bulk liquid. It is difficult to avoid complications due to buoyancy or convection when L_2 is of lower specific gravity than the bulk liquid. In such cases, if solidification occurs from below L_2 liquid can float out into the bulk liquid whereas if solidification is in a downward direction, the unfavorable thermal gradients can lead to excessive convection.

The feasibility of growing composites with off-monotectic compositions has been demonstrated (ref. 105) but the growth on a systematic and practical scale is complicated on Earth by segregation of the primary phase. Directional solidification of these materials in space could avoid these problems.

Directionally solidified monotectics may have applications as filters, thermal protection materials (ref. 106), fiber strengthened materials, superconductors or may be useful in the production of fibers.

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*L_2 is the liquid in a monotectic system having a composition on the side of the miscibility gap opposite to the monotectic composition. The liquid in the vicinity of the monotectic composition is L_1.

Objectives

The objectives of the work on liquid phase immiscibles are:

1) To understand the evolution of the microstructure of these types of systems in the absence of gravity induced coalescence mechanisms such as convection and Stokes migration.

2) To determine the propensity of these systems to form spinodal structures and to study their stability and their ability to be retained during the solidification process.

3) To understand the fluid-flow processes that occur in immiscible liquids.

4) To obtain accurate measurements of surface tension, interfacial energies and viscosities of the component liquids in the immiscible systems under study in order to be able to interpret the evolution and stability of the microstructure.

With regard to space studies on monotectic and near-monotectic alloys, the following objectives are pertinent:

1) To determine the relationship between the structures of these materials and their growth conditions and composition.

2) To determine the relationships between imperfections in the structure and the presence of convection currents.

Justification

The reduction in buoyancy forces and convection currents brought about by the micro-gravity environment should provide a clearer understanding of coalescence mechanisms in liquid phase immiscible systems. It should also allow the isolation of convection and buoyancy effects in the study of solidification processes in these systems and in monotectic materials. Finally, preparation of these materials in space should afford us the opportunity of obtaining materials with microstructures unattainable at 1-g for subsequent study on Earth.

Approach

Experiments on liquid phase immiscibles would be geared toward determining the effect of material composition, cooling rate through the miscibility gap and solidification conditions such as thermal gradients and interface velocity on the microstructure (distribution of second phase, presence of spinodal structure) and properties of these materials. Such experiments would usually begin with a homogeneous liquid equilibrated at a temperature in the single phase liquid field above the miscibility gap and would be followed by controlled cooling within the miscibility gap and during solidification. Liquid droplet agglomeration kinetics would be studied for materials of composition within the miscibility gap, both in space and on Earth.

The effect of interfacial energies, surface tension and viscosity on agglomeration kinetics and on the stability of droplets would be determined through investigation of a number of systems with a wide range of properties. It would also be important to obtain as part of the study accurate measurements of viscosity and surface tension as a function of composition and temperature. Finally, since fluid-flow processes appear to be important in determining the final microstructure of these materials, such phenomena would occupy an important place in these studies. Experiments of this type would not only be carried out on opaque metallic systems, but also on transparent model materials.

Directional solidification at 1-g and in the micro-g environment under various G/R growth conditions (G is the temperature gradient in the liquid at the solid-liquid interface and R, the solidification rate) and for both monotectic and off-monotectic compositions should provide us with an understanding of the influence of gravity driven processes on the evolution of coupled growth monotectic structures. The structural parameters of interest would include the size and spacing of the aligned fibers, and the presence or absence of banding or other microstructural imperfections. These studies should provide insight into the nature of defects in these materials, the conditions required to form such composite structures and the influence of surface and interfacial energies.

Materials

Materials having a wide range of surface and interfacial energies and viscosities would be chosen for these studies. We would start with some of the better characterized systems such as Al-In, Pb-Cu and Pb-Zn but would then expand the selection to other materials such as organic transparent systems in which direct observation of fluid flow processes, agglomeration and purification is possible.

D.2 SOLIDIFICATION OF FOAMS

Background

The production of stable foams of crystalline metallic materials requires two essential steps: 1) generating the gas-liquid metal foams; (2) solidifying the foamed liquid. Whereas considerable knowledge exists concerning the fundamentals of step (1), virtually nothing is known about step (2). Solidification of liquid metal films supporting small pressure differentials has become a matter of practical interest for such relatively new processes as edge-defined film fed growth (EFG) (ref. 109) and melt shaping (Stepanov process) (ref. 110). In these processes one deals with a solid-liquid interface growing in contact with vapor-liquid and vapor-solid interfaces. It is safe to say that the meniscus conditions to achieve stable solidification of a liquid film without rupture remain obscure. Surek and Chalmers (ref. 109) for example, have conclusively shown that the meniscus angle which must be maintained for constant thickness solidification of silicon was 11^{0} and not zero, as previously thought. This angle is a function of crystallographic orientation (e.g., 8.5^{0} for an average polycrystalline specimen) and different for different materials, e.g., 13^{0} for germanium. The foregoing discussion is presented to underscore the point that foam solidification is a complex phenomena, and that production of metallic foams under reduced gravity will require considerable study into basic solidification phenomena in liquid films.

Objective

The main objective of this experiment is to determine the interfacial relationships (meniscus conditions) for crystallization of thin metal films. The relationships among the solid-vapor, liquid-vapor, and solid-liquid interfaces would be measured under reduced gravity conditions. This information has applicability to the crystallization of foamed alloy melts during the preparation of low-density metallic foams.

Justification

Under near zero-g conditions, films of liquid metals in various configurations could be solidified to investigate the phenomena of interest. Besides meniscus equilibrium, the redistribution of solutes, including gas forming properties, would also be of interest, since gas bubble formation within a foam film would disrupt the integrity of the foam.

Approach

Molten films of various alloys would be shaped by supporting them on wire frames (in the manner of soap bubbles) and observing the freezing process under various conditions. Experimental variables include film composition, film thickness and freezing rate. Measurements include contact (ref. 111) and dihedral angle determinations and observation of film stability during crystallization.

Materials

Both technologically important and model systems are of interest with respect to foam formation at low g. Water containing surfactants would be an ideal system to study, since the formation of aqueous foams is well known, although their solidification behavior is not. Terrestrial studies of bubble formation in aluminum (again with surface active additions) have been carried out on a limited basis. Extension of such studies at low-g seems reasonable, especially since aluminum-gas foams might have some interesting properties. With sufficient experience, and assuming positive results with the simpler materials, one should consider study of foam formation in stainless steel or other structural alloys. The engineering possibilities of a new class of composite materials involving metals and gases is so intriguing that numerous alloys and gas mixtures might be studied in an attempt to achieve truly novel behavior and properties.

E.   EXPERIMENTS DEALING WITH SURFACE PHENOMENA

INTRODUCTION

The reduction of gravitational forces on homogeneous fluids or mixtures of fluids often accentuates phenomena resulting from forces which are second order at 1-g. Surface or interfacial tension forces are a good example. These forces may at micro-g interfere with the operation of a space system (e.g., filling and emptying of fuel tanks) (refs. 112,113) or with experimental processes (ASTP and SPAR II experiments on immiscible materials (refs. 100,101). However, they may also be used to advantage in the forming of complex shapes, films or ribbons. The potential of doing so has been demonstrated by Darbro in a Skylab Science Demonstration (ref. 114).

Solidification experiments on confined systems conducted under reduced gravity conditions have demonstrated unexpected and previously unobserved wetting behavior of various melts with their respective confinement materials. Thus, for example, the crystal growth experiments on Skylab and ASTP involving InSb and Ge in quartz ampoules exhibited, contrary to experience on Earth, a wetting behavior which appears to be a strong function of the chemical nature and composition of the melt (refs. 51,55). Specifically, it was found that the actual contact area between melt and confining quartz ampoules was less than about 1% for Ga-doped Ge and Te-doped InSb while it was 100% for Sb-doped Ge and Sn-doped InSb. From a study of surface morphological features of the solidified melt it was concluded that the contact between the melts and the confining quartz ampoules was restricted to narrow (5 to 20 μm) melt ridges (of 1 to 5 μm height) spaced randomly and oriented predominantly along the established thermal gradient (growth direction). This wetting phenomenon, which is also encountered in metallic systems, is fundamentally different from that observed on earth and at present cannot be explained on the basis of the established wetting theory.

In view of the importance of solid-liquid contact (wetting) behavior not only for materials science but also for biological, medical and other basic and applied research to be conducted in space, it is evident that the potential implications of the observed wetting effects warrant their detailed and systematic investigation.

