NATIONAL BUREAU OF STANDARDS

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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Applications of Space Flight in Materials Science and Technology

NATIONAL BUREAU OF STANDARDS

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The National Bureau of Standards was reorganized, effective April 9, 1978.

Applications of Space Flight in Materials Science and Technology

Proceedings of a Conference held at the National Bureau of Standards, Gaithersburg, Maryland, April 20-21, 1977

Edited by

Shirleigh Silverman (Posthumous) and
Elio Passaglia

Center for Materials Science
National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

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Preface

This conference is the outgrowth of a letter from Dr. James Fletcher, the Administrator of the National Aeronautics and Space Administration (NASA), to Dr. Ernest Ambler, Acting Director of the National Bureau of Standards (NBS). The letter requested the assistance of the NBS in setting up a conference devoted to the subject of the Applications of Space Flight in Materials Science and Technology. It was felt that the NBS would provide a most suitable location for such a conference in view of its established commitment to measurement sciences and to the characterization, properties, and performance of materials.

The Program Committee decided upon a program that would first review those experiments that had been done in the Skylab and Apollo-Soyuz flights and the SPAR rocket program, and then devote itself to an examination of future prospects and opportunities for research and materials processing when the Space Shuttle becomes operable.

Program Committee:
Shirleigh Silverman, Chairperson
James Bredt, NASA
Mark Nolan, NASA
Elio Passaglia, NBS
John B. Wachtman, Jr., NBS

It was largely through the efforts of Dr. Shirleigh Silverman that this conference took place. He was instrumental in causing it to happen, and provided the leadership necessary for its organization. He was also to have been editor of these proceedings, but his efforts were halted by his untimely illness and death. These proceedings are offered in his memory.

Abstract

This conference was held to review the materials science experiments carried out in space, and to assess the possible future applications of space in materials science and technology with the advent of the space shuttle. Experiments carried out on Skylab, the Apollo-Soyuz Test Project, and recent sounding rocket experiments were reviewed. Specific discussions were directed at possible future applications in metals and alloys, ceramics, semiconductor materials, biological materials, crystal growth, transport properties, critical phenomena, thermodynamic data, containerless processing, combustion, and convection effects.

Key words: Containerless processing; materials science; micro-g; Sky-lab; space processing, space shuttle.

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Introductory Comments

Shirleigh Silverman
Conference Chairperson
National Bureau of Standards

I am Shirleigh Silverman and it is my pleasure to have the privilege of being the Chairperson for this morning's session. I am sorry to be starting a few moments late, but apparently a number of the people who are staying in town at the Holiday are having a little bit of delay in getting out here by transportation. I think, however, that there are enough of us here to start it off. First I would like to make a few comments as to how this Conference came about.

Some months ago there was a letter that came from Dr. James Fletcher, who is the Administrator at the space agency, to Dr. Ernest Ambler, who is the Acting Director of the Bureau of Standards. The letter requested the assistance of the Bureau in setting up a conference here that would be devoted to the subject of this particular conference--The Applications of Space Flight in Materials Science and Technology. Dr. Fletcher felt that the Bureau of Standards would be a very suitable location for such a conference in view of the Bureau's commitment to measurement science, to the characterization of the properties of the materials, and, in general, to things which relate to the subject at hand. As a result of this, a committee was established and the members of the Bureau were, aside from myself: Dr. Passaglia, who had been until recently the Chief of the Metallurgy Division here, a Division which had been actively involved in some of these matters; and Dr. Jack Wachtman, who is the Chief of the Inorganic Materials Division, in whose Division the interests also impact upon materials. The people from NASA were Dr. James Bredt and Dr. Mark Nolan.

At the time that we met to set this program up, we concluded that perhaps the best thing to do would be first of all, to have a review of those things which had been done, both in Skylab and in the Apollo flight and to cover also those experiments which had been done in the SPAR program, the rocket program. And then we felt that following that, it would be good to take a good hard look really at what the future might involve; so, today will be devoted essentially to the past and to the future. Now as some of you know, NASA made a request to the Space Applications Board, that the National Academy of Sciences take a look at what had been done in this area, to review, and to make recommendations. This request was forwarded within the Academy structure to the Solid State Sciences Committee of which several of us here including myself happen to be members, and it was that Committee report to the Academy which led to the establishment of a Committee whose Chairperson is Dr. William Slichter of Bell Labs and from whom you will hear a little bit later on.

Well, with that brief summary of the history first of this Conference and of some of the activities that sort of relate to it, I would now like to start the program.

Welcome Address

John D. Hoffman

Director
Institute for Materials Research
National Bureau of Standards

Welcome to the National Bureau of Standards and to this Conference on the Applications of Space to Materials Science and Technology. We at the Bureau are pleased to co-sponsor this meeting with NASA. Some of you may be visiting NBS for the first time and may not be familiar with the range of activities at the Bureau. I would like to take just a few minutes to describe some of our activities.

The Bureau was created in 1901 to develop and disseminate the national standards of measurement to determine physical constants and properties of materials, to develop test methods to aid in the establishment of standard practices, and to provide technical services to other government agencies. More recently, legislation has given NBS new and specific responsibilities in the area of computer technology, standard reference data, fire research, energy conservation, and materials conservation. The work of the Bureau is carried out in four Institutes: the Institute for Basic Standards, the Institute for Applied Technology, the Institute for Computer Sciences and Technology, and the Institute for Materials Research. Measurement, standard practices and data are common themes in all of our work and we are perhaps best described as the Nation's measurement laboratory.

The Institute for Materials Research is concerned with the development of methods for measuring the key properties of materials, the development of methods for relating these properties to performance of materials in service, and the development of Standard Reference Materials. Our work covers a wide spectrum; metals, alloys, polymers, ceramics, and the diversity in our program is reflected in some of our ongoing work. For example, failure analysis, nondestructive evaluation of materials, laser isotope separation, clinical standards, and measurements for air and water quality, The Institute for Materials Research has a long history of involvement in the space processing program. Recent planning efforts in the Metallurgy and Inorganic Materials Divisions of this Institute have been directed towards the NASA mission with emphasis being placed on the planning of the development of measurement techniques, standards, and benchmark data important for the space environment. I believe that this Conference will contribute substantially to the fund of practical knowledge on materials processing and materials properties generally. Once again, welcome to NBS, Gaithersburg, and have a good meeting.

USES OF SPACE FLIGHT FOR MATERIALS RESEARCH

John E. Naugle

National Aeronautics and Space Administration
Washington, DC 20546

It is a pleasure for me to participate in this coming together of the world of space flight with the worlds of solid state physics, surface chemistry and materials research to form a union which I expect to be turbulent and hope will prove productive. Some previous relations have existed between NASA's world and yours, because we have exploited the results of materials research in aeronautics and space flight and some of you have begun to use space flight for some preliminary experiments in the program we call "Materials Processing in Space." However, I think we are still some distance from a mutual understanding of what is important for you to do in this program and what NASA should seek to accomplish in it.

Since all research in space is difficult and expensive, it is important that we agree on a clear and definite understanding of these issues. This was not such a problem in my field, cosmic ray research, because we had an obvious need to operate instruments above the atmosphere for long times, and NASA had to understand the radiation environment in which men and automatic satellites would have to fly and had to know how and whether they could survive in it. Moreover, space research on cosmic rays proved to be an exciting field because new discoveries were made on every flight. We found research in space to be difficult and time consuming despite this background of mutual understanding and interest, but it was ultimately rewarding.

The main difficulty in space research is the blending of research, which is one of the more undisciplined and unpredictable kinds of human activity, with space flight engineering and operations, which are necessarily among the most highly organized and disciplined of human activities. It can be done and it can produce substantial results, as one can see from the cosmic ray program. Another example, which happens to be documented in the current issue of the Journal of Applied Optics, is the solar research conducted on the Skylab missions. The lead article by Dick Tousey of the Naval Research Laboratory accurately and eloquently describes the fortunes and vicissitudes of the solar physicists who joined forces with NASA in 1965 to study the sun and finally achieved their goal eight years later. I recommend it as a classic study of the troubles one may encounter in space research and the ultimate results that one may achieve.

Throughout the Skylab solar program, there was a mutual understanding that good solar research would be done in space, and NASA and the participating scientists shared a common desire to make that happen. This mutual understanding of the solar program's value and goals was essential to its success, and I think that a similar understanding will be indispensable to the success of any kind of research in space.

I suggest that the kind of understanding I have described in these two examples has not yet been fully achieved between NASA and the several materials communities. In my opinion, the most important current business of our program in Materials Processing in Space is to develop this essential background of mutual interests and shared goals with the scientific world. In order to contribute to that development, I want to state as clearly as I can why NASA has a program in Materials Processing in Space, what our objectives are, what we hope to obtain, and what steps we have taken or are taking to accomplish our objectives.

The Space Act says that we are to "expand human knowledge of phenomena in the atmosphere and space," and we are interested in the behavior of materials in space for both science and applications. Space flight provides a laboratory setting in which everything is weightless, to a good approximation, so that materials and living systems can be studied in isolation from the effects of gravity. It also affords other resources, such as abundant solar energy and means to develop ultrahigh vacuum, but it is not yet certain that these provide unique advantages; however, there is no other way to turn off the earth's gravity, in effect, for as long as we wish and study complex phenomena in its absence.

We believe that the phenomena that are accessible to study in weightless materials should be understood, but I think we are taking more of a gamble here in other fields because the worth of such studies will depend on the resourcefulness and creativity of scientists in exploiting the resources of space to elucidate effects that occur in materials on the ground as well as in space. That is, the basic laws of physics that govern the behavior of materials are not different in space; whatever materials do there they will also do on the ground, and the attraction of space is simply that one may find it possible to do some experiments on materials that are not feasible on the ground or implement controlled processes that cannot be done in the ground. The same might be said of cosmic ray research or solar physics, but in these cases it was obvious that important fractions of the radiation we wanted to study could not penetrate the earth's atmosphere. In the case of materials research, there is not such a clear-cut barrier to accomplishment on the ground, and there is room for some perfectly understandable skepticism regarding the necessity of doing experiments in space.

Nevertheless I am curious, as I am sure some of you are, about what we may learn if some very clever people ask some very penetrating questions and make some very careful measurements on materials in space. We think the question is worth examining, and we have asked the Space Applications Board to take a deliberate and careful look at it and give us their advice on it. Dr. William Slichter chairs the group that has been assembled to do this, and its activities will be described in this address.

Our first reason for having a program called Materials Processing in Space, then, is our responsibility for the expansion of human knowledge. NASA does not take this responsibility lightly; we have, in concert with groups such as this, conceived, developed, obtained funding for, and carefully executed over $5 billion worth of programs whose primary, and in most cases, sole justification was science. What we undertake in the name of science must not only be sound, it must be the very best science because it is so expensive. If we are to undertake a program in materials research in space that may cost up to $100 million annually, then it must be good and it must be perceived as the best way to obtain the results in question by the majority of materials scientists, and not only by those whose work is supported by the program.

The second reason for our program in Materials Processing in Space is rooted in NASA's charter for application of the knowledge and technology of space flight for the benefit of the human race. Here, we want to explore the potential of using the resources of space flight to develop and manufacture new products or to produce familiar products more cheaply or with less hazard to the environment. The possibilities in this area will depend a good deal on what inventions arise from materials research in space as well as on future developments in space flight capabilties, but they may have far-reaching implications.

Those are the major reasons why we are interested in understanding the behavior of materials in space. What actions are we taking that can give you some confidence that our interest is serious? I have found that a good research program in space rests on three supports like a three-legged stool, and we have been taking active measures in all of these necessary areas.

In the first place, a successful program must have strong and knowledgeable leadership. Mr. Johnston has recently brought Dr. John Carruthers from the Bell Laboratories into NASA Headquarters to direct the program, and we feel that he has the full confidence and respect of people in NASA as well as in the scientific community.

Secondly, there must be a strong, interested group at a NASA field center to design and develop the flight hardware and help to handle the program's day-to-day operations. We have such a group in the Marshall Space Flight Center.

Finally, one must have several highly competent research groups participating in the program: groups in universities because of their high caliber and in order to attract bright students to make their careers in space activity; groups in the field centers to interact between non-NASA scientists and space systems engineers; and groups especially in industry and other government laboratories to incorporate space research results into their other activities.

These three elements are necessary for a successful program, but they are not sufficient unless the program also has funding and flight opportunities. The funding for the Materials Processing Program has been steadily increasing. It was $6 million in FY 1976, $9 million in FY 1977, and we are requesting $15.5 million in FY 1978. We expect a further increase for FY 1979, provided our current review shows that there is indeed something worthwhile to be done. As regards flight opportunities, we have assigned the Spacelab 3 mission to materials processing. An artist's concept of the mission is shown in Figure 1; Spacelab 3 is scheduled to fly in January of 1981, and further materials processing missions will be assigned as required.

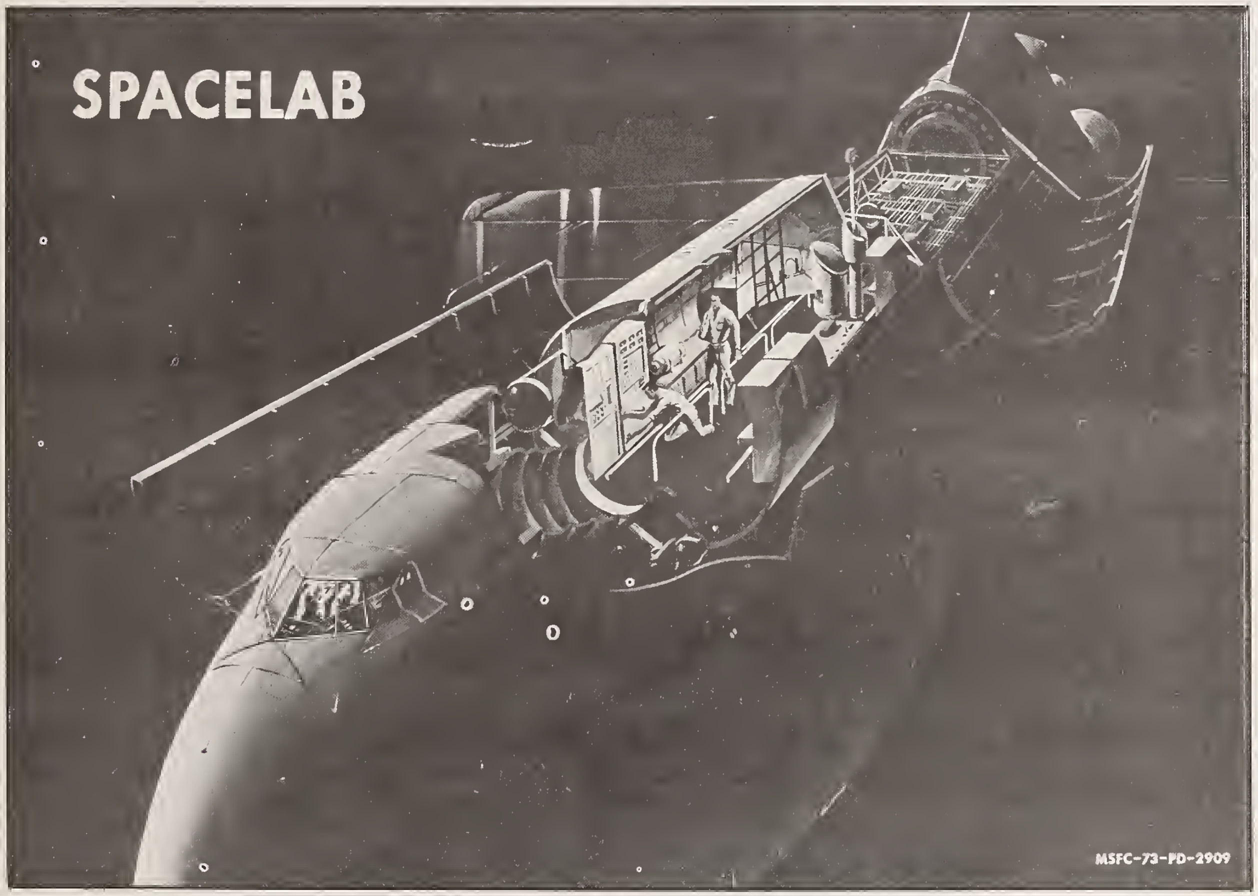

Figure 1. Spacelab for space processing (artist's concept).

In summary, we in NASA are serious about conducting a program to understand the behavior of materials in space and to exploit that knowledge for the benefit of all the peoples of the world. We invite you to join us in this enterprise, whose success will depend on ideas you generate, the steadfastness of the NASA commitment and some help from the gods who watch over the secrets of nature.

Discussion

Question: Are there any plans to have a polar subsynchronous orbit of the shuttle subsequent to these early flights when you have Vandenberg in operation?

Answer: Yes.

Question: Will there be a solar collection of energy as opposed to a battery operated furnace?

Answer: Well, I think the answer to that is certainly yes. I do not think we necessarily have to go into a polar subsynchronous orbit to get solar energy. I mean, we are looking at using solar energy on flights out of Cape Canaveral.

Question: For melting materials?

Answer: Yes. That is certainly under consideration. Now for space lab three, I do not think we will be doing that. I think we will be using the fuel cells on board there; but you probably know there is at the drawing board stage a proposition to have a solar energy source that we could use over and over again for space processing.

THE NATIONAL RESEARCH COUNCIL STUDY

William P. Slichter

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The broad question of the scientific and technological aspects of materials processing in space arose through discussions several years ago among persons and groups with the National Research Council and with the National Aeronautics and Space Adminstration. The history of this thought has been described by Dr. Silverman in his introduction. One consequence of these discussions was the planning, with the combined interest of NASA and of the NRC, of a general study of technical aspects of materials processing in space. Under the aegis of the Space Applications Board of the NRC, and with funding by NASA to examine these technical aspects, a committee was established in late 1976 to carry out this broad study.

The charter of the committee is purposely general. The study plan, which was agreed upon as central to the NASA-NRC arrangement, included the following objectives:

(1) an assessment and evaluation of the scientific and technological significance of what has been learned to date about processing organic and inorganic materials in the space environment;

(2) a judgment of the merit of a program on materials processing in space (possible benefits, if any, values, advantages and disadvantages); and

(3) recommendations regarding the nature and scope of NASA's future program of experiments on materials processing in space as well as on a program of complementary experiments in ground-based facilities, or theoretical studies designed to provide a sound scientific basis for the program.

Inevitably, the study committee required an acronym. Accordingly the designation STAMPS (Scientific and Technological Aspects of Materials Processing in Space) was adopted as a label for the Committee. The membership was drawn from a broad spectrum of persons active in work on materials. In choosing the Committee, attention was given to people whose technical interests were in the broad area of materials science, including the fundamental disciplines. Some familiarity with space programs was considered to be advantageous. However, the membership of the committee expressly excluded persons whose professional activities were or might soon be supported by NASA research grants. The Committee consists of William P. Slichter (Bell Laboratories, Chairman), Robert H. Bragg (Berkeley), John M. Deutch (Massachusetts Institute of Technology), David Jacobus (Merck, Sharpe, and Dohme), Morton E. Jones (Texas Instruments), William Klemperer (Harvard), Richard A. Oriani (U.S. Steel), Walter S. Owen (Massachusetts Institute of Technology), Albert Rubin (Cornell University Medical Center), L. E. Scriven (University of Minnesota), Robert F. Sekerka (Carnegie-Mellon University), and John Wachtman, Jr. (National Bureau of Standards). Liaison with the Solid State Sciences Committee is provided by Shirleigh S. Silverman (NBS), and liaison with the Universities Space Research Association is provided by Henry Leidheiser (Lehigh University).

To carry out its charter, the Committee has organized a series of conferences on selected technical topics. The purpose of the conferences is to gather and discuss information bearing on the Committee's objectives. Topics were chosen by the Committee in early meetings. The conferences feature active participation by invited experts from the scientific and technological community. The topics addressed or planned include fluid dynamics, biological separations (especially electrophoresis), containerless processing, solidification, and combustion and flames. Emphasis is being given to principles and phenomena, rather than to the behavior of specific materials. The Committee has no intention of passing judgment on specific programs that may be candidates for prosecution in the space environment. Rather, it will deal with generalized problems.

Certain reactions have evolved from the early meetings of the Committee. One clear opinion is that experiments in space should be linked closely to strong earth-based science and technology. Another reaction is that if the fundamentals of science and technology from terrestrial experiments are unknown, then space experiments on a try-and-see basis are unlikely to be fruitful. Although the Committee feels that the present prospects for commercial processing in space are very limited, it recognizes the possibility that by proper planning some activities in space might present unique opportunities to produce prototype materials or pilot processes.

The Committee recognizes the need to go forward with its work expeditiously and to produce a report at the earliest reasonable date. To that end, a concentrated workshop will be held during the summer. That session will draft a report which will then go through the usual review procedures of the National Research Council. The workshop may reveal the need for additional conferences to complete the study, but every effort will be made to complete the report in a timely manner. Upon the completion of review and revisions, the report will be issued through the NRC. It will specifically go to the Administrator of NASA and will also be a public document.

Discussion

Question (Paul Meijer, Catholic University): I heard you say something about containerless processing; if so, what kind?

Answer: Well, that's largely to be determined, but one can think of the preparation of refractory materials for example, or materials of interest in which purity is of particular importance on a scale unobtainable by present experience with containers. Now I would hasten to say that it is not obvious in light of experience in various excellent earth-bound experiments that it is a necessity to use space experiments for this, but one may learn things.

Question (M. Foster, IBM): Will your committee make recommendations based on your conclusions?

Answer: We don't have more than partial conclusions. I cited a few of them earlier and they are highly preliminary. There will be a meeting this summer which will bring together the judgments and points of view that we have developed through interactions with the community of materials science and related topics and in light of our discussion. That is when the report will be generated and I refer to a report that will go through the review procedures of the National Research Council as it must under charter. It will be delivered to NASA and will be a public document. The report will be delivered as expeditiously as possible subject to the review procedures.

Question (Charles Johnson, Arthur D. Little): You indicated that you would like to develop experiments that are uniquely useful to probe in space. I wonder if your committee has established certain criteria already that you are using to screen what is uniquely useful.

Answer: I think I may have mislead you if I allowed the words "uniquely useful" to enter. I do not think we are seeking to prove the uniqueness of something. We would like to develop clarity of information and basic knowledge if that is to be done by appeal to a low gravity environment. It may turn out that there is something that is uniquely useful, but we are not just going out on a search for that because we think that is rather a futile search. That would be almost a try and see kind of search. We think that with the brain power that is already been brought to bear on all of these things that if there is something really uniquely useful, it would have been thought of already. But there may be ramifications or aspects or clarifications or extensions of knowledge which may indeed turn up things that are surprising and lead to new lines of thought. So it is with an intended openness that we are approaching the study. I do not know if I have answered your question, but I hope I have.

Reply (Charles Johnson, Arthur D. Little): I don't quite get the sense of the criteria that you plan to use to establish this openness that you are referring to. I was trying to get a sense of what the committee would use as a screen against which to select various kinds of experimental projects.

Answer: We are not going to select experimental projects. That is for investigators to propose. We hope that our information made public in short time will clarify fundamental issues related to materials processing, broadly speaking, and based soundly upon scientific concepts and purposes will emphasize those things that are perhaps to be revealed or exploited by a microgravity experiment. I don't want to elaborate on this too much because of lack of time, but I think you will hear some of these things cited in a couple of talks tomorrow. It is not the function of this committee to screen the validity of experiments. This is not a review committee. Peer review process handles that, and we must not get into that kind of activity. We can be indicators of fruitful lines of endeavor perhaps, but that will depend on whether they emerge. And we are not chartering ourselves to say we will struggle until we get this kind of information and reveal to the world that here is where you ought to be working. Rather, we are going to make a collective assessment as best we can of what one knows about the influence of gravity upon important phenomena and do this in scientific terms with a strong awareness of the behavior of materials and materials processes.

Question: You are chairing the science committee of the Space Applications Board. Is there an Engineering Committee being formed?

Answer: There is not really what you call an Engineering Committee, because we are it too. This committee is science and technology and the word technology is meant to embrace the concept of engineering. There is to be formed, but not yet actually formed, a committee which you might call "Commercial Aspects". That has not yet come into being, but it will rather shortly, I believe.

Comment (Clo Wood, SAB): The concept is that after the scientific and technological group has tried to establish some sort of basis for what it would be useful to do, another committee would address the institutional aspects of how industry and commerce could participate. It would address such questions as proprietary rights, prices for a ride on the shuttle, and the general barriers to outside participation. But it is not useful for that committee to start its work until some directions of useful activity begin to emerge from this committee.

Speaker: Let me emphasize in this general context that communication between the committee we have been talking about and the people at NASA has not waited, and is not going to wait until the report is written and is reviewed. That would be unfortunate and would offer no opportunity for feedback or for continuing information. On the contrary, the communications occur on a consistent basis and will continue to do so, through verbal reports and attendance at the meetings of the committee by members of the NASA organization who have a direct interest in this area, and by members of the Space Applications Board of the Academy of Engineering. The report will be for the record, but the information ought to be largely known.

MATERIALS PROCESSING EXPERIMENT CAPABILITIES IN SPACE

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The purpose of this paper is to provide a background for the understanding of the physical capabilities of the materials experiments on Skylab, Apollo-Soyuz, and the Space Processing Applications Rocket (SPAR). To understand the experiment capabilities and limitations in the scientific context, we need to understand the mission, its profile and objectives, in addition to the capabilities of the spacecraft itself to provide the supportive environment and, finally, the capabilities and limitations of the experimental apparatus.

The Skylab mission provided a manned orbital space station with the primary purpose of studying the physiology of man operating in space for long periods of time in a large spacecraft in which he could move around. Medical experiments had first priority.

Skylab is made up of a laboratory complex involving the orbital workshop, docking adapter, Apollo spacecraft, and Apollo telescope. It still revolves around the Earth at an orbital altitude of 440 km. The mission profile required the spacecraft to be put in orbit in early May 1973, followed weeks later by the first manned mission which had a duration of 28 days, a deactivated period until the next manned mission of 59 days, followed by another period of deactivation, and finally, a manned duration of 84 days. Materials experiments were performed in each of the missions.

Two different attitudes were maintained while on orbit. One involved the perpendicular to the local vertical to Earth and the other involved a solar inertial attitude. A major amount of thrusting was required for changing attitudes, but once in a specific attitude, momentum for holding was provided largely by the control moment gyros. This system was capable of maintaining an angle of ± 6 arc minutes to any particular axis. It is important to realize that there were forces operating which caused minor accelerations to the materials experiments of less than 10^{-4} g's.

From the thrusting of the many reaction systems and vents, so much gas was being expelled that, surrounding the spacecraft, the pressure was much higher than the local pressure of that point in space. The vacuum chamber vented overboard could not achieve extremely low pressures. The cabin was maintained at a pressure of 25 cm Hg during habitation and slightly less than that during the deactivation periods. The temperatures rose as high as 49 °C in the cabin but the humidity was maintained close to 50 percent. This was the environment which surrounded the experimental apparatus.

Electrical power was supplied by many sources. The housekeeping required an average of about 400 watts. Individual experiments took much more than this for short periods of time. The experiments requiring the electron beam gun were powered by their own nickel-cadium battery. The rest of the experiments in the furnace were powered from spacecraft sources, through 28 volt dc bus.

The materials experiments were performed in the M512 apparatus, which consisted of the vacuum work chamber vented overboard, the electron beam gun, the control panel, and several experiment modules and inserts which went into the vacuum chamber, including the M518 furnace in which most of the solidification and melting experiments were carried out. The chamber was a sphere 40 cm in diameter and, when vented overboard, it took two hours to get to 10^{-4} torr. The vacuum achieved without a pump or a wake shield was not very good. This is the reason why we are enthusiastic about a vacuum wake shield, which will provide much lower pressures for materials experiments.

Fourteen materials experiments were completed on Skylab. Two used the electron beam gun for melting specimens, one used an exothermic chemical for heating, and the other eleven were out in the electrical tube furnace. Since this furnace was similar in design to that used on the Apollo-Soyuz, it will be described later.

The primary purpose of the Apollo-Soyuz Test Mission was to demonstrate international cooperation in space. It showed that with a docking adapter, American and Russian spacecraft could perform rescue operations in space. Twenty-nine scientific experiments, eleven in materials sciences, were performed by the American crew. The mission profile involved a separate launch of the two spacecrafts, with a rendezvous and docking on the second day in orbit, followed by several docking tests and separation, after which most of the scientific experiments were performed. The altitude was lower than Skylab, 220 km. The materials science experiments were conducted in three pieces of apparatus: the tube furnace and two electrophoresis devices.

The tube furnace was 15 cm in diameter, and it had three tubes, 2 cm diameter, surrounded with an insulation of nested radiation shields. The windings were Kanthal A-1 imbedded in an alumina cement, which provided a capability to heat each tube to 1150 °C, using 250 electrical watts. The second part of the furnace was the programmable controller which provided variable heating and cooldown rates. Heating was accomplished at 5 to 8 °C per minute and cooldown from 2 to 17 °C per minute. There were three chromel-alumel thermocouples in the furnace for control.

The third part of the furnace was the helium cooldown system, which provided a gas in the evacuated insulation area to cool the outside of the furnace rapidly so that the astronaut could handle the equipment. Typically, the interior of the furnace could be heated to 1150 °C in an hour or more, while the outside remained below 100 °C. Cooldown rates in the interior also could be controlled by the helium cooldown apparatus. Helium was provided between the radiation shields and then evacuated for the next experiment. There were 11 materials experiments and 8 of these were accomplished in the furnace. The experiments are described in the Final Science Report of the Apollo-Soyuz Experiments, recently published, by Marshall Space Flight Center as NASA TMX-73360.