E.1 BASIC STUDY OF SURFACE AND INTERFACIAL TENSION PHENOMENA AT MICROGRAVITY

Objective

The major objective of studies dealing with surface and interfacial tension phenomena is to understand the influence of these forces on equilibrium configurations of fluids in contact with solids and of mixtures of fluids. A second objective is to understand the fluid flow mechanisms by which the equilibrium forms are achieved and the kinetics of the processes involved.

Justification

The space environment accentuates surface tension phenomena because they are no longer dominated by gravitational effects as is usual on Earth. It is critical that we become intimately acquainted with these basic forces so that we can understand and control them. Knowledge of this behavior could ultimately lead to processes involving the intricate shaping of materials.

Approach

Theoretical and experimental research would be conducted on surface tension dominated phenomena. The research would include studies of 1) equilibrium shapes obtained on wire forms (See also Experiment D.2), 2) equilbrium forms of mixtures of liquids both in containers and in a containerless configuration, 3) bubbles and 4) the stability of all these forms. The mechanisms and kinetics involved in going from one geometrical configuration to another would also be included in this study.

Owing to the exploratory nature of at least part of this study, some of the experimentation should be conducted in a "shirt-sleeve" environment so that direct observation of the phenomena by a trained observer may uncover some unknown or unexpected effects that can guide future research.

Materials

A full range of materials having a wide spectrum of surface and interfacial tensions and viscosities would be studied in the previously delineated investigations in order that a comprehensive understanding of the phenomena involved be obtained.

E.2   THE WETTING BEHAVIOR OF CONFINED MELTS
UNDER SOLIDIFICATION CONDITIONS IN REDUCED GRAVITY

Objectives

The primary objective of the proposed research is the determination of the wetting characteristics of high temperature melts in contact with potential confinement materials and the quantitative exploration of the phenomena responsible for the reported wetting anomolies in confined solidification systems. Ultimately, this study should contribute to our quantitative understanding of wetting in reduced gravity.

Justification

While the study of basic wetting phenomena has already been identified as an important subject to be pursued in the realm of fluid physics (ref. 11), wetting associated with solidification processes warrants special attention within materials science activities because of the prevailing complex boundary conditions. Specifically, the existence of temperature and compositional gradients gives rise to conditions in reduced gravity, under which forces other than the conventional interfacial free energies become operative and may control the liquid-solid contact behavior. (For example, it has been suggested that surface flows of the Marangoni-type may locally modify the surface composition and result in wetting anomolies.)

The exploration of liquid-solid contact behavior becomes of paramount importance for the optimization of the design of non-conventional materials processing systems required for reduced gravity operations. Several crystal growth methods such as "Czochralski pulling," ribbon growth by the EFG method and others presently considered for space processing require "melt shaping" to be accomplished by appropriate dies for which the wetting behavior with the melt is the most essential characteristic. Furthermore, a multitude of systems considered for space processing will require confinement because of evaporative losses at high temperatures. For such systems it is essential that the wetting behavior be known and solid-liquid contact be minimized if the full advantage of reduced gravity environment is to be realized.

One of the most attractive features of solidification in space is the possibility of conducting experiments in an unconfined configuration, and thus eliminating contamination from the confinement material and avoiding the introduction of stresses and associated defects.

Acoustic and electromagnetic systems have been designed (refs. 41, 115,116) to assure melt stabilization in an unconfined configuration. These approaches, however, involve the application of body-forces which may interfere with internal melt stability and thus may reduce the effectiveness of low gravity in providing convection-free conditions. A viable alternative to the proposed stabilization systems may be the use of partial non-wetting confinement by solid structures of appropriate design. This approach, however, is contingent on our knowledge of the wetting characteristics of solids in reduced gravity. Preliminary indications from experiments in space suggest that the solid-liquid contact behavior of melts in space is in some instances fundamentally different from that observed on Earth. Thus, a systematic study of the wetting characteristics of high temperature melts in contact with potential confinement materials appears essential for the assessment of the potential of space processing.

Approach

The first phase of the suggested study would be devoted to ground-based research. All solidification experiments conducted in space would be re-examined for indications of unusual melt-container contact characteristics. Subsequently, experimental approaches for the determination of wetting behavior under reduced gravity would be developed. In the second phase, preliminary experiments involving relevant solidification systems and potential confinement materials would be conducted for the ultimate purpose of verifying the reported wetting anomolies and optimizing the experimental approach considered for Spacelab operation.

The Spacelab experiments would be devoted to a systematic investigation of the wetting characteristics of those melt-container systems showing unusual wetting behavior. Since an understanding of the wetting anomolies in reduced gravity is essential for the optimization of particular growth configurations, wetting experiments should be conducted under equilibrium conditions as well as under dynamic steady state growth conditions. The equilibrium experiments should include the determination of static and dynamic contact angles as well as contact angle hysteresis.

Materials

In view of the apparent sensitivity of the wetting behavior in reduced gravity on minority components (impurities or intentionally added dopants), all materials studied must be of known, controllable composition with starting materials of the highest degree of purity obtainable. The study should include semiconductor, metallic and ceramic systems of scientific and technological interest. The confinement materials to be considered should include those identifiable from ground-based experiments, as well as those potentially suitable for confinement.

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F. BASIC MATERIALS SCIENCE EXPERIMENTS DEALING WITH VAPOR-SOLID PROCESSES

F.1 CRYSTALLIZATION FROM THE VAPOR

Background

Crystallization from vapors (vapor growth) has gained ever increasing importance in the preparation of semiconductors, insulators, and metals. Vapor-to-solid processes are employed for the preparation of bulk materials and, on a particularly large scale, for the production of thin films. Bulk materials (large crystals and polycrystalline components) are grown by Physical Vapor Transport, PVT (sublimation-condensation in closed and open systems), and by Chemical Vapor Transport, CVT ("reversible" chemical reaction mostly in closed systems). Thin films for electronic and optical devices are largely obtained by Chemical Vapor Deposition, CVD ("irreversible" chemical reactions of gases and vapors in a hot reaction zone in open systems).

The advantages of vapor growth over, say, crystallization from melts, result mostly from the lower temperatures involved: (1) Many materials that decompose before melting or that exhibit high temperature solid-solid phase transitions can be grown at lower temperatures from vapors; (2) high purity conditions are achieved more readily because of reduced interaction with containers; (3) vapor-solid interfaces exhibit considerable shape stability against non-uniformities in heat and mass transfer, a feature that is important for the compositional uniformity obtained during growth; (4) lower temperature gradients and hence lower dislocation densities can be more easily obtained; (5) less expensive heat sources, requiring less energy, can be employed; (6) improved flexibility can be obtained over melt and solution growth particularly in epitaxial processes due to the control on a macroscopic basis of the vapor flux to growth interfaces.

The performance of solid state devices depends to a large extent on the compositional and structural perfection (homogeneity) obtained in the solid during growth. This perfection, in turn, depends strongly upon mass and heat transfer conditions in the vicinity of the growing interface. Non-steady transport can result in inhomogeneities that severely limit device performance. Hence a quantitative understanding of non-steady transport in vapors in flow geometries and under physical and chemical conditions relevant to materials preparation is of utmost importance.

Unfortunately, with a few outstanding exceptions, the current understanding of the transport mechanisms that prevail in vapor-solid processes is rather limited and most of a qualitative nature. In addition to mass diffusion in a concentration gradient and streaming (displacement flow due to a change in the number of vapor molecules during interfacial reactions), complex interactions between buoyancy-driven and externally produced convection are encountered which readily lead to non-steady, oscillatory transport. Furthermore, as is typical of various semiconductor processes, if vapors (gases) having differences in molecular weight are employed (e.g., H_2 + $SiCl_4$), thermal diffusion can strongly contribute to the transport and also produce convection currents as a result of destabilization. These phenomena are typically ignored in the crystal growth literature. This complex picture becomes even more complicated when evidence is introduced from recent investigations (refs. 117,118) which show that in certain chemical vapor-solid processes the interplay between mass and heat transfer very close to the interface can cause oscillatory phenomena. Note that this mechanism can be expected to prevail even in the absence of gravity.