The Space Processing Applications Rocket, approximately 43 cm in diameter, provides a capability to carry out some low-gravity materials experiments and thus, provide program continuity during the hiatus between the end of the Apollo Program and the beginning of the Space Shuttle. There are many limitations involved with the rocket, such as, the high launch accelerations and vibrations and the spin-down before the five minute period of weightlessness. Nevertheless, this provides the capability to checkout and develop apparatus at a much lower cost than that of larger spacecraft. It also helps to better understand melting, solidification and levitation, and to learn how to integrate many experiments at a time on a rather short schedule.

The payload on the solid rocket includes a measurements module, recovery system, a support module, and then the various pieces of apparatus. The total experiment payload can be 180 to 320 kg providing the five minutes of weightlessness. Of course, a lower payload weight can provide longer times and a Nike booster can launch a larger payload. The mission profile consists of launch from White Sands, New Mexico, northward into the desert with a high acceleration launch, spin-up to provide flight stability, and spin-down. A coast period occurs for the next 300 seconds, in which the rocket reaches a maximum altitude of 240 km and, during which the accelerations are low, below 10^{-4} g. This is followed by a heat shield and parachute deployment and a soft landing in the desert so that the specimens may be retrieved. Of course, all solidification and other processing have to occur before the depletion of the coast, and parachute deployment. Accelerations have been measured by gyros, accelerometers and by specific experiments on flow of materials to show that the accelerations are in the neighborhood of 10^{-4} or less after despin.

The roll rates during the spin increase to about four revolutions per second in thirty seconds and continue until about 60 seconds into the flight. The acceleration in the thrust vector rapidly increased to about 13 g's during the thrusting of the engine and dies out rapidly at about 32 seconds when the engine firing is completed. Starting at sometime after 60 seconds, the conditions of the rocket are very quiescent and, very closely, simulate the conditions obtained on orbit in terms of weightlessness or virtual free fall.

At first, it was thought that a non-spin platform would be required to protect the experiments from roll axis accelerations. There was concern that there would be a long-lasting vortex motion in fluids on the rocket caused by despin. However, Marshall Space Flight Center's Space Laboratory made experimental measurements on spin-down time for typical fluids in various positions simulating flight experiments. They simulated conditions of rotations rates, deacceleration rates, on- and off-axis, wetting and nonwetting, with and without damping. The results were that a non-spin platform was not needed for vessels of less than 1 cm diameter.

The apparatus on the rocket includes: (a) a tube furnace which is similar to the Apollo-Soyuz furnace, (b) directional solidification furnace, (c) thermal control unit which provides for heating and cooling at lower temperatures for model materials such as organics and salt solutions, (d) an acoustic levitator, (e) an electromagnetic levitation apparatus, and (f) a continuous electrophoretic separator.

In summary, low gravity levels in the range of 10^{-4} g's or less have been provided by each of the spacecraft on orbit or the ballistic rocket. The furnaces have been provided with controlled temperatures up to 1150 °C on Apollo-Soyuz (1000 °C on Skylab) and about 970 °C on the General Purpose Rocket. Specimens in the furnaces were less than 2 cm in diameter and as much as 10 cm long. These specimens sizes have been adequate for metallographic analyses and interpretation. The time available on the rocket is short but on Apollo-Soyuz and Skylab longer periods of time were available. However, there have been limitations on the amount of electrical power provided and that has placed a limitation on the total time and temperature available.

In the tube furnace experiments, each experiment has been solidified and melted in a sealed tube in which the environment surrounding the specimen was controlled. Other special apparatus, such as the wake shield, will have to be provided for very high vacuum experiments in the future. The experiments provided so far, 14 on Skylab, 11 on Apollo-Soyuz, and 20 on the three SPAR rockets, have provided much valuable data in weightlessness. We have gained much experience in flight apparatus design and operations showing that we can provide a useful experimental capabiltiy in space.

Discussions

Question: What is the status of the wake shield facility at this time?

Answer: Currently it is still in the planning stage. The Langley Research Center has done some excellent work in defining the feasibility of the wake shield and we at Marshall Space Flight Center are further defining the engineering layout for such a facility. I think I should say that most of us closely involved with the program want it very much. We see some real advantages to be able to attain extremely high vacuum and weightlessness at the same time. That would be something which I believe would be a unique capability of the space environment for experimentation. It is in the stage of feasibility and engineering definition although it is not yet approved. We hope that it will get funded and then we will be most happy to develop that facility. I think the question whether it does go on and gets funded would depend very much on the scientific community determining whether they saw a need for it or not.

Question: What is the principle of operation?

Answer: Let us see if I can describe it in a few words. Essentially, the space craft in orbit is piling up molecules on the front but is causing a rather clean wake behind it because its velocity is about as fast or faster than most of the molecules or atoms at that altitude. Therefore, if you put a chamber, particularly a hemisphere, facing backwards, you can achieve a very high vacuum. Of course, you would have cleaned the chamber up, baked it out, before you would have put it up there. The vacuum science people at

Langley Research Center, who I think are here somewhere, really could give a much more precise answer about the operation of the wake shield. There have, by the way, been experiments on some early satellites which had vacuum measurement gauges facing forward and backward and measured these large pressure differences.

METALLURGICAL STUDIES IN SKYLAB AND APOLLO-SOYUZ FLIGHTS

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A number of experiments were performed in the Skylab missions and in the Apollo-Soyuz Test Project to evaluate the role of near-zero gravity on the structure and properties of metals, alloys and related model systems. These experiments can generally be divided into three principal categories: (a) engineering processing studies, (b) fundamental segregation studies, and (c) directional solidification studies. In the first category, experiments have been conducted in Skylab to study the feasibility of brazing in low gravity environments, which have produced rather encouraging results. For example, it was shown that, in a low gravity environment, surface tension forces drive capillary flow, which on earth must compete with gravitational forces. This result indicates that braze gap clearances will be far less critical in space for future construction. Additionally, the low gravity environment alters liquid-metal interactions; a liquid Ag-Cu alloy dissolved Ni more rapidly than is observed at 1-G and solid stainless steel dissolves Cu from liquid Ag-Cu more rapidly in space than on earth. While it is not entirely clear why this result was obtained, there may be possibilities of improving studies of liquid-metal interactions at low gravities. Another experiment in this category includes electron beam melting of an aluminum alloy, a stainless steel and pure tantalum. These experiments indicated that surface tension forces allow the use of electron beam welding in low gravity environments. Additionally, the presence of elongated grains near the melt back region was observed in ground-based experiments while only equiaxed grains were observed in low gravity, apparently due to convection effects. Other experiments in this category included a relatively unsuccessful sphere forming experiment and an attempt to study pore retention in fibrous and powdered aluminum samples. In the latter case, surface tension caused agglomeration of the samples, effectively eliminating porosity.

In the second category, that of phase separation, experiments have been performed on Au-Ge, Pb-Zn-Sb and Pb-Sn-In alloys at compositions where the phases are known to exhibit a liquid or solid miscibility gap. These experiments resulted in the observation of unknown x-ray diffraction lines in the low gravity processed materials, suggesting unpredicted morphological changes. Additionally, unusual superconducting transitions were observed with low gravity Au-Ge specimens showing a transition, with no transition observed in ground-based samples. Samples of Pb-Zn and Al-Sb were flown in ASTP and results, when compared with ground-based samples, showed that microscopic and macroscopic homogeneity was greatly improved. Some problems were encountered in the PbZn system but a number of fine Pb particles was observed in the Zn matrix indicating enhanced homogenization.

In the third category, directional solidification alloys of Al-Al_2Cu, NaCl-LiF and Bi-MnBi have been studied. For the Al-Al_2Cu alloy, the investigators reported improved structures although the results were not unequivocal, with Skylab 3 results showing worse structure than ground-based produced structures and Skylab 4 results showing superior structures to ground-based results. Experiments have also been performed on a model eutectic system, NaCl-NaF in which continuous NaF fibers were produced in low gravity, apparently due to reduced convection in the melt ahead of the planar interface. Additionally, improved optical properties were observed due to the improved alignment of the transparent fibers. Similar experiments were performed on the NaCl-LiF system in ASTP with similar results. In the latter case, dissolution of the NaCl matrix in water clearly showed a much improved aligned structure in the low gravity experiments when compared with ground-based experiments. These specimens showed improved axial light transmittance, also indicating improved fibrous structures with fewer terminations.

The Bi-MnBi system is a ferromagnetic alloy with rod shaped fibers which exhibits a strong magnetic anisotropy. This property is maximized if the fibers are of the critical magnetic domain size, a structure which can be obtained by directional solidification. In ASTP grown samples, room temperature coercive forces of 11.2 KOe, with 135 KOe being measured at 77 K, values approximately 100 percent better than observed in earth-grown samples. Additionally the shape of the magnetic hysteresis loops is changed for the space grown materials, with hysteresis loops for samples grown at micro-g at 3.1 cm/hr being comparable to samples grown at 1-g at 75 cm/hr. These results are not as yet totally explained and work is being continued in the SPAR program.

In conclusion, metallurgical processing in Skylab, and ASTP, while not totally successful, in many cases resulted in some unusual and intriguing structures and properties. Considering the priorities of these experiments relative to the total space program, these results must be viewed as encouraging for future studies aimed at understanding metallurgical processing under low-g conditions.

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Discussion

Question (Jeff Ledlos, Massachusetts Institute of Technology): I have a question regarding the superconducting properties of these alloys. The first question is, how positive one can be that this gold-germanium alloy is really superconducting? Were other criteria checked like critical field and the presence of an energy gap? You mentioned that there were changes in the superconducting behavior for the second alloy. The second question is, were there any changes in critical temperature and critical magnetic field for this alloy?

Answer: This is, of course, a review of someone else's work. However, as far as I know field measurements were not made. At least the data I had available indicated they were not made. This particular transition was simply done by lowering the temperature and making resistivity measurements. The important aspect seems to be that this transition is not observed at all if the material is grown on earth, whereas you do see a relatively sharp transition if the experiments are done in a microgravity environment. In the second case, this large critical temperature difference is the same independent of where the material is processed, but there is a second transition which occurs at a higher temperature only for the space-grown material. And again, I do not believe that critical field measurements were made. It is simply a resistivity measurement as a function of temperature.

Question (Stan Gelles): I wanted to make a comment on the extra x-ray diffraction lines that have been observed on some of the immiscible materials. I have seen a recent report that tried to confirm that fact without any success so I would say that that still needs some confirmation. Would you care to speculate as to what causes that anomalous superconducting transition?

Answer: I am sorry, I really do not know. It is very preliminary data. I want to emphasize that many of these experiments, as Stan has pointed out, have not necessarily been confirmed. They were one shot experiments. There is certainly possibility for error.

Question (Foster, Massachusetts Institute of Technology): Is it a function of USRA to make suggestions to the PI's on following up data?

Answer: I think that is exactly what our committee is supposed to do. However, let me toss in some criticisms on that one. In many cases, by the time any USRA committee sees the data the PI is no longer a PI for NASA. In some cases where there is a NASA PI in house, we can still give positive input which we hope he will follow up on. The committee serves totally an advisory role. If we see some data from a PI that we think does not seem to make sense, we can ask them to follow up on it. We cannot tell them to follow up on it. We can only advise NASA that we think that there is something funny about that particular data and it ought to be followed up on. Which we try to do. We hope that our input is of a constructive nature in that if we see something anomalous, we are not saying, "Look, that is something stupid," but, "maybe you ought to try something else to prove what you have got there." Or perhaps improve your experiment before it flies. The committees in NASA, frankly in my opinion, are still waltzing together and still trying to decide just where they stand with each other. In the final analysis what would be nice to do (since most of us we hope are objective since we do not have an immediate program with NASA on the same subject) is to simply give PI's another point of view. That is we do not want to denigrate what PI's have done or what they are going to do, but make suggestions to them which might be helpful. And our hope is, as I say, to react very positively with both NASA and the PI's. And we hope that the PI's will, in fact, take advantage of us.

Comment: I think you might be too generous. I think it might be time for somebody to say, look you are on the spot. You told us something, either it is right or it is wrong. I think the PI has a responsibility.

Answer: I think we have done some of that.

Question (Lacy, NASA Marshall Space Center): In the superconducting transition which was observed in that particular experiment, I think the PI's noted their independent confirmation of this kind of activity through splat cooling. I think you quoted one or more papers in the open literature. People had splat cooled the same kind of material and also noted these transitions. And so I think, at least in the case of certain metastable phases, that they were able to form in zero g, splat cooling giving you an independent way of looking at this.

Answer: Thank you.

Question (Gilbert Moore, Thiokol): Has any consideration been given to the study of organic superconductors?

Answer: Not to my knowledge. It might be a very interesting kind of proposal to put in if it can be documented.

Comment: There is no Danish experiment for the first Space Lab mission. They are going to attempt to grow an organic superconductor. There is not any United States work.

Comment (Martin Glicksman): There is not one shred of evidence that there is any organic superconductor, or one on the horizon. I doubt, therefore, if there would be one in orbit.

FLUID BEHAVIOR IN A MICROGRAVITY ENVIRONMENT

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The availability of a reduced gravity environment for extended periods of time in earth-orbit laboratories has stimulated interest in its utilization for new material processing techniques. To date, three major areas have been identified which define the uniqueness of reduced gravity for materials processing and these are listed in Table 1 together with some of the associated advantages and disadvantages. These factors will define not only what kind of materials science can be performed in support of earth process studies and applications in space now, but also what new materials and processes can be generated in space in the future which will be useful for new applications. Since each of these factors involves some knowledge of fluid behavior under reduced gravity conditions, then this subject is reviewed in some detail here.

Table 1. Advantages and disadvantages of various aspects of space processing of materials

Space environments use for materials processing	Advantages	Disadvantages
1) Containerless handling of liquids	Container contamination avoided; thermodynamic study of reactive materials at high temperature; studies of liquid-solid nucleation phenomena possible; preparation of new reactive phases and amorphous solids made easier; stable length of liquid floating zones increased.	Need for position control of drops with external force fields; surface tension-gradient driven convection possible; liquid shape changes will induce convection in liquid.
2) Reduction of density-gradient driven flows	Mass transport by diffusion alone results in uniform macrosegregation in grown crystals; elimination of time-dependent convection phenomena and microsegregation striation in grown crystals.	Heat transfer by thermal conduction alone in melts produces undesirable crystal-melt interface shapes; constitutional supercooling instabilities more favored in convectionless melts; bulk mixing of melts not possible; other sources of uncontrolled convection may become dominant.
3) Reduction of sedimentation and Stokes flows (of solids and bubbles in melts)	Controlled monotectic solidification possible; microphase separation possible in glasses; reduction of equi-axed zone formation in ingot solidification; Preparation of uniformly dispersed composite materials.	Elimination of bubbles in melts very difficult.

There have been many detailed studies of the behavior of fluids under weightless conditions because of early interests in propellant tank design, spacecraft thermal control, liquid venting, and biological functions such as astronaut feeding, waste disposal, personal hygiene and blood circulation. Many of these problems are documented in a review by Habip [1][1], but a brief overview here is necessary as a background to our present interest in performing studies of fluid behavior in space.

The operation of liquid propulsion systems on spacecraft in a low-g environment requires some means of insuring the supply of gas-free propellent from the tanks to the engines. Many spacecraft use containment devices such as bladders or diaphragms to position and control the propellent. However, certain systems make use of the fluid mechanics of liquids in low-g to control the propellant.