An additional shortcoming often found in many vapor growth studies is the very limited knowledge of the vapor composition and the actual chemical reactions taking place. For many of the experiments reported in the literature the underlying reactions are merely hypothesized, and because of the lack of reliable thermochemical data only crude analogies and estimates are presented. This uncertainty in the chemical parameters is subsequently reflected in the calculations of concentration gradients, diffusion coefficients, viscosities, thermal conductivities, etc., and such uncertainty strongly limits the quantitative evaluation of heat and mass transfer. Furthermore, the level of impurities or excess components in "stoichiometric" vapors and solids, which can have significant effects on growth habits and growth rates is frequently underestimated. Hence, one of the mandatory prerequisites of a research program in which Earth-bound and low-g transport studies are conducted in a comparative manner is a rigorous thermochemical characterization of the vapor-solid systems to be used.

Objectives

The primary objective of the suggested ground-based and space experiments is to obtain a quantitative understanding of the various transport phenomena occurring in well characterized PVT and CVT systems. The space experiments will allow us to separate gravitationally induced transport phenomena from those that are dominant in the microgravity environment.

A secondary objective, once the transport mechanisms are understood, is to determine the relation between vapor transport mode and the compositional and structural defects in the deposited solid.

Justification

Progress in transport studies, even in vapor growth systems of great technological interest, has been slow. The main reason for this is the complexity of the transport mechanisms involved. The microgravity environment offers the unique opportunity of drastically reducing this complexity and creating experimental conditions more amenable to quantitative analysis. Carefully performed comparative studies on Earth and in space will yield quantitative descriptions of buoyancy-induced and kinetically-conditioned non-steady transport. This isolation of vapor transport mechanisms cannot be achieved without space experiments. Furthermore, more complete definition of the transport modes will help in clarifying their relationship with compositional and structural defects in the deposited solid.

Carefully designed vapor-solid transport studies, Earth-bound and in space, will yield the insight necessary to produce more homogeneous and hence more efficient device material. It is also expected that once the complex superposition of the various (sometimes opposing) transport mechanisms is quantitatively understood, higher vapor-solid growth rates can be obtained through a more educated choice of the transport conditions.

The possibility of performing vapor-solid processing in space has been demonstrated with experiments performed on Skylab (ref. 119) and Apollo-Soyuz (ref. 120). Considerable improvement of crystal size and morphology, and a quite unexpected increase in transport rate was obtained in closed ampoule vapor transport experiments. The experiments have pointed out the

need for additional ground-based transport studies oriented to the assessment of fluid-dynamic behavior. Moreover, since open tube vapor-solid experiments which are technologically more important have not yet been performed in space, an appraisal of the potential of reduced gravity for vapor-solid space processing is considered to be highly speculative at this point.

The series of materials science space experiments suggested in general terms in the following sections is specifically designed to provide scientific criteria for deciding (1) which processes are apt to yield adequate materials on Earth by a more appropriate choice of operating conditions, and (2) which processes cannot be improved sufficiently on Earth and will greatly benefit from a zero-g environment.

Approach

Since the effectiveness and productivity of space experiments depend to a large extent on the quality of supplementary ground base research, such research would be emphasized in the suggested program.

Considerable ground-based efforts would be devoted to the chemical characterization of the vapor-solid equilibria in systems to be studied terrestrially and in the micro-gravity environment. Particular attention would be paid to the fact that many of the vapor-solid reactions of interest take place under conditions that are far off equilibrium. Vapor characterization would be carried out by mass spectroscopy and by matrix isolation spectroscopy (ref. 121).

Experiments on physical vapor transport will provide a basis for understanding the more complex CVT modes. The following ground-based and space experiments would be conducted:

1) Determination of the flow patterns in transport ampoules by high-resolution thermometry or, by the probeless techniques of laser Doppler anemometry (ref. 122) and/or holographic interferometry (ref. 123).

2) Terrestrial determination of transport rates under convectively stabilizing and destabilizing conditions (transport along and opposite to the direction of gravity). Comparison with transport rates in the convection free environment of space.

3) Crystal growth at 1-g under oscillatory transport conditions and correlation to compositional and structural inhomogeneties. Comparison with space experiments similarly conducted.

4) Determination of the onset of morphological instability (breakdown of interface shape) under the convective conditions prevailing at 1-g and under micro-g conditions. In situ microscopy of the interface and an analysis of the resulting inhomogeneities in the solid would be performed in this research.

Similar experiments would be conducted in the more complex CVT research area. Ground base research would have high priority and simple approaches

such as conducting experiments in different orientations with respect to the gravitational field would be stressed. This type of experiment is rarely performed.

Experiments on chemical vapor deposition would be oriented toward understanding the influence of buoyancy-driven convection when superimposed on externally imposed forced convection. Comparative ground-based and flight experiments would be conducted as follows:

1) Determination of flow patterns and convective instability conditions (believed at this point to be solely due to buoyancy) in open tube (displacement reactor) geometries.

2) Establishment of the relationship between oscillatory convection modes (as determined by thermometry or optical means) and compositional and structural inhomogeneities (as determined by high resolution selective etching, electron probe analysis, etc.)

3) Determination of the onset of non-steady transport in "oscillatory chemical deposition reactions," believed to be oscillatory even in the absence of gravity.

Materials

It is very tempting to base a program such as the above upon materials of maximum "technological utility." Yet in some cases these materials, may not be the ideal systems to study because of experimental limitations in the zero-g environment or from intrinsic deficiencies. Moreover, choice of some materials will have to be made based on results obtained within the program. Hence the following brief list should be understood to be tentative.

Physical Vapor Transport

Iodine (in some inert gas). In the vapor state its composition and physical parameters are very well characterized. It has been extensively used in various basic transport studies (refs. 124-126) and is convenient because of the low experiment temperatures needed and the resulting negligible contribution of radiation heat transfer.

Zinc (in some inert gas). Near equilibrium behavior can be expected in the monatomic vapor.

CdTe. This material offers the possibility of adjusting non-equilibrium interfacial conditions (and variations of transport conditions) by altering the stoichiometry in the vapor (without introduction of an "inert" species). In contrast to other II-VI compounds, CdTe can be obtained by PVD in both n- and p- type (ref. 127). This allows the vapor composition to be checked by conductivity measurements on the solid.

Chemical Vapor Transport

Transport of ReO_3 with Iodine. This system exhibits sizeable temperature oscillations in relatively small temperature gradients (ref.128).

This phenomena possibly results from chemical convective instabilities (ref. 129). rather than from convection arising solely from density differences caused by thermal expansion.

Transport of Ni with Ni(CO)$_4$ (Nickel Carbonyl). Experiments in this system can be conducted at low temperatures. The transport reaction is well understood and relatively simple kinetics are involved.

Transport of GeSe and GeTe with GeI$_4$. These systems were used in Skylab III and IV. Considerably more ground-based experiments (fluid dynamics studies and chemical characterization of vapors) are needed to unravel the transport results obtained in space.

Transport of GaAs with HCl or I$_2$. The particular advantage of this system is its technological importance. There is a wealth of information on its structural and compositional characteristics.

Chemical Vapor Deposition

Silicon Deposition From SiCl$_4$ or SiH$_4$. This undoubtedly is one of the most important CVD systems in device production. It is very well characterized with respect to vapor composition and reaction kinetics.

Silicon Carbide Deposition from SiCl$_4$ and CH$_4$. This system exhibits dynamically conditioned oscillatory transport (refs. 117,118). Due to the very narrow compositional range of SiC, deviations from stoichiometry can readily be identified from Si or C precipitates.

G. TRANSPORT PHENOMENA IN LIQUIDS

INTRODUCTION

The orbital environment provides two conditions beneficial to investigations of transport phenomena in liquids. (1) Convection-free transport of heat and matter and (2) containerless configuration of fluids. Transport property measurements in liquids are especially sensitive to the presence of a gravitational body force, because transport phenomena generally relate a flux of matter, energy, or momentum, to a force, manifested by a spatial gradient in temperature, composition, stress, etc. Invariably, liquids display convective instabilities in the presence of such gradients when body forces are present. Thus, the reduction of the gravitational force by many orders below its terrestrial value should lead to nearly ideal conditions for observing transport phenomena in non-convecting fluids. The freedom from contact with container walls also greatly expands the possibilities for conducting experiments on reactive liquids, especially those at high temperatures. A good example of the limitations imposed by container compatibility is the lack of viscosity data (momentum transport) for silica melts above 1800°C. Such data would be of extreme interest to glass scientists studying the structure and behavior of molten glasses, as well as to glass technologists concerned with processing of high-temperature glasses.