Settling rockets, as were used for the Apollo Service Module main engine, can orient the liquid to the required position. Capillary structures located within the tank can use the force of the liquid surface tension as a means of controlling and positioning the liquid since the contact angle between liquid and container is near zero. Screens, perforated plate, or sheet metal vanes are used to form the capillary structure of the device. The Viking Orbiter has and the Space Shuttle Orbiter will have capillary devices in their propellant tanks.

Such propellent tank systems require a detailed knowledge of the static and dynamic behavior of liquids in a low-g environment. Some of the phenomena that have been investigated with regard to these systems are the shape and stability of gas-liquid interfaces in various shaped tanks, wicking and capillary pumping of the liquid through narrow passages, liquid from or into a tank in low-g, and the response of the liquid to disturbances of a periodic, steady, and transient nature. Propellants for such systems cover a wide range of storage temperatures, surface tensions, densities, contact angles, and are usually highly reactive (e.g., hydrogen, oxygen, fluorine, nitrogen tetroxide, hydrazine, and cesium).

Spacecraft thermal control is primarily achieved by the use of heat pipes using the large heats of liquid evaporation and liquid condensation. Liquid return is accomplished by capillary forces with wicks and is enhanced by low gravity. However, gas entrapment is a problem with certain wick designs which seriously degrade the heat pipe performance.

The earliest fluid mechanics experiments in reduced gravity were carried out in the short term environments of drop towers (a few seconds) and aircraft flying in a Keplerian trajectory (∿30 sec.). This early work allowed engineering design concepts to be tested. The first fluid mechanics experiments in space were performed on Apollo 14 [2] and 17 [3] flights during translunar coast. Two types of experiments were performed; convection and heat flow. In one group, thin layers of oil were heated at the solid-oil interface, and surface tension gradient driven (Marangoni) convection cells were observed at the free surface by means of aluminum particles suspended in the oil. In the other group, completely confined fluids (argon gas and Krytox 143AA oil) were heated in a variety of ways and temperature changes monitored by means of color changes shown on liquid crystals. In the Apollo 14 flight, heat transfer was 10 to 30 percent greater than for pure conduction, while in Apollo 17 no such enhancement was observed. It is thought that vibrations from the spacecraft and astronaut motion were greater on Apollo 14 because the experiments were performed on the return flight without the added mass of the lunar lander as opposed to those on Apollo 17 where the lander was still attached.

A series of six ad hoc science demonstrations relating to fluid mechanics were performed on the last two Skylab missions [4-8] and three additional demonstrations were performed in the Apollo-Soyuz Test Project (ASTP) [9]. These are listed in Table 2. In these demonstrations, mostly on-board equipment was used. However, the experiments were recorded in real time by either the data acquisition camera or on videotape for subsequent ground analysis. The experiments on mass and heat flows (in water) indicated that no unexpected convection phenomena were present in space (including Marangoni flows). The Skylab experiments on liquid floating zones (TV101) and liquid drops (TV107) yielded valuable insight and information regarding the static, rotational, and vibrational stability of cylindrical zones and spherical drops (of water and soapfoams). Both zones and drops showed non-axisymmetric rotational instabilities (C-shapes for zones and peanut shapes for drops) and vibrational/oscillation behavior which departed from expected theoretical behavior because of the presence of higher order modes due to the large

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[1] Figures in brackets indicate literature references at the end of this paper.

amplitudes induced experimentally. The ASTP experiments on liquid films, liquid spreading, and capillary wicking confirmed the expected minimum surface area shapes adopted by films and external liquid surfaces on wetted solid surfaces. The experiments on immiscible liquids and chemical foams showed that the distributions of a second phase liquid or gases in a liquid matrix were uniform. The films and foams were stabilized by the absence of liquid draining that occurs on earth but still coalesced or disappeared eventually by capillary and evaporation.

TABLE 2

Demonstrations and experiments relevant to fluid behavior on Skylab and ASTP missions

Science demonstrations (showing fluid behavior)

(a) Skylab
- Diffusion in liquids (water)
- Ice melting
- Liquid floating zones (TV101)
- Immiscible liquids (TV102)
- Liquid films (TV103)
- Fluid mechanics series (liquid drop behavior) (TV107)

(b) ASTP
- Chemical foaming
- Liquid spreading
- Capillary wicking

Space processing experiments (showing fluid behavior)

(a) Skylab
- Vapor growth of II-VI compounds (M556)
- Immiscible liquid alloy compositions (M557)
- Radioactive tracer diffusion (M558)
- Microsegregation in germanium (M559)
- Growth of spherical crystals (M560)
- Indium antimonide crystal growth (M562)

(b) ASTP
- Surface tension induced convection (MA041)
- Monotectic and syntectic alloys (MA044)
- Interface markings in crystals (MA060)
- Zero-g processing of magnets (MA070)
- Crystal growth from the vapor phase (MA085)

There were six materials processing experiments performed on Skylab [4,10] and five on ASTP [9,11] (listed in Table 2) which revealed fluid mechanics phenomena in high temperature processing configurations. One set of experiments (M556, MA085) involved the vapor phase transport and growth of IV-VI semiconductor compounds in a closed tube. The results showed that mass transport in the vapor under reduced gravity conditions was, in fact, faster than for the earth experiment in a low pressure regime which had thought to produce convectionless, diffusion-controlled growth. More extensive fluid dynamics analysis needs to be done here. All other experiments involved the unidirectional melting and solidification of high temperature melts to demonstrate diffusion and convection phenomena to grow single crystals, and to prepare various types of multiphase solids with geometrically-controlled distributions of the second phases. Some general conclusions regarding the fluid behavior of these melts can be inferred from post-flight compositional analysis of the segregation behavior and bulk mass transport during solidification as well as from the overall shape and appearance of the resolidified melt:

(a) all contained melts change shape to the equilibrium dicatated by the contact angle and filling factor;

(b) the wetting behavior depended sensitively on doping in contained semiconductor melts, although few investigations reported the surface appearance of their specimens; and

(c) there were no detectable influences of convection effects on segregation or mass transport processes in containered melts. Unfortunately, the one containerless crystal growth experiment (M560), where Marangoni convection might have been expected, was not compositionally analyzed.

More recently, fluid behavior and materials processing experiments have been carried out on the rather constrained environment of sounding rockets which provide 5 to 7 minutes of reduced gravity. To this date, however, no new information has been obtained about fluid behavior except as an indicator of the unusual aspects of sounding rocket flight; segregation due to despin accelerated flows, inadequate specimen equilibration times, residual acceleration due to non-zero rocket spin during free coast, and fluid flow due to meniscus shape changes over the experiment time as contained liquids achieve their equilibrium shapes (determined by the contact angle and filling factor). However, apparatus such as acoustic field and electromagnetic liquid drop positioners are being tested which will be used for extensive experiments being designed for Spacelab.

Some of the future space experiments being designed to study fluid behavior on Spacelab include:

(a) A liquid drop dynamics module is being designated for Spacelab by the Jet Propulsion Laboratory to provide information for a wide range of problems including superfluid helium behavior, nuclear fission, raindrop oscillations, containerless space processing, and binary star formation. Some tentative experiments are:

° Equilibrium shapes of rotating drops with uniform body charge.

° Equilibrium shapes of large rotating drops with negligible surface tension.

° Equilibrium shape of rotating bubbles.

° Fission processes of uniform body-charged drop (rotation or oscillation).

° Large amplitude oscillation of a uniform body-charged drop.

° Large amplitude oscillation of a surface-charged drop.

° Coalescence of neutral drops.

° Coalescence of charged drops (surface or body).

° Internal motion within drops due to rotation, oscillation, fission, and fusion.

° Capillary wave on a spheroid.

° Non-Newtonian fluid drop dynamics.

° Accretion and evaporation of drop in controlled environment.

° Surface tension and solution driven convection in drops.

° Dynamics of a superfluid drop.

° Spontaneous nucleation.

° Ice crystal formation.

(b) A fluid physics module is being designed for Spacelab by the European Space Agency to study the quantitative behavior of rotating liquid columns at ambient temperature. Some tentative experiments are:

° Quantitative assessment of end disc misalignment and non-planarity.

° Effects of other variables such as unequal end diameters and rotation rates, non-cylindrical zone shapes (nodoids and catenoids), and partially wetting end discs.

° Behavior of other types of liquids, composites, quantum liquids, charged, and non-Newtonian.

° Use of floating zone as a "tubeless test tube" for studies of Marangoni convection, complex crystal growth (e.g. TTF-TCNQ), and containerless electrophoresis.

(c) A cloud physics laboratory is being designed for Spacelab by NASA and McDonnell Douglas Astronautics Company [12]. A summary of experiment classes is given below:

° Condensation nucleation

° Ice nucleation

° Ice multiplication

° Charge separation

° Ice-crystal growth habits

° Scavenging

° Riming and aggregation

° Droplet-ice cloud interactions

° Homogeneous nucleation

° Collision-induced freezing

° Saturation vapor pressure

° Adiabatic cloud expansion

° Ice nuclei memory

° Terrestrial expansion chamber evaluation

° Condensation nuclei memory

° Nuclei multiplication

° Drop collision breakup

° Coalescence efficiencies

° Static diffusion chamber evaluation

° Unventilated droplet diffusion coefficients.

(d) Containerless high temperature melts will be positioned by an acoustic field in a facility being contemplated by NASA. Such an apparatus would have wide potential for different types of studies in material science including those concerning Marangoni convection and static rotational and vibrational behavior.

The reduction of density gradient driven natural convection in low gravity environments leads to a consideration of other sources of residual fluid motion which may become dominant. It is important to understand that only very slow flows may influence mass transport in crystal growth systems significantly but will exert no influence on the overall heat transport in the systems. Consequently, natural convection arising from the variation of fluid properties, other than density with temperature and concentration, must also be considered at reduced gravity. Flows from surface tension gradients (thermocapillary convection) have already been mentioned. Variations in other fluid properties such as viscosity, thermal conductivity, and thermal expansion will generate slow flows. Such fluid properties are known to contribute non-Boussinesq terms to the Navier-Stokes flow equations for thermal convection at one-g and to alter the flow stability criteria [13-15]. Although not studied, their influence at reduced g in generating fluid velocity may be very important. Other sources of uncontrolled convection may arise in gases from pressure gradients due to chemical reactions, low level g-jitter [16] (variations of 10^{-3} g may be common in spacecraft at average levels of 10^{-4} to 10^{-3} g), and to boundary layer thermal transient contributions (such as thermoacoustic convection) [17].

The processing of materials in space is unique because of the altered behavior of fluids in a reduced gravity environment. Therefore, this review has addressed our current state of knowledge concerning the behavior of fluids under reduced gravitational conditions. Many gaps in knowledge have been identified which require further clarification by ground-based experimentation without need for recourse to a space environment. However, there will always be an element of the unexpected because of our unfamiliarity with the space environment. Hence, in order to fully utilize the characteristics of reduced gravity to innovate new and unique materials processing techniques, it is essential that space experiments be conducted in conjunction with well-conceived and highly competent ground-based research program.

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Discussion

Comment (Bredt): Hans Walter did do a considerable amount of compositional work on his indium antimonide crystals. It is not in the NASA report and has not yet appeared in print. One of the things he saw that was unusual was a series of growth bands that he attributes to what you might call the inverse interface breakdown due to constitutional supercooling. What he thinks he sees is the pile up of impurities that effectively decreases the melting point and temporarily arrests the growth.

Answer: For the record, Jim Bredt is clarifying the situation with regard to Hans Walter's experiment on Skylab involving the freezing of a spherical drop of molten InSb. Compositional profiling was performed in the initial region of the regrowth. Walter did, in fact, find a series of striations spaced with an increasing spacing from the start of the regrowth region. The analyses of these, which by the way is not universally accepted by those in the business was published in the Journal of the Electro Chemical Society last year. I believe that at this particular juncture that those kinds of striations, which, by the way, had been also reseen on the MIT germanium experiments on ASTP, may be associated with the problems of the starting transient. In other words, the remelting is first carried out and regrowth has to take place under the conditions we want in the mission. I think the problem of turn around involves a transient heat flow problem that we do not understand and may be primarily responsible for the kinds of instabilities that we are observing. The explanation that Walter proposed was a very detailed dynamic interplay between the compositional gradients present in the melt and the temperature gradients present which, of course, control the solidification rate. This explanation had been put forward many years ago by the Russians and was not believed here primarily because we had always had thermal convection present and it was thought they were looking at thermal convection striations. I would at this point say that without further work in the area that I am pretty much neutral and I guess there are people on both sides of the fence about the interpretation of the striation behavior.

Comment (Jerry Wouch, General Electric): Some of the most beautiful work in rotating droplets was done during the 1890's in working out the stability of figures of revolution. It seems like in the weightless environment of space we have the opportunity to truly check some of the mathematics developed in that period by measuring the droplet stability figures, and also by studying the coupling between surface tension, oscillations, and rotations.

Answer: Yes, you are absolutely correct and this is one of the primary motivating factors of the Jet Propulsion Lab experiment. What you have just posed is the basic mechanism, for instance, of the formation of neutron stars on the one hand and of nuclear fission on the other. Conceptually, at least, the same principles apply and can be studied very effecively over the dimensions that we can accommodate in the drop dynamic module that JPL is contemplating. They do have that kind of physics input to their module and if you are interested, you could talk to Taylor about that. I am sure he would be interested in talking too.

Taylor Wang commented that the experimental conditions that will be imposed on the liquid drops will look at all the equilibrium rotating unstable modes.

Answer: The work that is going on right now as a prelude to this has to be basically an evaluation of the characteristics of acoustic field positioning and how they interact with the liquid drop shape. I guess those studies are almost complete and they are really fascinating. When I first heard about these studies at the Jet Propulsion Lab I was very skeptical, but, in fact, only very low levels of sound energy are needed in order to maintain the position of drops of very large size. It turns out to be eminently practical to do this sort of thing, not only for the physics studies that JPL is going to carry on, but also for containerless processing experiments more relevant to materials science that we have in mind.

CRYSTAL GROWTH IN MICRO-GRAVITY - AN OVERVIEW

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1. Introduction

The common objective of the experiments performed in space was to explore the effects of microgravity on crystal growth. The aim of the experiments was multi-fold: firstly, to obtain basic information which could lead to the improvement of present theoretical concepts and crystal processes on earth, secondly, to establish a realistic basis for future space processing applications, and thirdly, to observe unexpected phenomena. The experiments were not designed to produce "perfect" single crystals for specific applications.

Except for the solution growth (MA-028), all crystal growth experiments were performed in the multi-purpose gradient furnace which contained three tubular reaction cavities allowing the simultaneous processing of three experiment ampoules sealed individually in metal cartridges. A summary of the experiments performed during the Skylab and Apollo-Soyuz missions and of the principal investigators is given in Table 1.

Table 1.

SKYLAB and ASTP crystal growth experiments.

Skylab	ASTP	Investigation	Principal Investigator	Organization
M 559		Melt growth and microsegregation in Ge	J. T. Yue	Texas Instruments
M 560		Containerless solidification of InSb	H. U. Walter	U. of Alabama (D.F.V.L.R.)
M 563		Directional solidification of InSb - GaSb alloys	W. R. Wilcox	U. of Southern California (Clarkson College)
	MA-028	Crystal growth from aequeous solutions: $CaC_4H_4O_6.4\ H_2O$, $CaCO_3$, PbS	M. D. Lind	Rockwell International
M 562		Melt growth and segregation in InSb	H. C. Gatos and A. F. Witt	Massachusetts Institute of Technology
	MA-060	Melt growth and interface marking in Ge		
M 556		Crystal growth from the vapor phase: GeSe, GeTe	H. Wiedemeier	Rensselaer Polytechnic Institute
	MA-085	$GeSe_{0.99}Te_{0.01} - GeI_4$, $GeS_{0.98}Se_{0.02} - GeCl_4$, $GeS - GeCl_4 - Ar$		

2. Experiments and Results

2.1 Melt growth and microsegregation in Ge: M 559

For terrestrial crystal growth from the melt, gravity-driven convection effects on segregation are intrinsically coupled with contributions arising from temperature gradient differences and fluctuations. The aim of this experiment was to isolate the effect of gravity on microsegregation. For this purpose Ge [111] single crystal cylinders doped with Ga (8×10^{16} atom/cm^3) were partially remelted and then refrozen in space at growth rate of about 5 μm/sec.

For characterization, spreading resistivity measurements were performed by the two-probe method at 5 μm intervals on flat polished crystal surfaces. A comparison of the radial resistivity profile at 0.5 cm away from the original solid-liquid interface for the Ga doped Ge crystals resolidified in space and on earth (fig. 1) reveals that fluctuations in the macrosegregation of the space crystal are reduced by about a factor of 6 relative to the ground-based crystals. The improved compositional homogeneity in dopant distribution is attributed to the absence of gravity-driven convection during solidification in space. The existence of microsegregation, although small in the space crystal, could indicate the presence of other sources of solute mixing, such as surface tension gradient driven.

2.2 Containerless solidification of InSb: M 560

In this experiment, the solidification of a partially remelted InSb crystal Czochralski-grown on earth and enclosed in a graphite mold (one end of the crystal was free) was studied to investigate the feasibility of containerless processing, crystal perfection, and dopant homogeneity in space grown crystals. About 1.6 cm of the seed crystal was remelted and subsequently solidified in space at an average solidification rate of 12 mm/hr.

The InSb crystal grown in space (fig. 2) clearly shows the boundary between seed and space grown portion. The morphology of the upper part indicates that the melt was in contact with the graphite heating cavity during final solidification. Optical photomicrographs of differentially etched longitudinal sections of a Se doped (10^{19} atoms/cm^3) InSb crystal

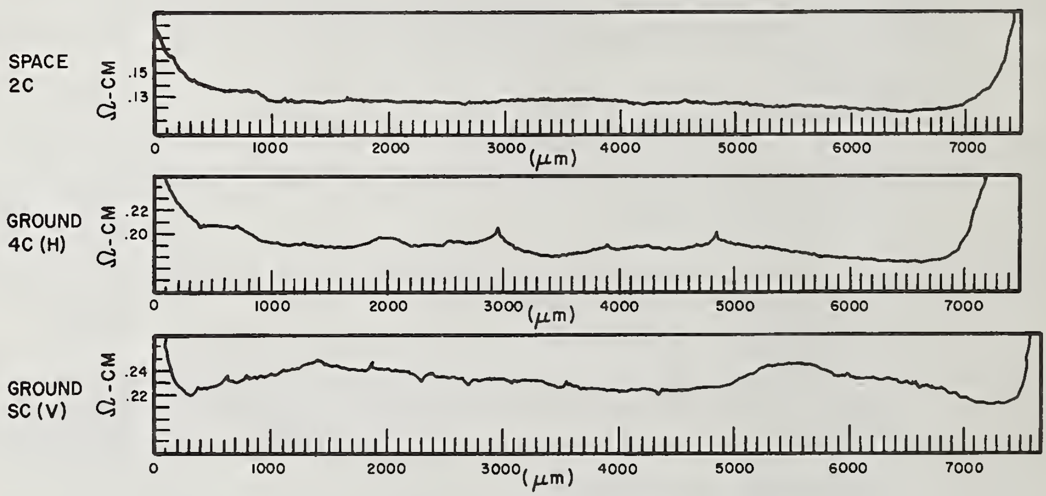

Figure 1. A comparison of the radial resistivity profile of the three Ga doped Ge crystals. The upper curve is for the crystal resolidified in space while the lower curves are for crystals resolidified terrestrially in horizontal (H) and vertical (V) temperature stabilizing positions. All three curves are made with the two probe spreading resistance methods at 5 μm steps. The radial profiles are measured at 0.5 cm away from the original solid-liquid interface. Each unit on the horizontal axis is 100 μm.

Figure 2. InSb crystal grown by a containerless method in space. Czochralski-grown seed mounted in graphite support at bottom. Boundary between seed and space-grown crystal (top portion) is clearly visible.

reveal a system of very distinct impurity striations (fig. 3). Rotational striations in the Czochralski-grown seed in the lower half and in the space grown section (upper half) off-facet striations at right and on-facet striations at left are visible. The causes for these growth discontinuties in the space grown crystal portion could not be explained in terms of existing theory. The principal investigator proposed a new concept based on kinetic supercooling which would explain the striations in space-grown InSb and also possibly certain non-rotational striations observed in crystals processed on earth.

2.3 Directional solidification of InSb-GaSb alloys: M 563

In this experiment the resolidification of concentrated InSb-GaSb polycrystalline ingots containing 10, 30, and 50 percent InSb was studied to determine the effect of microgravity solidification on the degree of single crystallinity and defects. In both space and ground tests about half of the ingot was melted back and then resolidified at a cooling rate of 0.6 °C/min. Microscopic examination of the surface morphology of corresponding sections of space and ground processed ingots of InSb-GaSb showed that both contained twin and grain boundaries, microcracks, and voids. The portion solidified in space was not bulk single crystalline.

A comparison of the distribution of twin boundaries for the 30 percent InSb ingots processed under different conditions (fig. 4) indicates that the number of twins in the Skylab samples is less than in the ground specimens after the first few mm of resolidification. Similar studies revealed that the number of grain boundaries appeared to be slightly less in the Skylab ingots than in ground samples. The number of microcracks was about the same for space and ground samples showing no systematic dependence on gravity. The investigators attribute the observed differences in defect densities between space and ground processed ingots to the effect of foreign particles at a growing interface causing nucleation of gas bubbles, twins, and grain boundaries. From microprobe composition analysis of Skylab ingots compared to those predicted by computer analysis of surface tension-driven convection, the investigators conclude that gentle Marangoni convection did occur.

2.4 Crystal growth from aqueous solutions: MA-028

The main objectives of this experiment were to grow crystals from aqueous solutions (analagous to crystal growth in gels) according to the reaction: A(soluble) + B(soluble) + ... = C (crystal) + D(soluble) + ... At low gravity, convection and sedimentation are negligible and the gel is not needed for suppressing these processes and can be replaced by a region of pure solvent. In the three reactions studied, calcium tartrate was grown from aqueous solutions of $CaCl_2$ and $NaHC_4H_4O_6$; $CaCO_3$ from solutions of $CaCl_2$ and $(NH_4)_2\ CO_3$; and PbS from $PbCl_2$ and CH_3CSNH_2. The starting solutions initially contained in separate compartments diffused towards each other in a central chamber where the reaction occurred at ambient temperature (16-24 °C) of the space craft.

The largest crystals obtained in space were calcium tartrate crystals (fig. 5) of well-formed clear and plate-like habit with dimensions up to 10 mm. The calcium carbonate experiment produced numerous clear rhombohedral crystals up to 0.5 mm edge length similar to those on earth (Fig. 6). The lead sulfide crystals were much smaller, up to 0.1 mm in size. Despite of time limitations and the lack of temperature control, the crystals obtained in microgravity appear to be at least equal in size and quality to those grown in gels on earth. These results indicate that this technique can be developed to a useful method for crystal growth from solution in space.

2.5 Melt growth and segregation in InSb: M 562

In this experiment, the resolidificaiton of partially melted cylindrical InSb single crystals, Te-doped, was studied to investigate controlled solidification and segregation behavior in space. The InSb Czochralski-grown (on earth) seed crystals contained in quartz ampoules, were melted back in space about 6 cm and subsequently resolidified at an estimated average regrowth rate of 10 μm/sec.

The external morphology of the Te-doped ($10^{18}/cm^3$) InSb crystal regrown in space (fig. 7) reveals surface ridges which apparently isolated the semiconductor melt from the

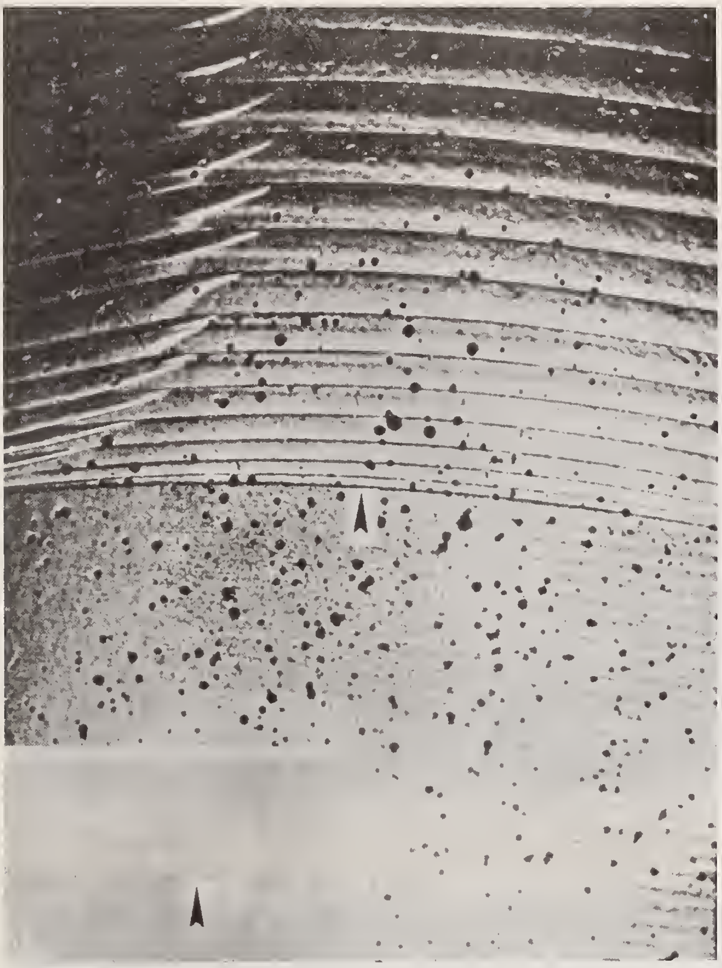

Figure 3. Etched (111)A longitudinal section of InSb(Se) single crystal (sample E3-SL4). Arrow indicates demarcation between Czochralski-grown seed at bottom with rotational striations and space-grown section. (111)B solid-liquid interface facet striations at upper left, off-facet striations at upper right. Etch pits due to In-dislocations. Magnification approximately 17X. Inset (b) Meltback interface, 125X.

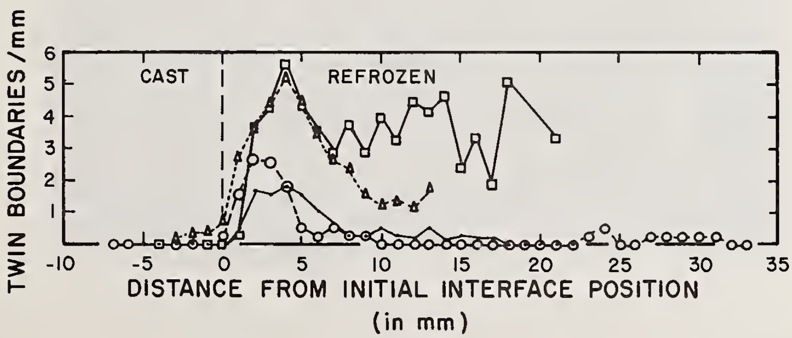

Figure 4. Distribution of twin boundaries: (Δ) vertically processed, (□) horizontally processed, (o) SL-3 processed, and (●) SL-4 processed.

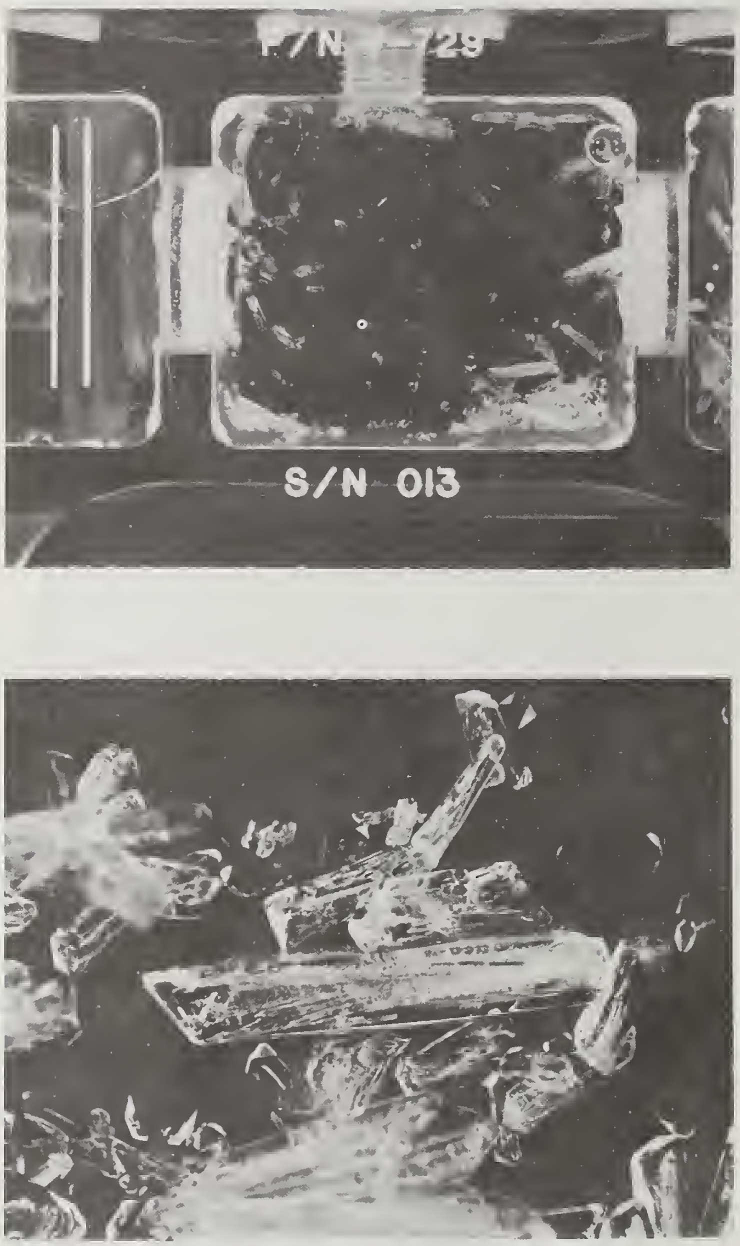

Figure 5. Calcium tartrate crystals grown from aqueous solution in space.