Properties of interest include, but are not exclusively limited to solute and tracer diffusion coefficients, thermal diffusivity and conductivity, thermo-solutal diffusion coefficients (Soret effect), viscosity, electro-

migration and various thermo—magnetic coefficients. Development of novel techniques which permit "contactless" measurements would be especially desirable. For example, the measurement of oscillatory damping of a liquid unduloid can be used to measure the viscosity of a high temperature melt. Such techniques must be developed before the full potential of the microgravity environment can be exploited for liquid state transport property measurements. Ancillary techniques such as temperatures and positioning control, must also be developed in order to implement advanced measurement methods in the Space Shuttle/Spacelab. Finally, with appropriate experimental problems solved, high—accuracy measurements could be made of transport properties on systems of scientific and technical importance.

In the following we have limited our attention to two types of experiments, "Diffusion in Liquids" and "Convection Effects in Liquid Electro-transport Experiments."

G.1   DIFFUSION IN LIQUIDS

Background

The two liquid phase diffusion experiments that have been conducted in space (refs. 56,57) have shown that a complication arises in these types of experiments on melting the sample to initiate the experiment and on freezing it to terminate the experiment. The volume change accompanying these phase transformations will produce fluid flow which, in turn, may alter the diffusion profile. Likewise, solute redistribution during solidification may complicate the interpretation of experimental results.

The problem of convection in Earth—bound diffusion experiments has been overcome by employing capillary size tubes oriented in the vertical direction under conditions where vertical density gradients due to concentration gradients are stabilizing and density gradients due to temperature gradients are essentially zero, or if present, are stabilizing. At the present time there is good evidence that Earth—bound experiments can be conducted in the absence of convection, and diffusion coefficients measured to a precision of around 5% in opaque high temperature materials, such as liquid metals, and to a precision of less than 1% in aqueous systems (ref. 130). There is no reason to believe that space experiments would offer an improvement in precision and consequently it does not seem justified to propose space experiments to measure liquid diffusion experiments in general.

However, there are many high temperature materials whose liquids are too corrosive to be held in capillary containers for Earth—bound diffusion experiments. A potential technique for measuring the liquid diffusion co-efficient in such materials is the float zone melting technique. Convection is inherently present in this technique in Earth—bound experiments due to density gradients induced by temperature and concentration gradients. Analysis of the initial transient in such terrestrially conducted experiments does allow a measurement of solute diffusion coefficients in liquids, but a know-ledge of the solute boundary layer thickness is required (ref. 131). Since these thicknesses are very difficult to measure accurately, the float zone melting technique conducted on Earth is not accurate enough for measuring liquid diffusion coefficients. However, if it can be demonstrated that Marangoni convection may be eliminated from such experiments in space, then analysis of such experiments would allow accurate determination of diffusion coefficients in corrosive metals.

Another novel method which may be applied to the measurement of the self diffusion coefficients in liquid metals and alloys circumvents the solidification problem. This method not only can be used where suitable capillaries are unavailable, but can also be used as a means of checking the capillary methods in systems where both methods can be used.

Objectives

To develop a method for measurement of interdiffusion coefficients in corrosive high melting liquids employing the float zone technique and to apply the method to measuring diffusion coefficients in model liquids and those of scientific and technological importance.

To develop a radioactive tracer method for measurements of self-diffusion coefficients in liquid metals and alloys and to apply the method to the determination in space of the self-diffusion coefficients in pure liquid metals and alloys which are too corrosive for terrestrial determination.

Justification

Liquid interdiffusion and self diffusion coefficients cannot be measured accurately on Earth in liquids sufficiently corrosive that they become contaminated when held in capillary containers. The space environment provides a unique set of circumstances, namely, an environment with minimum convection that provides an opportunity to do experiments without containers.

Approach

Initial experiments to measure diffusion coefficients through measurement of the initial compositional transient occurring during solidification would be carried out on non-reactive low melting metal point systems so that a comparison can be made between the space experiments and those conducted on Earth in capillary experiments. The experiments would be done in the presence of both slightly oxidizing and reducing atmospheres in an effort to determine if Marangoni convection would be controllable in the space experiments. Once it is established that the technique performs satisfactorily then experiments could be extended to high temperature materials.

For the self diffusion measurements, a layer of tracer material would be deposited while on the ground on the surface of a sphere of the material to be studied. The sample so prepared would be suspended in a furnace in the space environment, melted symmetrically and heated quickly to the desired temperature. In order to avoid distortion of the diffusion profile during freezing, the diffusion process would be monitored in situ by measurement of the radioactivity at the surface of the liquid sphere as the tracer diffuses inward.

A newly developed technique provides a still better approach to self diffusion measurements (ref. 132). This method takes advantage of the annihilation of positrons emitted from specific radioactive tracer atoms. This annihilation gives rise to two gamma rays with momenta that are 180° apart, which are detectable through coincidence counting. By using slit systems, it is then possible to define the penetration plot with extremely high precision. (Any minor distortion of the profile which takes place during the original melting of the sample would be known from the profile obtained at very short time periods after melting.) Experiments would be carried out at separate

temperatures for different specimens so that D(T), the diffusion coefficient as function of temperature, can be obtained over a sufficiently wide temperature range.

Materials

For the float zone experiments, Sn containing various solute elements would be used as model materials. Accurate measurements of diffusion coefficients in these materials by the capillary method can readily be made on Earth for comparison purposes. Once the technique has been checked out, measurements on corrosive liquids would follow.

Similarly, radioactive tracer experiments would be conducted initially on low melting point metals for which capillary experiments can be performed on Earth. After the technique has been developed, self diffusion measurements would be made in reactive materials of scientific and technological interest.

For the self diffusion experiments by the position annhilation technique, the host material can be selected by interested scientists. The diffusing tracer must be one which is a positron emitter, and is limited to the following isotope: ^{22}Na, ^{55}Co, ^{58}Co, ^{57}Ni, ^{64}Cu, and ^{90}Nb. Nevertheless, those isotopes offer the opportunity to study a range of systems. The ^{22}Na isotope is particularly convenient, and diffusion of Na in many systems is of current interest. In particular, high precision self diffusion measurements over a wide temperature range in liquid Na are still lacking and are of great fundamental interest.

G.2 CONVECTION EFFECTS IN LIQUID ELECTROTRANSPORT EXPERIMENTS

Background

When a DC current is passed through a metal alloy it is generally found that a transport of the solute element occurs toward either the cathode or anode. The transport velocity per unit electric field – the mobility – is relatively small and large current densities are required to produce significant transport velocities. However, the mobilities of interstitial solutes (O, N, C) in solids are sufficiently high that some of the purest metals in the world have been prepared using electrotransport (ref. 133). The mobilities in liquid metals are also high enough that significant purifications should be obtainable by means of electrotransport. Perhaps more importantly, electrotransport should be useable in conjunction with zone refining to further enhance the purifying action of zone refining. This technique is sometimes called field-freezing (ref. 134). Electrotransport studies on liquid metals have shown (ref. 135) that the large currents required for extensive purification produce sufficient convection in the liquid that significant purification cannot be obtained. Also field freezing studies have shown essentially the same results. Significant purification is obtained only by using very small tube diameters, around 1 mm (ref. 136).

The convection currents must result from either natural convection due to the temperature profile induced by the electric current, or from forced convection associated with the electric current. Models for these mechanisms of convection have been proposed and a recent study (ref. 137) has shown that these mechanisms, alone or in linear combination, cannot explain the experimental data. Hence, the mechanism responsible for the electric current-induced convection remains a mystery.

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Objective

The objective of this experiment would be to determine the relative importance of gravity induced convection in liquid metal electrotransport experiments.

Justification

If, in fact, gravity-induced convection is the main source of convection in liquid metal electrotransport experiments, then space experiments would be quite beneficial. They would provide information that could aid in resolving the theoretical problem concerning the mechanism of convection. They would also allow a method of producing small quantities of ultra-high purity metals, either by electrotransport experiments alone or by field freezing experiments. The purified materials would be used for basic materials science studies on Earth.

Approach

It is suggested that a study of convection during electrotransport on liquid metals be carried out utilizing the most sensitive available technique, which appears to be that employed in ref. 137 . Analysis would be accomplished by comparison with Earth-bound experiments and with theoretical models. If results show that a significant reduction of convection occurs in the space experiments, it is recommended that space experiments then be conducted on zone melting in conjunction with field freezing. The purpose of these experiments would be to evaluate the extent that the purification effect of the zone melting technique could be enhanced by the addition of electro-transport.