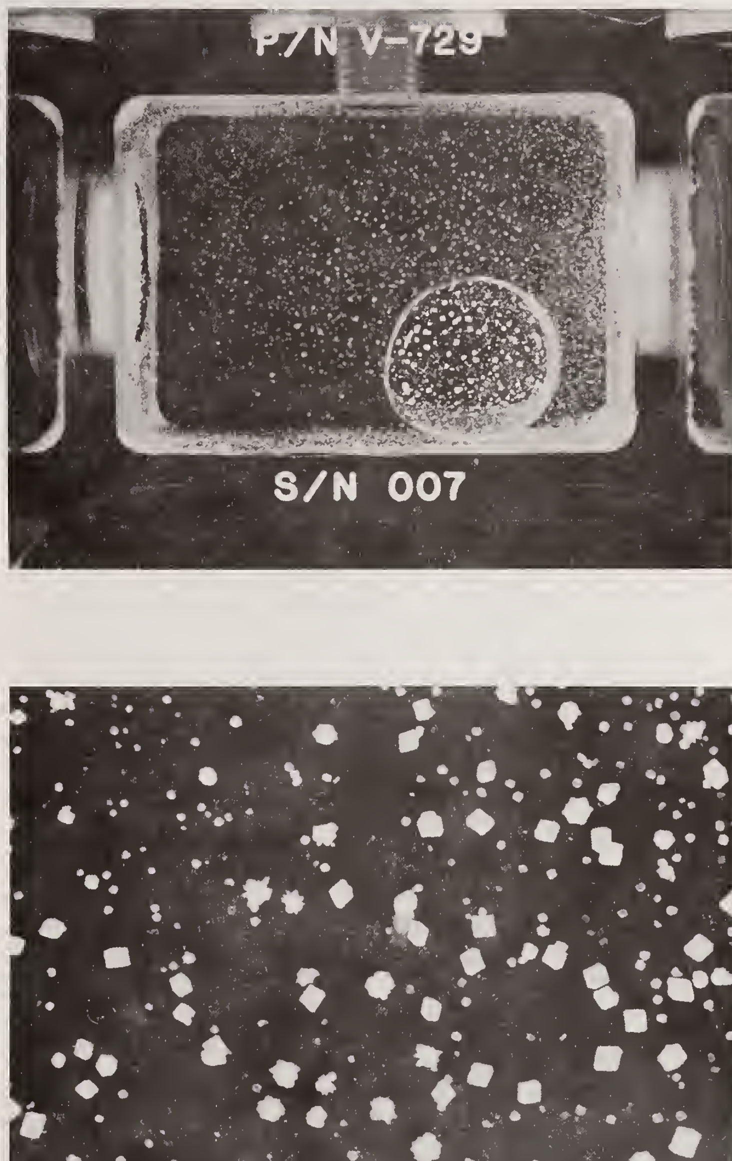

Figure 6. Calcium carbonate crystals grown from aqueous solution in space.

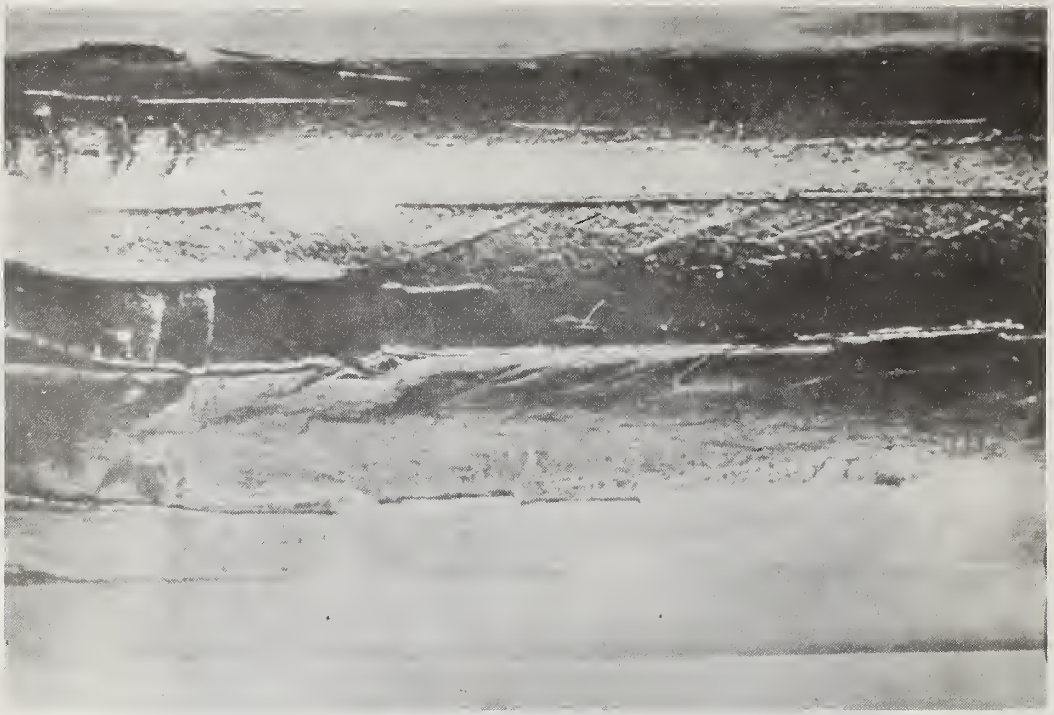

Figure 7. Surface ridges on InSb grown on Skylab.

quartz ampoule. The nature of these ridges, which were never observed on earth, is not yet explained, but it is presumed to be related to surface tension effects of the melt. The Te segregation behavior revealed by high-resolution etching (fig. 8) showed that compositional fluctuations are absent in the portion of the crystal regrown in microgravity. The earth-grown part of the crystal reveals compositional inhomogeneities due to rotation effects and uncontrolled gravity-induced thermal convection. Hall measurements of a Te-doped space grown InSb crystal show that the carrier concentration is constant after an initial transient. This indicates steady state growth and segregation with an effective distribution coefficient of unity, yielding compositional homogeneity on both the micro- and macro- scale in the absence of convective flow.

2.6 Melt growth and interface marking in Ge: MA-060

This experiment was designed to measure the effects of microgravity on the microscopic growth rate, on interface morphology, and on dopant segregation behavior. The same regrowth procedures as on Skylab were performed on Ga-doped (10^{18} atoms/cm^3) Czochralski-grown Ge single crystals. During resolidification periodic current pulses were transmitted across the crystal-melt interface which caused a brief transient in the dopant concentration pattern which can be revealed by subsequent high-resolution etching techniques.

The photomicrograph of an etched crystal segment of the Ga-doped Ge crystal (fig. 9) reveals the original seed portion (top) with pronounced compositional inhomogeneities (rotational striations). This is followed by a region of apparently uncontrolled growth and segregation (center). The faint lines in the regrown-in-space section (bottom) of the crystal of steadily increasing spacing are the deliberately introduced interface demarcation lines. The photomicrograph reveals unambiguously the absence of turbulent natural convection as well as surface-tension-driven convection in the bulk of the melt during growth in space.

The microscopic growth rates, based on the interface marking in 4 s intervals, increase rapidly from zero to about 7 μm/s during an initial transient region (fig. 10). After that, the growth rate slows down and approaches a value of about 9 μm/s after about 2 cm of growth. The growth rate behavior observed in space is virtually identical to that observed during ground-based testing under "stabilizing" vertical thermal gradients indicating the same heat transfer characteristics and predominance of conductive heat transfer. The existence of pronounced initial transient periods in the observed microscopic growth rates in space and on earth is not taken into account in presently accepted theoretical models dealing with segregation under convection-free conditions, indicating a basic deficiency in these models.

Figure 8. Te segregation behavior revealed by etching in InSb. Top portion: Seed crystal grown on earth. Bottom portion; Regrowth in space.

Figure 9. Ga segregation behavior in Ge revealed by etching. Top portion: Micro-segregation associated with growth in earth. Bottom portion: Micro-segregation associated with growth in space.

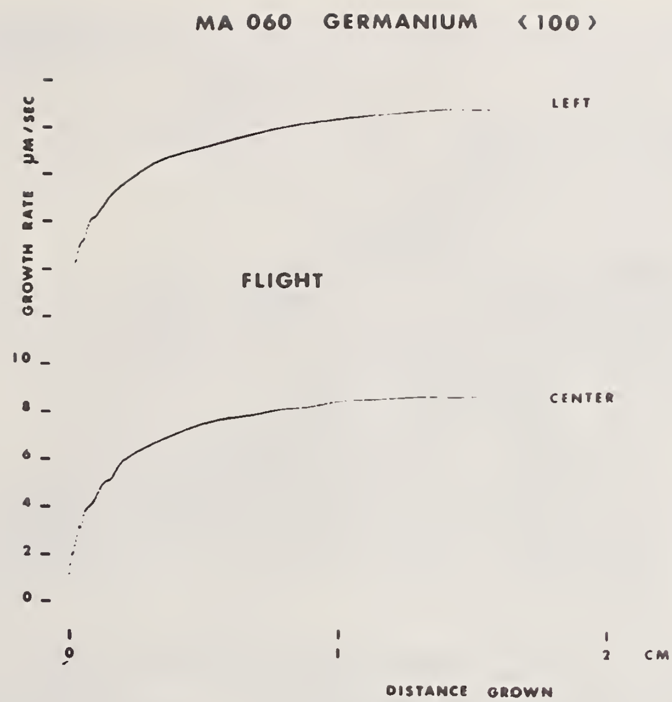

Figure 10. Microscopic growth rate of Ge crystal grown in space.

2.7 Crystal growth of GeSe and GeTe from the vapor phase: M 556

This experiment is concerned with the investigation of microgravity effects on crystal growth and transport phenomena of IV-VI compounds. In a chemical vapor transport system based on the reaction

$$A(s) + B(g) = C(g) + D(g) + \ldots,$$

the necessary concentration gradient for gas motion is based on a temperature gradient. The relative contributions of diffusive and convective flow to the overall transport process are temperature and pressure dependent. The primary objectives of Skylab experiments were to examine the crystal growth morphology and to measure absolute transport rates in the absence of gravity-driven convective interference. For this purpose, GeSe and GeTe were transported with $GeI_4(g)$ as a transport agent in evacuated closed ampoules of fused silica in a temperature gradient of 524° → 422 °C. The evaluation is based on a direct comparison of crystal morphology and transport rates observed in space and under identical conditions on earth.

Under dominant convective transport conditions on earth, dendritic growth (fig. 11, bottom) is observed with distinct curvature of individual dendrites (length up to 10 mm). In microgravity, well developed large single crystal platelets (maximum size 4 mm x 18 mm) of (001) orientation are obtained (fig. 11, top). The differences in bulk crystallinity are revealed by thermal etching of cleaved (001) faces of GeSe crystals grown at a pressure corresponding to minimum convective conditions on earth. The high etch pit density of the ground-based crystal ($\sim 10^5/cm^2$) (fig. 12, bottom) reflecting the number of dislocations is sharply contrasted by the considerably lower pit density of the space crystal ($\sim 10^3/cm^2$) (fig. 12, top) revealing the considerably improved crystallinity of the latter. The mass transport rates observed in microgravity are four to ten times greater than predicted based on diffusion limited vapor transport. The Skylab 4 mission experiments performed at different temperatures (412 °C → 346 °C) and pressures confirmed the positive effects of microgravity on crystal morphology and confirmed the greater mass transport rates in space than expected. These results are of basic scientific importance.

2.8 Vapor growth of mixed IV-VI compounds: MA-085

In the ASTP experiments, GeS and mixed compounds of GeSe-GeTe and GeS-GeSe were transported with different transport agents (GeI_4, $GeCl_4$, $GeCl_4$ + Ar) in the gradient 604° → 507 °C to determine the microhomogeneity of solid solution crystals and to further elucidate the unexpected mass tranpsort phenomena in micro-gravity.

Transmission Laue x-ray diffraction patterns of GeSe-GeTe solid solution single crystal platelets of (001) orientation (fig. 13) reveal a significant degree of strain, plastic deformation and distortion of the ground-based specimens (fig. 13, left), which is completely absent in the space-grown samples (fig. 13, right). Microprobe studies confirm the considerably improved chemical microhomogeneity of the ASTP crystals. Scanning electron photomicrographs (fig. 14) reveal significant differences in surface morphology between space (fig. 14, top) and ground (fig. 14, bottom) crystal. These are consistent with the results of chemical etching which indicate the considerably improved crystallographic bulk properties of the space-grown solid solution crystals.

The observation of significantly greater mass transport rates than predicted for microgravity confirms the trends of the Skylab experiments. These discrepancies between theory and experiment indicate that present models of vapor transport are incomplete and provide the basis for their extension.

3. Summary and Conclusions

The solution, melt, and vapor growth experiments demonstrated the favorable conditions of microgravity for crystal growth and, in some cases, for the observation of basic phenomena which could not have been observed at normal gravity. The observation of unexpected results in the melt and vapor growth experiments is of basic scientific and technological significance.

The data obtained indicate that some of the presently accepted theoretical models are incomplete. On the basis of all space experiments performed, the feasibility of space processing, in principle, has been established. The positive effects of microgravity on crystal growth have been demonstrated. The results also indicate the need for further ground-based research.

Figure 11. Condensation region of a GeSe transport ampoule. Bottom: Dendritic growth observed on earth. Top: Well developed single crystal platelets grown in space.

Figure 12. Optical photomicrographs (125 X) of thermally etched cleaved (001) faces of GeSe crystals. Bottom: Crystal grown on earth. Top: Crystal grown in space.

Figure 13. Laue x-ray diffraction transmission photographs of (001) oriented GeSe-GeTe solid solution single crystal platelets. Left: Crystal grown on earth. Right: Crystal grow in space.

Figure 14. Scanning electron photomicrographs of native faces of GeS-GeSe solid solution single crystals. Top: Crystal grown in space. Bottom: Crystal grown on earth.

DIRECT OBSERVATION OF DENDRITE REMELTING AND
MACROSEGREGATION IN LOW-GRAVITY

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The transition between the columnar and the equiaxed zone in casting has been the subject of numerous publications [1-3][1]. Theories dealing with this phenomenon have depended on gravity as the driver for fluid flow and subsequent crystal multiplication [3-4]. The only theory which is active in the absence of gravity [1] suggests that the equiaxed zone forms due to constitutional supercooling ahead of the interface.

Experiments have attempted to circumvent the gravity influence by use of magnetic fields [5], metal screens [6], or other impediments to fluid flow. None of these techniques actually eliminates the gravity force. Through the Space Processing Applications Rocket (SPAR) project, the present experiment was operated at a gravity acceleration around 10^{-5} g, a level perfectly adequate for eliminating acceleration influences on casting phenomena. The purpose of the experiment was to observe the growth of dendrites in the columnar solidification region in order to determine the influence of gravity driven flow on the formation of the equiaxed zone. In order to observe the actual solidification process in low-g, a transparent "metal-model" material was selected for this experiment.