Materials

It is recommended that initial experiments be conducted on mercury alloys because of their ease of handling and because of the extensive data available on them.

H. MATERIALS SCIENCE EXPERIMENTS INVOLVING FLOAT-ZONE SOLIDIFICATION AT LOW GRAVITY

INTRODUCTION

The float zone technique is a very powerful experimental technique which has been used terrestrially for several purposes:

> To purify materials which are very reactive and cannot be held in containers without contamination. The purification occurs by two principal means: (1) the tendency of the impurities to concentrate in the liquid zone, i.e., the usual zone melting purification, and (2) preferential evaporation of impurities from the hot liquid zone, especially if the process is conducted in vacuum.

To prepare single crystals of reactive materials which cannot
be held in containers without contamination. In addition to solid
solution crystals and congruently melting compounds the technique
is also applicable to incongruently melting compounds.

To prepare uniformly doped single crystals of reactive materials
by the zone leveling technique.

The microgravity and vacuum environment of space offers potential
opportunities to apply float zone solidification to materials science problems.
These opportunities stem from the interaction of the technique with the en-
vironment to produce (1) enhanced zone stability, (2) reduction of density
driven convection currents, (3) purification by evaporative processes. The
last advantage is not unique to space and is considered to be a convenience
to be utilized with the most important attribute of space, long-term micro-
gravity.

Three experiments are suggested that take advantage of zone-solidifi-
cation in space.

H.1 GROWTH OF SINGLE CRYSTALS OF INCONGRUENTLY MELTING MATERIALS

Background

A major effect of low gravity for the float zone technique is that
the maximum length of a stable zone is increased significantly. Theoretical
analyses (refs. 138,139) have shown that the maximum stable zone length, ℓ_{max},
is independent of zone diameter, d, for large d,

$$\ell_{max} = a(\gamma/\rho g)^{1/2}$$

where γ = surface tension at the free surface of the liquid zone, g is the gra-
vitational constant and ρ is the density difference between the molten zone
and surrounding medium. The value of a is calculated as either 2.8 (ref. 138)
or 3.6 (ref. 139). These theoretical treatments have been confirmed fairly
well by terrestrial experiments; for example ℓ_{max} is around 0.7 cm in Au and
1.5 cm in Si (ref. 140). Note: The value of ℓ_{max} may be enhanced by utilizing
a levitation force with R.F. heating. In Si values as high as 3 cm have been
reported (ref. 141).

For the case where the value of g approaches zero, the theoretical
value for ℓ_{max} approaches the well-known Rayleigh limit: (e.g. see refs. 139
or 142)

$$\ell_{max} = \pi d$$

Experimental confirmation of this result has recently been obtained both in
simulated zero-g experiments (ref. 142) and in zero-g experiments aboard
Skylab (ref. 143). Consequently in zero-g the maximum zone length for a 2
cm diameter rod of Si would increase from 1.5 cm to around 6 cm.

Although there does not appear to be any obvious advantage of an
increased zone length for purification or preparation of uniformly doped
materials, there may well be quite a significant advantage in the prepara-
tion of incongruently melting materials. For example, in attempts to prepare

a single crystal or even a polycrystalline compound which melts incongruently by a peritectic reaction, it is often found that the solid-liquid interface is unavoidably dendritic. Basically, this is caused by the difference in composition between the crystal and the liquid from which it is forming, and it is inherent to the process. If the composition difference is fairly large (as it often is) then the dendrites become quite long and the total zone length becomes so extended that despite the imposition of high temperature gradients the zone becomes unstable. Consequently, the enhanced zone stability at zero-g may prove to be a significant advantage when preparing single crystal peritectic compounds.

Objective

To determine whether the enhanced zone length stability at zero-g may be used to prepare single crystals of incongruently melting compounds which may not be prepared by float zone melting on Earth (due to the long zone length inherent to the dendritic interface generally found in such systems).

Justification

Many significantly important but highly reactive compounds melt congruently and their preparation on Earth is difficult because of zone stability problems. The enhanced zone length stability at zero-g may be sufficient to overcome this problem. Terrestrial materials science studies of the space-prepared materials should broaden our knowledge concerning the behavior of these types of compounds and should provide improved understanding of their crystallization behavior.

Approach

Peritectic compounds which are difficult to prepare on Earth would be selected for study. Comparative studies would then be carried out on Earth and in space to determine, if, in fact, the space environment does enhance the ability to prepare such materials by the float zone technique. The structure and properties of the Earth and space prepared materials would subsequently be studied and compared.

Materials

Examples of difficult to prepare peritectics which could be studied in this program are $TbFe_2$ and $Dy_{0.7}Tb_{0.3}$. These compounds exhibit a large magnetostrictive effect and are of current solid state physics interest.

H.2 CONVECTION AND DOPANT DISTRIBUTION IN FLOAT ZONE GROWN SEMICONDUCTORS

Background

The float-zone technique has established itself in electronic materials processing technology as uniquely suited for the production of contamination free single crystals. The primary drawback is the presence of excessive density-driven convection which results in uncontrollable compositional inhomogenities on a micro-scale. This technique must be considered

as extremely attractive in the context of space processing since dimensional limitations are eliminated and adverse density driven convection is absent. Moreover, this approach to materials processing will not require melt-positioning devices under reduced gravity conditions.

If Marangoni convection is absent in the float zone configuration, it should be possible to produce in space more perfect semiconductor crystals doped uniformly in both radial and axial directions. Proper care, however, must be taken to control heat flow conditions in order to produce planar, uniformly-moving crystal-liquid interfaces.

Objective

To determine whether convection may be completely eliminated in float zone solidification carried out in space and thus to ascertain whether semiconductor crystals uniformly doped in both radial and axial directions may be prepared.

Justification

Uniform axial and radial doping of semiconductors is not achievable in Earth-based growth from the melt because of convection problems. If this goal could be achieved in space it may be of significant interest to the semiconductor industry.

It is also probable that without convection and the need for sample rotation, crystals with fewer imperfections might be grown.

Approach

Space conducted zone leveling experiments would be carried out on semiconductor crystals such as Si and Ge. The uniformity of chemical composition of the prepared crystals would be analyzed using resistivity, etching techniques and radioisotope analysis. The extent of Marangoni convection would be evaluated by analyzing the solute profile in the initial transient region, and in the final quenched liquid zone.

H.3 SINGLE CRYSTALS OF HIGH PURITY CERAMIC MATERIALS

Background

Since ceramics constitute an important class of materials which have broad technological applications, an understanding of their basic properties is essential. Often, however, the electrical, optical and other properties of ceramic materials are critically affected by the presence of very low levels of impurities. The high level of purification which has made possible great advances in metals and semiconductors in recent years has not been possible for ceramic materials, largely because of the high melting points of these materials, and the difficulties associated with contamination (ref. 140). Very high purity, highly perfect single crystals which can be made available to the scientific community for all types of worthwhile experiments are required.

As previously noted, the vacuum level expected behind the molecular shield will be of the order of 10^{-13} torr and 10^{-17} to 10^{-18} torr with respect to elements other than H and He (ref. 4). Hence, there exists a good potential for evaporative purification in space for reactive materials which can be levitated (ref. 145). The float zone process offers an alternative technique for evaporative purification and does not suffer from the potential introduction of disturbances to the liquid from the positioning forces present in the levitation technique. In addition, the float zone technique also produces significant purification from the zone-melting process itself.

Objective

To explore the potential of space for generating high purity, highly perfect ceramic single crystals for subsequent terrestrial studies.

Justification

The combination of low gravity with a resultant minimization of convection (assuming the absence of Marangoni convection) and the high vacuum provide an ideal environment for producing highly perfect, high purity ceramic crystals.

The elimination of density-driven convection currents at low-g prevents growth fluctuations which lead to crystal imperfections. It also allows larger thermal gradients to be maintained in the liquid (ref. 140) and thus better control over the crystal growth process. Also, the high vacuum allows evaporative purification to be conducted during the zone refining operation.

Lastly, the presence of unattenuated solar radiation may through a solar collector system provide the relatively large amounts of energy which will be required for melting refractory ceramics (ref. 140). Radiation heating by means of a carbon arc has been successfully used on Earth (ref. 146). Alternatively, laser heating may be used in conjunction with more conventional energy sources. The question to be settled is whether the construction of a mechanism (lens or mirror system) which automatically adjusts for the sun's position is preferable to a more direct method which requires supplying the necessary power on the space vehicle.