The H_2O-NH_4Cl system has been used extensively as a metal-model material in the investigation of solidification phenomenon [7-9]. Experimentation has included such areas as growth morphology [10], growth kinetics [11], gravity segregation [12], and dendrite remelting and coarsening [13]. The observation of the remelt process during growth in the low-g environment was a primary objective of this experiment. Although several metallic systems have been solidified in space on Apollo, Skylab, and ASTP, this was the first direct observation of metallic-type solidification at low-g acceleration levels.

For all experiments, a solution of NH_4Cl was prepared by saturation at 72 °F. The resultant composition from the phase diagram [14] was 28.4 wt. percent NH_4Cl. This concentration was selected to preclude the presence of any solid NH_4Cl prior to initiation of solidification. The solution was encapsulated in a plexiglass cuvette. The cuvette was completely filled and sealed to eliminate air bubbles which, as a free surface, could become a nucleation site.

The capsule was mounted into a cuvette assembly consisting of two thermoelectric cooling units, three thermistors, and the mounting bracketry which also provided the heat sink for the thermoelectric devices. Power was supplied to the thermoelectrics by two HR5DC-7 3 volt batteries in series. The assembly was backlighted by a single tungsten filament lamp. The solidification process was photographed from the front of the cuvette with a 35 mm Nikon F2 camera. Using a motor drive unit and a 250 magazine back, it was possible to photograph a total of 240 frames at one frame per second.

A series of ground-based tests (GBT) was made in the "flight" hardware to characterize the solidification process in the one-g environment. All tests were made in a vacuum chamber with a thermally controlled shroud. The cuvette temperature versus time curve for the GBT runs and the low-g flight were comparable. The direction of the gravitational force directly affected the fluid flow in the cuvette. One-g tests were therefore made with the cuvette perpendicular (horizontal) as well as parallel (vertical) to the gravity force. Differences in temperatures for the two orientations are attributable to the thermal transfer caused by convective fluid flow.

[1]Figures in brackets indicate the literature references at the end of this paper.

During the low-g portion of the rocket flight, the entire solidification sequence occurred and was photographed. Selected photographs are shown in figures 1 and 2 of ground-based and low-gravity solidification in the same time frame.

Figure 1. Photograph of low-g solidification.

Figure 2. Photograph of one-g solidification.

Length versus time measurements of secondary dendrite arms and dendrite array "interfaces" for low-g and one-g growth were made. The first crystal to appear in the low-g solution had what appeared to be a (100) growth direction and a slow growth rate of 0.29 cm/min. Other dendrites in the low-g case, and all measured dendrites that were attached to the wall in the one-g experiment, grew at rates ranging from 0.85 to 1.0 cm/min and apparently had a (110) growth direction. Except for the initial low-g dendrite, there was no significant difference in individual dendrite growth rates between the low-g and one-g crystals; however, there was a difference in the rate of interface growth. The low-g interfaces grew at approximately 25 percent of the rate of individual dendrites. This indicates that the controlling factor on the single dendrite growth rates is the cooling rate and crystallographic direction of the system. During interface growth, the matrix depletes the surrounding solution. In the one-g experiment, there is fluid flow supplying fresh solute to the growing interface. In the low-g experiment, fluid flow does not occur, so growth is limited by diffusion in the quiescent liquid. This diffusion limited phenomenon could also be seen in the low-g experiment when an individual dendrite merged into a dendrite array. The growth rate decreased and momentarily halted.

The measured spacing of secondary and tertiary dendrite arms for both one-g and low-g crystals is shown in Table 1. The flight secondary arm spacing is greater than that of one-g material. Tertiary arm spacing is less affected by the gravitational levels. It was found, however, that the standard deviation for ground-based material ranged from 26 to 38 percent. This contrasts sharply to the deviation of only 13 to 20 percent for low-g arms. The greater deviation in one-g arm spacing is most likely a result of breakoff caused by convective fluid flow. This flow leads to an enhanced coarsening process, whereas the absence of fluid flow causes the low-g material to retain more of a fine substructure.

Table 1. Dendrite arm spacing.

	Secondary		Teritary			
	X ± σ, mm	σ, %	Side	σ, %	Center	s, %
Flight	0.102 ± .020	19.6	.034 ± .005	14.7	.044 ± .006	13.4
Vertical GBT	0.072 ± .019	26.4	.031 ± .012	38.0	.056 ± .015	26.8
Horizontal GBT	0.061 ± .020	32.3	.030 ± .009	30.0	-	-

An obvious but immeasurable difference between the one-g and low-g solidification was seen in the growth symmetry. During the early stages of one-g solidification, secondary and tertiary arms grew almost exclusively towards the wall. Growth arms towards the center were impeded by the upward flow of warm liquid.

In the low-g experiment during the rocket flight, the dendrite arms grew symmetrically, regardless of their orientation in the assembly. There was obviously no inhibiting influence such as fluid flow to disturb the crystal symmetry.

Some fragmentation or breakoff of dendrites was observed in the one-g experiments. The results of the fragmentation were apparent in the numerous crystallites being carried by the convection currents. No fragmentation was observed in the low-g samples. This supports the conclusion that there was negligible fluid flow in the low-g case.

Although necking was observed in all experiments, no actual remelting was visible. This is due to the short period of time available for the experiment. According to Kattamis, Coughlin, and Flemings [13], for dendrites with the stated arm spacings, it would take 3×10^4 minutes for secondary and 1.2×10^3 minutes for tertiary arms to melt off.

It can therefore be concluded that gravitational acceleration is the dominating influence on the zone transitions in casting structure. Without grain fragmentation and the subsequent flow of the particles into the central fluid, there is no equiaxed center zone. The obviously quiescent liquid ahead of the low-g interfaces was not conducive to secondary nucleation and growth.

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Discussion

Question (Glicksman, RPI): Will there be follow up experiments to this particular experiment?

Answer: We do have two more experiments that are flying. They are not a similar configuration to this experiment and we are following it up with some metal systems. Now the proposals did not cover going any further into follow up experiments. We did attempt to do that, but it was not agreed upon.

Question (Meijer): In the movie it was clear that the first two spots started near the wall. Do you think that is an accident?

Answer: In this particular cuvette, and it was the same cuvette in both movies, I feel that the first nuclei began actually on a flaw in the cuvette wall. We were attempting to nucleate on the walls, so it was not an accident. We wanted to come closer to stimulating castings. We were not really looking at the nucleation process itself.

THERMAL MIGRATION OF BUBBLES AND THEIR INTERACTION
WITH SOLIDIFICATION INTERFACES

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Weightless melts are expected to contain more bubbles than their terrestrial counterparts because of reduced bubble mobility and easier bubble nucleation [1][1]. The production of void free material by solidification in low gravity will therefore be more difficult unless ways are found to manage bubbles or to suppress their incorporation into the solid. This paper is a progress report on a sounding rocket experiment whose objectives are to study the interaction between solidification interfaces and bubbles and the thermal migration of bubbles in weightless melts.

A sounding rocket apparatus capable of gradient freeze solidification of low melting temperature materials has been built and flown successfully on SPAR I and SPAR III [2,3]. The progress of solidification is recorded photographically by a 35 mm camera at a rate of one frame per second and a magnification of one-half. Three specimens of gas-saturated commercial purity CBr_4, a transparent model material, were solidified on SPAR I with an initial temperature gradient of 5 °C/cm; on SPAR III the temperature gradient was increased to 20 °C/cm, and one high purity and three commercial purity specimens were processed. The appearance of the specimens shortly after the beginning of the low gravity interval is shown in figure 1 for SPAR I and figure 2 for SPAR III. In both cases, the lower, bright portion of the specimen tube is solid CBr_4 and the upper portion is the transparent liquid; all the specimens are situated in an initially linear temperature gradient with the highest temperature on top.

Inspection of the photographs shows that gas evolution occurred at the solidification interface. This continued at a roughly constant rate throughout the remaining 220 s of observation. The evolved gas was always trapped in the growing solid; in SPAR I the bubbles are trapped as roughly spherical voids, and in SPAR III the gas formed long cylindrical voids (wormholes). The beginnings of cylindrical voids can be seen in specimen C, figure 2. Comparison of the flight specimens with identically processed ground based simulation specimens shows that the gravity level (10^{-4} g vs. 1 g) had no effect on the void morphology. The high purity specimen (D, fig. 2) was an exception to this observation; it grew cylindrical voids at 1 g and spherical voids at 10^{-4} g. Other work had led us to expect that the void morphology would be a function of the growth rate, impurity concentration, and distribution coefficient [4,5,6,7]. Our results show that the void morphology is also strongly dependent on the temperature gradient at the interface, and influenced by the gravity level only in the case of the high purity specimen.

The predominant effect of the reduced gravity environment was to favor a greatly increased number and total volume of voids trapped in the crystal. This effect was documented by optical observations and by radiography. The optical observations also showed that a void nucleation burst had occurred in SPAR III at approximately t_o + 70 s. This time coincides with the establishment of low-gravity conditions in the rocket and, hence, may be indicative of a gravitational effect on nucleation, but there is also the possibility that nucleation was simply caused by impurity build-up and the timing was a coincidence.

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[1] Figures in brackets indicate literature references at the end of this paper.

Figure 1. Appearance of the specimens at 105 s after lift-off, SPAR I. The left-hand specimen is napthalene with small particles added; it was part of experiment 74-15 of MIT. The next three specimens are CBr_4 and designated A, B, and C from left to right. The width of each specimen is 7 mm.

Figure 2. Appearance of the specimens at 101 s after lift-off, SPAR III. The specimens are designated A through D from left to right. Vertical fiducial grooves in the heat leveler block are spaced 10 mm center to center.

Figures 1 and 2 show that bubbles were present in the liquid portion of all of the specimens. In SPAR I, the bubbles vary from 0.1 mm to 4 mm diameter; in SPAR III, the bubbles tend to be more uniformly sized at approximately 0.1 to 0.2 mm diameter with several larger bubbles also present. The large, 4 mm diameter bubbles in SPAR I and SPAR III were due to incomplete filling of the sample tube. They were pushed down from their original position at the top of the sample tube by rocket spin induced fluid flow. The smaller bubbles, none of which were present before launch, were nucleated by a particular vibrational frequency of the rocket motor or by the reduction in gravity (i.e., hydrostatic head) or were released by the solid CBr_4 during interface erosion by the spinning liquid. It is unlikely that interface erosion would give rise to the uniform bubble size and spatial distribution observed in SPAR III.

Continual gas evolution resulted in growth and coalescence of the bubbles situated at the solid-liquid interface in all of the SPAR I specimens and in specimen D of SPAR III. These bubbles were trapped by the growing solid without any indications of macroscopic pushing (minimum detectable motion would have been 0.2 mm). Specimens A, B, and C of SPAR III achieved a steady state equilibrium between gas evolution, interface motion and void growth such that cylindrical voids of constant diameter were found. Bubble detachment from the interface was not observed for either of the imposed temperature gradients.

No steady state thermal migration of bubbles was observed. Initial estimates based on previous work [8] suggested that bubble velocities of the order of millimeters per second should have been observed. Alternatively, Marangoni numbers of the bubbles in SPAR III are calculated (on the basis of measured values of the physical constants of CBr_4) [9] to be 3, 300, and 5000 for 0.1 mm, 1 mm, and 4 mm diameter bubbles, respectively. Pearson calculates that for a planar geometry, significant thermocapillary flow should occur for Marangoni numbers of 80 or greater [10]; however, recent experiments [11] show that significant thermocapillary flow occurs in bubbles with Marangoni numbers of the order of 10^{-4}. The most likely cause for the observed bubble immobility in our experiment is thought to be contamination of the bubble surface by impurities.

Although steady state large scale thermal migration of bubbles did not occur, significant bubble motion was observed in specimen B, SPAR III and specimen C, SPAR I. In SPAR III, the lower edge of the large bubble just visible at the top of specimen B moved downward by 1.3 mm. This motion occurred in a relatively uniform manner over a 60 s time interval. The flight film shows that the motion of the large bubble caused the small bubbles in its vicinity to be pushed along apparent streamlines of fluid flow. A similar observation was made on specimen C, SPAR I in which the abrupt coalescence of two bubbles at the solid-liquid interface caused pushing of neighboring small bubbles. These observations document an additional source of fluid flow in weightless melts, namely, fluid motion due to bubble coalescence or due to the motion of large bubbles.

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Discussion

Question (Taylor Wang, JPL): Are the temperature gradients quoted, measured values or extrapolated values?

Answer: Those are the temperature gradients that existed at launch. We have measurements on the back of the metal block of the temperature gradient during flight and those measurements show that the temperature gradient is about the same when it cools, as we expect. We have no direct measurement of the temperatures in the liquid. It is almost sure that despin causes fluid motion and causes leveling of the temperature gradient. We are fairly sure that it is not completely leveled because of the fact that we still get good specimen growth. But, we have proposed in the next flight to make an ampoule with temperature sensors inside the specimen material to determine exactly what the temperature gradient is during the experiment.

Question (Taylor Wang, JPL): Can the lack of motion of the bubbles and the lack of difference between the voids in the earth-grown and space-grown samples be explained on the basis that you are really looking at isothermal conditions?

Answer: The lack of bubble motion can be explained by no temperature gradient, definitely. The velocity is supposedly directly proportional to the temperature gradient. But, one observation that I think shows that there was a good temperature gradient left is that we still get cylindrical void morphology during flight on SPAR III, whereas if the temperature gradient had been lower, we would expect to find a spherical morphology as we have seen before with the low temperature gradient. You are right--we should have good measurements of the temperature gradient and we expect to do that in the next few months.

Question (Ostrach): What is the Marangoni number for this particular system?

Answer: I do not know. When we started the experiment we had two fluid dynamicists look into this and they are the ones who made these estimates of the velocities. These were based on the parameters for this particular system, the measured temperature dependence of the surface tension, the viscosity, etc. I am sure that the Marangoni number could be given to you rapidly by these fluid dynamicists.

Question (Glicksman, RPI): What was the resolution in the measurement of bubble pushing?

Answer: The resolution or the minimum motion that we could observe was gross. It was on the order of a few tenths of a millimeter. So it was not a fine measurement. We could not make a fine measurement, we only took the pictures at a half-x magnification.

Question: What was the minimum bubble size that could be tracked?

Answer: Well, in the second flight, the small bubbles are on the order of a tenth of a millimeter. And I could say in that particular case I could detect the motion of maybe three or four tenths of a millimeter without problem. This is not a very good limit. The shrinkage flow would give you only about two tenths of a millimeter motion. So the resolution of our measurement of bubble pushing is poor and, in fact, for large bubbles I suppose that nobody would predict that you would get bubble pushing, especially by a dendritic interface.

Question (Glicksman, RPI): Is there any evidence that there is something peculiar about the contact angle of the bubble at the interface that might preclude bubble pushing?

Answer: I am not sure I can answer that. No, I really cannot.

Question (Passaglia, NBS): It seemed as if the specimens had a very extensive mushy zone and in the mushy zone there was repetitive nucleation of new grains which would not allow pushing.