Approach

Material for space zone melting would be prepared in rod form ($\sim$ 2 cm diameter) by sintering material of the highest purity available. This material could then be zone melted terrestrially several times in high vacuum to remove volatile impurities and effect zone purification. Alternatively, this latter operation could be combined with the space zone refining. Here several passes of a molten zone are required. As discussed above, heating by focussed solar or laser radiation should be strongly considered. An alternative method is induction heating with the use of a high purity graphite susceptor (ref. 140). The choice may be dependent on the material (its melting point, whether or not an oxygen atmosphere is needed to maintain stoichiometry, etc.). The final stage (which may, in fact, be combined with the previous stages) is crystal growth. In this step, one would have to consider the relative merits of introducing a seed crystal in order to control orientation and to be sure of obtaining a single crystal, as against carrying out the growth process without a seed.

The latter has the benefit of convenience and of not introducing contamination, but involves a greater risk of failing to obtain a single crystal. Ground based experiments for each material can provide the answers in each case. The crystal growth step must be carried out in an atmosphere in which the material will be close to stoichiometric. This may mean a substantial partial pressure of oxygen in some cases.

Materials

The materials to be considered should be those which can be considered prototype materials in the ceramics field, the measurement of whose intrinsic properties has been limited to date by the level of contamination and perfection. On this basis, the following are particularly worthy candidates: MgO, Al_2O_3, CeO_2, NiO and ZnO. The best candidates would be those whose vapor pressures at the melting point are not too high.

I. HIGH TEMPERATURE CHEMISTRY OF REACTIVE LIQUIDS

INTRODUCTION

The properties of liquid metals at high temperatures have been widely studied but in the past there have been serious limitations on the reliability of measurements at temperatures above 1000°C because of the problems of contamination by the container in which the liquid metal was held. Levitation devices on Earth or in a zero-g environment offer an escape from container problems and an opportunity to study conductors under conditions where contamination and thus the extraneous effects of chemical impurities are minimized. Studies of good electrical conductors with relatively low vapor pressures have, in fact, been done on Earth and reported in an extended series of publications (refs. 147-161). Ultrasonic and aerodynamic levitation devices are presently being developed and would have application to non-conducting samples (refs. 2,3).

There are several problem areas associated with terrestrial levitation devices which can be overcome by taking advantage of the weightlessness afforded by the Space Shuttle/Spacelab. One major disadvantage is that the agitation produced in a liquid sample by the levitation forces complicates the measurements of a number of properties such as viscosity, surface tension and diffusivity. Further, there is a large group of experiments and measurements that may be possible terrestrially but for which there may be some advantage afforded by space. Examples are the use of calorimetry to yield specific heats and equilibrium studies to yield free energies and heats and entropies of vaporization.

One advantage of applying electromagnetic levitation in space has to do with the separation of the controls for levitation and heating. In the traditional Earth-bound levitation devices so much energy is supplied for levitation that heating is inevitable and, in fact, the samples are usually overheated in the process of levitation. It is then necessary that the samples be externally gas-cooled with argon or helium in order to provide a range of temperatures for study. It is extremely important that the cooling gases are of ultra-high purity in order to minimize contamination. There is, further, the possibility that even "inert" gases like argon or helium will be appreciably soluble in liquid metals and thereby affect the measured properties. The

influence of dissolved gases in metals is of great interest and the space environment affords additional flexibility in its study.

The absence of large electromagnetic fields made possible by space levitation may be advantageous in the determination of the thermodynamic properties of liquid metals. It is important to establish that no unusual effects due to the electromagnetic fields are incorporated in existing data obtained in terrestrial levitation experiments. Comparative space experiments would establish whether such electromagnetic interactions are in fact a problem.

There are many cases where the heating of a metal near its melting point produces such a high partial pressure of vapor, that traditional levitation coils are electrically shorted and the sample can no longer be levitated terrestrially. This problem can be avoided in space by use of an open coil design, radiation heating, etc.

Levitation in a micro-g environment supplemented by continuous radiant heating or by laser heating to supply increments of known energy content would allow property measurements to be made on important metals like Mn, Be and Cr which have not been studied at or above their melting points because of excessive vaporization.

It is difficult on Earth to levitate and heat some of the highest melting point metals such as W and the binary carbides ZrC, TaC, beyond their melting points. Extremely high temperature substances will be interesting to study under space levitation conditions, assuming the availability of adequate electrical power to provide supplementary heating by radiation or to operate lasers or electron beam units which can supply incremental pulses of energy.

Most of the preceeding comments are based on the use of traditional drop calorimetric procedures for measurement of enthalpies, specific heats and other thermodynamic properties. Measurements of vapor pressures, decomposition products, viscosities, surface tension and electrical and magnetic properties for reactive liquids are also of interest.

In the following, two specific programs are suggested.

I.1   THERMODYNAMIC PROPERTIES OF REACTIVE LIQUIDS

Objective

To develop methods for measuring thermodynamic properties at micro-g. To make such measurements on materials that are difficult to measure on Earth or on materials for which terrestrial measurements are ambiguous.

Justification

Measurement of thermodynamic and other properties of reactive liquids requires that the sample be isolated from any container, i.e., be levitated.

Such measurements are needed to understand the chemical and physical behavior of these materials. For example, the area concerning the contribution of defect structures to the thermodynamic properties of liquids needs in-depth study.

Terrestrial levitation of some types of samples is extremely difficult and may be more conveniently effected in the weightless environment of space. However, work presently underway in the development of levitation devices for Earth applications may alter this situation.

The relatively high cost of space experimentation makes it imperative that experimental techniques be as efficient as possible. Hence, new, potentially more efficient approaches to high temperature calorimetry should be explored. One such approach would make use of temperature-time cooling curves from which various thermodynamic parameters as well as emissivities, thermal conductivities and similar data could be extracted. Such studies have already been started (ref. 147).

Approach

The drop calorimeter procedure for measurement of enthalpy and related thermodynamic parameters would be modified for the space environment. Initial measurements would be made on materials such as copper, silver and gold since measurements for these metals are available from other sources and would serve as excellent calibration substances to establish the experimental methods.

The studies would be extended to other materials for which there are ambiguities in the results of terrestrial levitation experiments and then to materials which are difficult or impossible to work with on Earth.

The method of evaluating thermodynamic properties from temperature-time cooling relations would be further developed. In this method a sample would be positioned with an externally applied electromagnetic field and heated by radiation. At this stage, when the sample has been equilibrated at a constant temperature, an additional increment of energy would be supplied by either an electron beam or by a laser. This energy would be absorbed and distributed throughout the sample leading to a new peak temperature. Finally, the temperature of the sample would decay with time as the sample radiates according to the Stefan-Boltzmann Law. In such a system there would be various opportunities for calibration and establishment of useful properties. When the radiant energy is reduced so that the sample is allowed to cool from above to below the melting point, then there would be an opportunity to determine the brightness temperature at the melting point. This quantity is fairly well known for most pure elements.

With a two color pyrometer there would be an opportunity to eliminate emissivity errors and thus to determine as a first approximation the absolute temperatures. Two color pyrometry also provides an opportunity to study emmissivities as a function of temperature. There are essentially no data on emissivities of liquid metals over a range of temperature above the melting point. The only reference points are the emissivities measured for the pure liquid metals at the melting points. Current work suggests that the emissivities

of most liquid metals as well as a number of other electronically determined properties (e.g., conductivities, reflectivities, Hall effect coefficients) are invariant over wide ranges of temperature. This flat temperature profile is quite surprising and drastically different from predictions based on current models for metallic liquids and assessments of electronic and anharmonic effects.

Materials

As previously described, copper, silver and gold could be used as calibration materials.

Studies on silicon, doped to produce a more easily levitated material for Earth-bound experiments, could be extended to space. Moreover, pure silicon would also be studied as a reference material in order to ascertain whether doping alters the thermodynamic measurements significantly.

Thermodynamic studies would also be carried out on the difficult to levitate, volatile liquid metals such as chromium, manganese and beryllium.

Finally, there is great interest in studying the thermodynamic and physical properties of refractory metals and their intermetallic compounds, metalloid alloys and refractory oxides.

I.2 VAPORIZATION STUDIES OF REACTIVE NON-CONDUCTING LIQUIDS

Objective

To determine vapor pressures, vapor species, and vaporized and condensed species from reactive non-conducting liquids. To study vapor interactions from more than one reactive liquid.

Justification

Most inorganic compounds do not conduct electricity sufficiently well to be levitated electromagnetically on Earth. Therefore, containerless chemistry and physical property measurements for these materials are not practical by the electromagnetic levitation techniques used on Earth by Jenkins, et al. (ref. 148), the Westinghouse laboratory group (refs. 149-151), the Rice University group (refs. 152-155), by Berezin, et al. (ref. 156) and by others (refs. 157-161).

For those measurements requiring a vacuum, it would not be possible to use other levitation systems such as the acoustic or aerodynamic techniques since they incorporate a gas atmosphere. Also, these devices may be quite inconvenient to use even for those experiments which can tolerate a gas atmosphere. Further development of these techniques could alter the situation, however.

Levitation in the space environment would allow reactive non-conducting liquids to be studied without contamination and without the ambiguity in results associated with such contamination.

Approach

Samples of various types of materials susceptible to container reactions would be studied in the suggested program. These materials would include binary and ternary oxides, various binary and ternary solids and most other high melting point covalent or ionic inorganic compounds which do not possess metallic character. Some materials such as metal sulphates, metal carbonates, metal nitrates, metal tungstates, metal silicates and metal borates, all of which have been studied in low pressure environments where contaimination is not a problem would be investigated in a higher temperature, higher pressure regime.

In a typical experiment, space levitated samples, heated by radiation from an electrically heated filament, furnace tube or solar device, would be made the subject of various kinds of studies and property measurements. For instance, weight-loss as a function of temperature and time-of-exposure at high temperatures could be determined and the type of vapor species could be analyzed by quadrupole or time-of-flight mass spectrometric sampling. Moreover, condensed vaporization products could be collected by use of matrix isolation techniques, and matrix reactions of vapor species by co-condensation with other reactants could be studied.

Materials

The following material systems are suggested for space levitation studies dealing with vaporization and related phenomena.

1. M_2SO_4
2. M_2CO_3
3. M_2CrO_4
4. M_2WO_4
5. $M_2B_2O_4$
6. $MX + CrO_3$, MoO_3, $CrWO_3$
7. $MX + AlX_3$
8. $MX + RX_3$
9. Metals/Alloys – poor conductors
10. Non-Metals – S, Se, Te, As, Sb and mixtures

where M = Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+

X = halogen
R = rare earth metal

EXPERIMENTAL AREAS CONSIDERED BUT NOT RECOMMENDED

RADIATION EFFECTS

The space environment can furnish various radiations. In particular there is the geomagnetically trapped penetrating-particle radiation (ref. 162) which includes the well known Van Allen radiation but which dips into lower altitudes in certain regions of space to produce what has been called the "South Atlantic Anomoly". This radiation involves electrons with energies approximately 0.5-7 MeV, at fluxes of 10^5 to $10^8/cm^2$ - sec and protons with energies greater than 100 MeV at fluxes 10 to $10^4/cm^2$ - sec. In addition, there is available ultraviolet radiation from sunlight with wave lengths down to 10 nm.

Although these radiations may be of significance from an engineering standpoint, they have little impact on materials science experiments in space, either because they are of insignificant energies to affect the properties of materials or because they can be produced artificially on Earth. For example, in the case of ultraviolet radiation, such radiation is available in higher flux and with a more focused beam from synchrotron sources. While such radiation facilities are not yet common, new ones are being contemplated and such sources will probably be much more readily available in the next few years. In addition, coherent UV light is currently attainable by the use of gas lasers combined with harmonic generation techniques.

Experimenters should be aware of the presence of these radiations in space and where materials that are sensitive to radiation are involved proper precautions should be taken to shield the experiments. It should also be pointed out that the ambient atmosphere at 556 Km (300 nautical miles) is mainly atomic oxygen (O) at a number density of $10^8/cm^3$, N_2 at $10^8/cm^3$, O_2 at $10^7/cm^3$ and atomic oxygen ions (O^+) at $10^5/cm^3$. Space experiments involving fluxes of these latter particles have been recently considered by a NASA sponsored study team (ref. 163).

SPACE VACUUM FACILITIES

Materials science experiments which are based solely on the availability of the space vacuum or even the ultra-high vacuum available behind the molecular shield facility cannot be justified unless large heat rejection rates or excessively large sample sizes are required. This conclusion was reached by the committee on the basis of conversations with personnel who have been involved with the operation of ground-based ultra-high vacuum facilities capable of better than 10^{-13} torr and those doing materials science research in such facilities (refs. 7,170).

The characteristics of one of the largest of these facilities, the Jet Propulsion Laboratory's "molsink" was kindly provided to the committee by G. Lewicki of that laboratory (ref. 171):

"In the molsink the "anechoic" working volume is a sphere 10.6 inches (26.9 cm) in diameter. Any oxygen or nitrogen molecule exiting that volume goes into a gaseous helium cooled sharp wedged fin array with a probability of between 1 and 2×10^{-14} of returning to that volume.

The pumping speed for oxygen and nitrogen is of the order of 3×10^7 liters per second.

The anechoic chamber surrounding the working volume can tolerate no more than 600 watts of heat from the working volume."

A similar facility exists at NASA-Lewis Research Center but is currently inactive. The latter facility could be activated if there were a demand for its services (ref. 7).

From a materials science standpoint, many if not most experiments requiring a high vacuum or high pumping speeds, e.g., purification, epitaxial growth, could be performed on a small scale in facilities on Earth. A space vacuum facility would be necessary for materials science experiments requiring a combination of long-term weightlessness and high vacuum. In this case, the wake shield facility previously discussed or some alternative (e.g. a space cryopumped facility) would be required. On the other hand, a space vacuum facility may be justified (more in terms of space processing than materials science) in those cases where large samples are necessary and/or large amounts of heat must be dissipated. The coating of large structures in space is one example which has been suggested.

RESEARCH ON POLYMERS

Prior to this contract and during the initial phase of the present study, more than 20 scientists from the academic and industrial communities were contacted to solicit ideas as to where the space environment may be useful in research on polymers. In addition, an announcement was also placed in the Journal of Polymer Science, Polymer Letters Edition, to solicit ideas in this subject area.

Some of the compelling reasons for space experiments on metals do not apply to polymeric materials. Synthetic polymers do not form large continuous single crystals when they solidify from the melt; spherulitic morphology generally predominates. Contamination due to containers is usually not a problem. For these reasons it was not surprising that there were few encouraging responses to our solicitation for ideas on materials science experiments involving polymers for conduct in space. There were two areas, however, that were suggested and merit further consideration.

Crystallization

There is a possibility that larger spherulites could be grown in some polymers. For example, it might be possible to avoid the transcrystallization phenomenon at the surface of highly purified polyethylene if a containerless configuration were used.

Glassy Polyethylene

It might be possible to produce glassy polyethylene by effecting large amounts of undercooling in these materials. Such undercoolings might be possible in a containerless configuration.

COMPOSITE MATERIALS

Since composite materials are made up of a mixture of two relatively insoluble materials, it has often been suggested that experimentation and processing of these materials in space would lead to more uniform mixtures of the phases, since buoyancy induced segregation would be minimized at micro-g.

This discussion is limited to composite materials which are produced by physically inserting particles or fibers into a molten matrix. It is not concerned with in situ grown materials such as directionally solidified eutectics, nor is it concerned with materials produced completely in the solid state. Moreover, it excludes composite materials made by vapor or electro-deposition techniques.

There appears to be little advantage to the processing in space of composite materials which consist of a dispersion of fine particles ($<\sim 1\mu m$) within a matrix. Particle motion in this size range occurs mainly by Brownian motion and settling velocities are minimal. Likewise, there is little advantage to be gained from processing continuous fiber reinforced composites. The configuration of the fibers within the structure is fixed by external means and by the matrix/fiber wetting characteristics. There is one area, however, in which the weightless environment of space offers an advantage namely in the production of whisker or chopped fiber reinforced composites and in particulate reinforced materials where the particles are appreciably larger than $1\mu m$. In both these cases, fiber, whisker or particulate settling would be expected to be alleviated by producing these materials in space. Confirmation of this fact has been obtained, for SiC whiskers in a silver matrix by Kawada, et al. (ref. 164) and Takahashi (ref. 165). The more uniform distribution of SiC also leads to a smaller variation in mechanical behavior.

EXPERIMENTAL AREAS NEEDING FURTHER CONSIDERATION

CORROSION STUDIES

Three specialists in the corrosion area were approached about the advisability of performing corrosion experiments in space. Two were somewhat negative in their opinions that the space environment would be useful for conducting corrosion studies. One of the corrosion specialists felt that this might be a fertile area, but he had no specific experiments to suggest. Some additional work is required to make final conclusions regarding this discipline.

SOLUTION GROWTH OF CRYSTALS

Solution growth techniques including liquid phase epitaxy (LPE), seeded aqueous solution growth, non-seeded aqueous solution growth and gel growth are important industrial crystal growth techniques which suffer, like melt growth techniques, to a varying extent from gravity induced convection. The theoretical framework of these processes is deficient and materials thus obtained fail to perform at their theoretical limits.

It should be noted that a small number of low gravity experiments have been conducted aboard Skylab (ref. 166) and ASTP (ref. 167) with mixed results. Also some ground based experiments and space experiment definition activities have been reported (ref. 168).

Whereas key experiments conducted in a reduced gravity environment may undoubtedly contribute to a better understanding of the associated growth mechanisms, no recommendations for specific experiments are made at this time for the following reasons: (a) the advantages of a low-gravity environment for solution growth are dependent on the absence of convection flows; verification of such conditions is the subject of some of the experiments suggested in the present study; (b) seeded solution growth requires defined, controllable solid-liquid contact - thus the design of meaningful experiments is contingent on experimental input from wetting experiments proposed in the context of melt growth and fluid physics; (c) aqueous solution growth experiments are by nature of long duration and should at this time be deferred until more basic data on systems behavior in reduced gravity become available.

ELECTRODEPOSITION STUDIES

This is an area that has received little attention from the committee and therefore no recommendations can be made at this time concerning this field. It should be noted that one experiment has been conducted aboard Skylab in the electroless deposition of silver (ref. 169).

CONCLUDING REMARKS AND RECOMMENDATIONS

During the four day sessions in which the committee discussed candidate material science experiments for the Space Shuttle/Spacelab, a number of general recommendations were made dealing with the conduct of such programs. The following are the committee recommendations:

Automated Versus Shirt-Sleeve Research

Although there are great economic incentives to automate space experiments, the committee feels that a fair proportion of the experiments should be performed in an interactive mode; i.e., in a mode in which the scientist observes the results of his experiment and can change the variables while the experiment is still proceeding or, alternatively, in a mode in which the scientist may be able to make changes in the experimental set-up and rerun it without excessive delay. Some of the more interesting Skylab experiments (fluid mechanics, liquid films, immiscible liquids) were performed in this manner and allowed the experimenter to interact directly with the space environment.

Ground Base Research

Extensive ground base research should be conducted to define and support the materials science experiments contemplated for space. It is very important that material systems be well understood and that characterization techniques be extensively developed so that maximum results can be obtained from the space experimentation.

Supporting Property Measurements

Most of the experiments conducted in space thus far have required knowledge of the properties of liquids as a function of temperature and solids at their melting temperatures. These properties include such characteristics as viscosities, surface tension, interfacial energies, all as a function of composition and temperature. It is very important that reliable data of this type be avialable. The committee feels that the National Bureau of Standards would be a logical organization to provide such reliable data.

Positioning Devices

Programs to develop electromagnetic or acoustic positioning devices for the space environment should include efforts to insure that these devices do not induce fluid flow in the sample materials. Such fluid flow would defeat one of the major attractions of space experimentation.

G As a Parameter

The orbiting Space Shuttle not only offers experimenters the microgravity environment in which to obtain results for comparison with one-g experiments, but it also affords the opportunity to obtain a continuous range of g levels between micro-g and 1-g. This capability would allow an experimenter to measure properties as a continuous function of g-level, and thus to compare

experimental results with a theoretical model involving g as a parameter.

Materials Science – Fluid-Flow Cooperative Efforts

Since fluid-flow is an important part of the phenomena of interest in materials science experiments in space, it is of prime importance that cooperative efforts between scientists representing these two disciplines be initiated and sustained. This cooperative effort is especially needed in the experimental design and result interpretation phases of many material science space programs.

Continued Experiment Definition Studies

Since the present study addressed only a select number of potential materials science experiments for conduct in space, and since even in those experiments discussed here in some detail there remain many details yet to be defined, it is recommended that further definition of materials science experiments for space be carried out. We have previously pointed out experimental areas needing further consideration. We are confident that other scientists expert in fields not represented on the present committee (e.g., physics of liquids) would offer other valuable suggestions for space research.

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APPENDIX A

A number of scientists were contacted by Committee members for information regarding various fields out of the direct expertise of the membership. In most cases the input consisted mainly of comments on whether space would provide opportunities for meaningful experiments in a particular discipline. However, for experiments on glasses and physical and chemical vapor deposition substantial inputs were contributed by M. C. Weinberg and G. E. Neilson of Owens-Illinois for the former subject and by Franz Rosenberger of the University of Utah for the latter. In addition, S. Ostrach of Case Western Reserve University attended our first meeting and presented background material on fluid-flow processes in space and on the activities of a previous committee organized to define space experiments in thermodynamics, heat-transfer and fluid dynamics. T. Cochran of NASA-Lewis Research Center also presented background material on the activities of the previous committees and their relation to the Lewis Research Center Spacelab Experiment Definition Program. A listing of the persons contacted and the subject matter of interest is presented in Table 2. The committee wishes to express our thanks to these scientists for their interest, advice and contributions to our activities.

Table 2. Non-Committee Scientists Contacted During the Course of the Present Study

Name	Affiliation	Subject
J. Cassidy	NASA-Lewis Research Center	Terrestrial Vacuum Facilities
T. Cochran	NASA-Lewis Research Center	Previous Studies
H. Doremus	Rensselaer Polytechnic Inst.	Ceramics
J. B. Hudson	Rensselaer Polytechnic Inst.	Surface Physics
I. M. Kreiger	Case Western Reserve Univ.	Gas Diffusion in Polymers
R. Laudise	Bell Telephone Laboratories	Hydrothermal and Flux Growth of Single Crystals
F. Lenel	Rensselaer Polytechnic Inst.	Powder Metallurgy
L. T. Melfi	NASA-Langley Research Center	Wake Shield Facility
R. I. Miller	Boeing Aerospace Corporation	Undercooling Effect
J. Newmann	UCLA-Berkley	Corrosion
E. F. Nippes	Rensselaer Polytechnic Inst.	Joining
R. Oriani	U. S. Steel	Foams
S. Ostrach	Case Western Reserve Univ.	Fluid Dynamics at Micro-g
R. A. Outlaw	NASA-Langley Research Center	Wake Shield Facility
F. Rosenberger	University of Utah	Physical and Chemical Vapor Deposition
F. W. Savage	Rensselaer Polytechnic Inst.	Joining
J. Stephens	Jet Propulsion Laboratory	Terrestrial Vacuum Facilities
R. Staehle	Ohio State University	Corrosion
D. Vermilyea	GE Research Laboratory	Corrosion
M. C. Weinberg & G. F. Neilson	Owens-Illinois	Glass Formation
R. R. Whymark	Intersonics, Inc.	Acoustic Levitation

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7. Author(s) S. H. Gelles, B. C. Giessen, M. E. Glicksman, J. L. Margrave, H. Markovitz, A. S. Nowick, J. D. Verhoeven, and A. F. Witt		8. Performing Organization Report No. None
		10. Work Unit No.
9. Performing Organization Name and Address S. H. Gelles Associates 2840 Fisher Road Columbus, Ohio 43204		11. Contract or Grant No. NAS3-20049
		13. Type of Report and Period Covered Contractor Report
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

16. Abstract

A committee of materials scientists whose members have expertise in various facets of the discipline has with the aid of colleague scientists defined a number of experimental areas and specific experiments that would utilize the space environment to further our understanding of materials science. The criteria used for the selection of the experimental areas and individual experiments are that the experiment or area must make a meaningful contribution to the field of material science and that the space environment is either an absolute requirement for the successful execution of the experiment or that the experiment can be more economically or more conveniently performed in space. A number of experimental areas and individual experiments were recommended for further consideration as space experiments. Areas not considered to be fruitful and others needing additional analysis in order to determine their suitability for conduct in space are also listed. In addition, recommendations have been made concerning the manner in which these materials science experiments are carried out and the related studies that should be pursued.

17. Key Words (Suggested by Author(s)) Space experimentation; Reduced gravity; Weightlessness; Nucleation; Convection; Solidification; Crystal growth; Containerless melting; Surface tension	18. Distribution Statement Unclassified – unlimited STAR Category 23		
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