Answer: The answer to the first part is yes, the mushy zone was very extensive. We had not anticipated before we started, but this carbon tetrabromide is a very difficult material to purify. You noted that in the fourth specimen the interface was much more planar than in the other three. But the supposition that there were a lot of crystals being nucleated in the mushy zone is incorrect. When you look at the specimens in a microscope, you find that they are all columnar and that there are about 7 to 8 grains in the specimen. These are not nucleated. We have nucleation of bubbles, but we do not have nucleation of new grains, so we have a columnar growth.

SPACE PROCESSING ROCKET EXPERIMENT 74-5
SPACE SOLIDIFICATION OF Pb-Sb EUTECTIC

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A three part experiment was undertaken to try to produce an eutectic structure of Pb-Sb free of primary crystallization products by using microgravity to eliminate gravitational segregation problems. The eutectic alloy was flown on SPAR I and a hypoeutectic alloy and a hypereutectic alloy were flown on SPAR II. A large number of various types of ground-based samples were prepared at 1 g and compared both mechanically and microstructurally with the flight specimens (over 1,000 photomicrographs were taken). In addition, a number of specimens were prepared under high g conditions, (ranging from 2 g up to 1,000 g and compared microstructurally with the 1 g and microgravity specimens (80 photomicrographs).

It was found that the ground-based specimens have bracketed the SPAR flight specimens with respect to mechanical properties and that there is no classification with respect to these properties that sets the SPAR flight specimens apart from the ground-based ones. The eutectic composition in both has apparently been shifted due to supercooling at the solidification rates involved, but this shift is not clearly defined due to the presence of dual primary crystallization product. This dual primary crystallization product is the result of thermal supercooling. High gravitational fields tend to sweep the nuclei responsible for primary crystallization from the melt, resulting in radial segregation. In the microgravity solidification environment, the primary crystallization products were homogeneously dispersed. All other gravity fields produced more erratic dispersion of the lead dendrites.

AGGLOMERATION IN IMMISCIBLE LIQUIDS[1]

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1. Introduction

Materials containing liquid phase miscibility gaps are presently used in electrical contacts and bearings and show potential as magnetic materials, superconductors, and superplastic materials. These systems are attractive subjects for space research because of terrestrial problems in producing in the bulk fine structures free of macrosegregation.

These materials show the potential of property improvement through alteration of their microstructure by processing in the microgravity environment of space. A finer and more uniform structure is expected in space-processed alloys containing a miscibility gap due to the reduction of buoyancy and gravity-driven collision processes. The possibility also exists that spinodal structures may occur in these systems and may be retained after processing in the microgravity environment.

We have been conducting experiments in the Al-In binary system (fig. 1) and have concentrated our efforts on two alloys, Al-40 wt. % In and Al-70 wt. % In, both within the miscibility gap. This program is part of a more general study aimed at determining the effect of composition, thermal treatment, and gravity on the structure and properties of alloys having a miscibility gap.

Both ground-based and flight samples were processed by holding the sample at a temperature in the single phase liquid field above the miscibility gap for fifteen minutes and then rapidly cooling through the two-phase field at a rate of approximately 15 °C per second. Flight samples were processed on the SPAR II rocket in the General Purpose Rocket Furnace by premelting the alloys on the ground and holding them for the fifteen minute period before launch at 950 °C. A temperature-time curve has been constructed from data telemetered from the rocket (fig. 2) and shows the thermal history of the rocket sample during hold and cool-down. The critical flight events are listed in table 1. As may be seen from figure 2 and table 1, cooling of the sample was initiated approximately one minute after microgravity conditions were reached and solidification was completed approximately 80 seconds before the end of the microgravity period.

2. Results

Macroscopic observations conducted on the ground-based alloys showed the expected layering of the indium and aluminum-rich regions in the gravitational field; the darker appearing, heavier indium-rich liquid is positioned at the bottom of the container (fig. 3). However, the results from the flight sample were surprising, Instead of the fine,

[1] Work conducted at Battelle Columbus Laboratories Under NASA Contract No. NAS 8-31543.

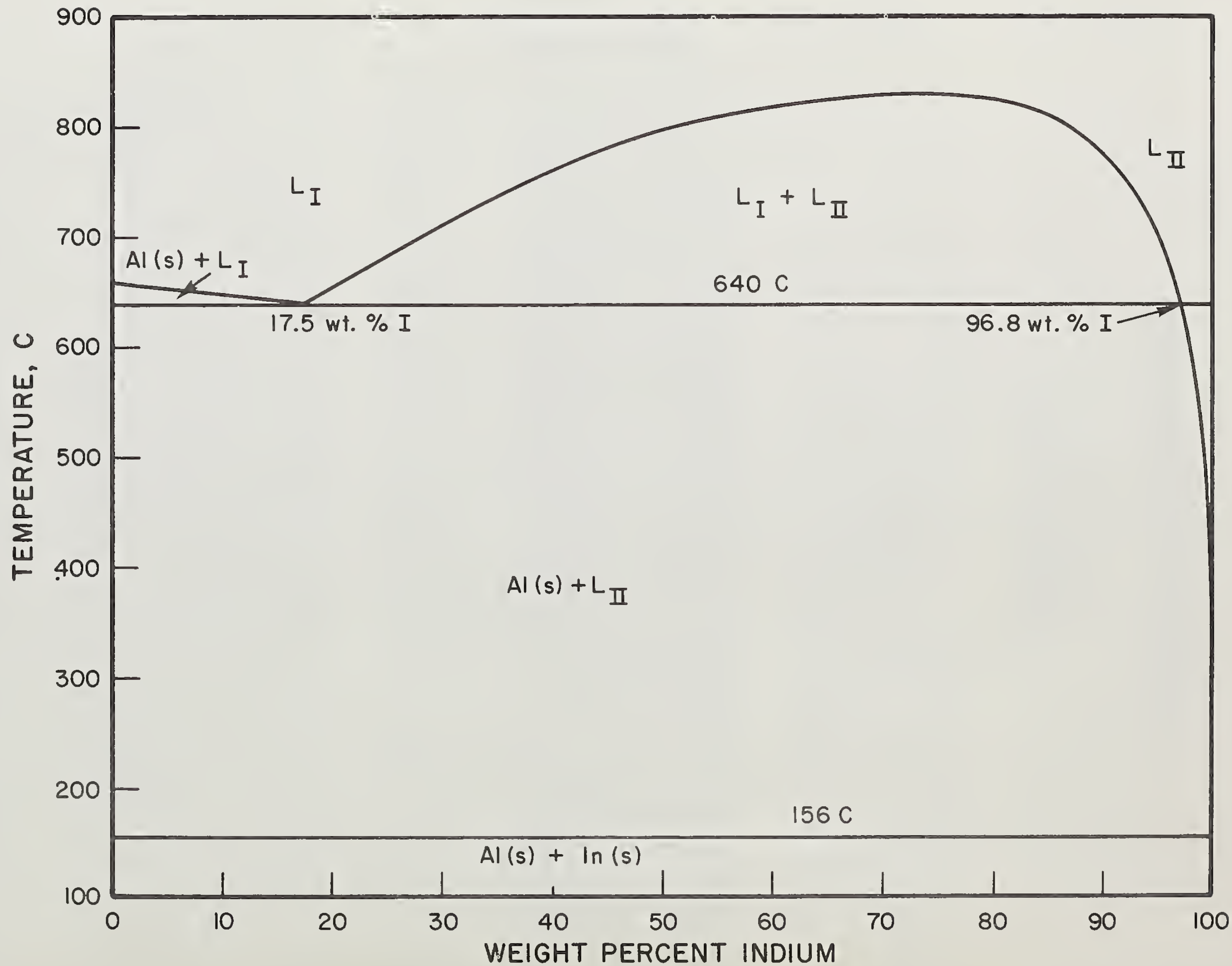


Figure 1. Aluminum-Indium equilibrium diagram[1,2].

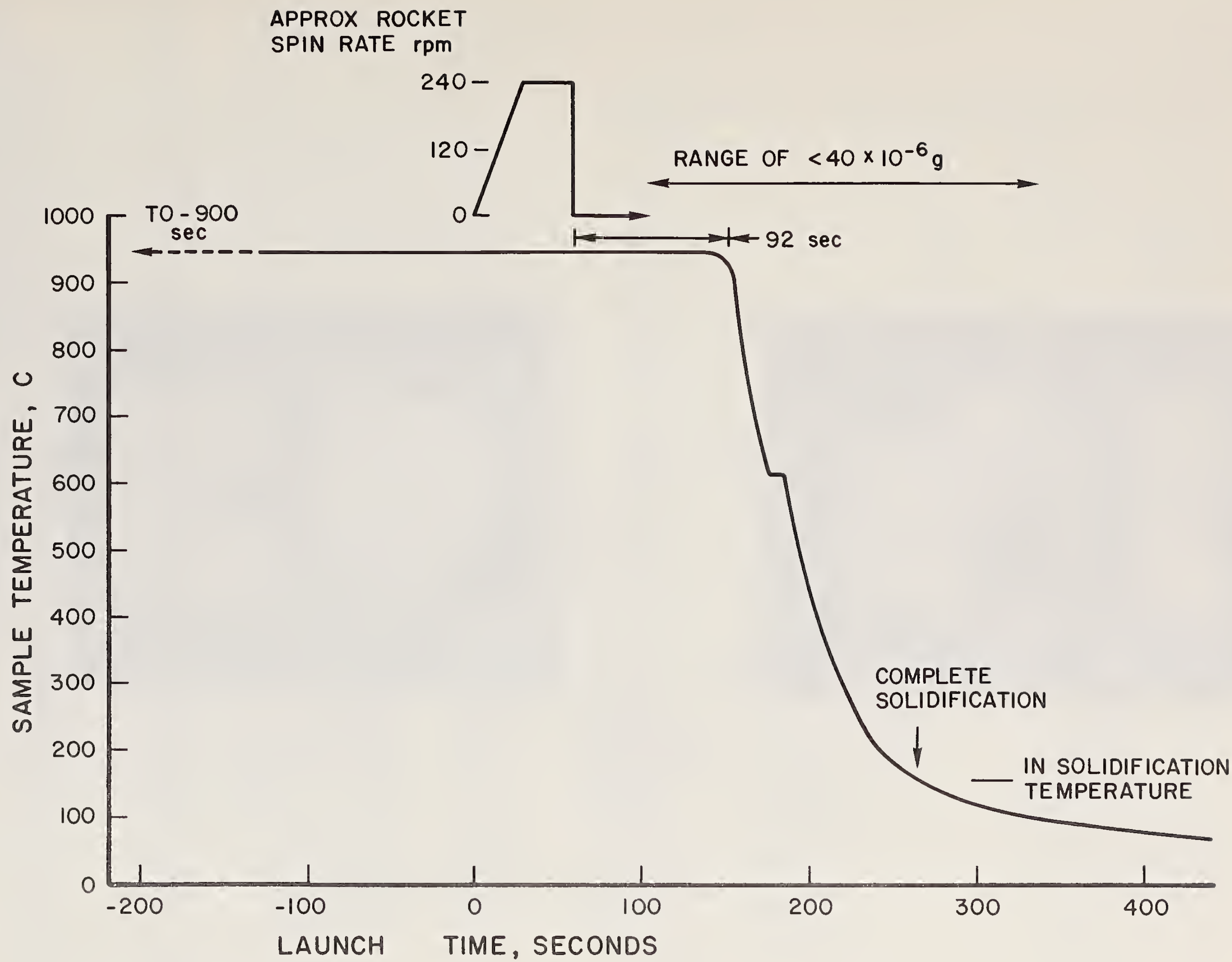


Figure 2. Thermal history SPAR II experiment 74-30.

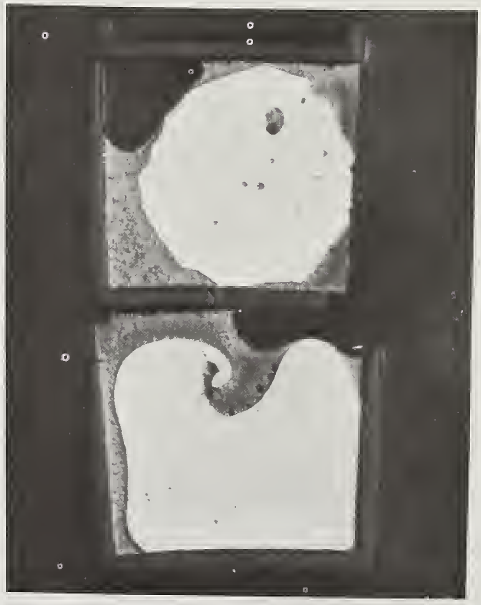
Al-70 Wt. % In

gravity

Al-40 Wt. % In

9H265 4X

Figure 3. Macroview of central polished longitudinal section of ground-based sample 74-30-18.



Al-70 Wt. % In

Al-40 Wt. % In

9H266 4X

Figure 4. Macroview of central polished longitudinal section of flight sample 74-30-21.

Table 1. Thermal history of specimen 74-30-21 and special events in the SPAR II flight.

Time, s	Sample Temperature, °C	Remarks
-900	950 (Est)	Start of preflight temperature soak
-220	949	First temperature data recorded
-200	948	
-150	952	
-100	950	
- 50	954	
- 25	953	
0	954	Launch
+ 25	954	
+ 50	943	
+ 60	-	Rocket despun, maximum acceleration 3×10^{-2} g
+ 75	947	
+ 91	-	Start of low g period; acceleration <40μ-g
+125	949	
+150	942	
+153.7	-	Start of sample cool-down
+176-+185	614	Monotectic arrest
+∿269	<155	Solidification completed
+∿348	-	End of low g period of acceleration <40μ-g

uniform macro- and microstructures expected, massive phase separation occurred (fig. 4). Both the Al-70 wt. % In and Al-40 wt. % In flight samples have structures which consist of a central aluminum-rich core surrounded by an indium-rich annular ring. The central core in the Al-70 wt. percent In alloy is roughly spherical.

The microstructure of the aluminum-rich regions of the ground-based samples consisted of indium particles within an aluminum-rich matrix. Marked segregation of the indium particles was observed in the aluminum-rich regions of both terrestrial processed alloys; larger more agglomerated droplets were found to be concentrated near the interface between the aluminum-rich and indium-rich layers. Similar segregation was found in the indium-rich layer with lower density aluminum-rich spheres floating up in the heavier indium-rich liquid and concentrating near the boundary between the layers. In addition to the aluminum-rich spheres, aluminum dendrites were also found in the indium-rich layer.

The microstructure of the aluminum-rich and indium-rich regions of the flight sample were more uniform and showed the same phases as present in the ground-based samples. The particle size range was qualitatively similar in both the flight and ground-based samples.

3. Interpretation of Results

Although the results have not been completely analyzed at this time, it is clear that the behavior of the ground-based samples was close to that anticipated, whereas the observations on the flight sample were totally unexpected.

The configuration of the flight sample is similar to those previously observed in gas-liquid mixtures held in containers at low-g. The fluid arrangements in such mixtures have been found to be dependent on the contact angle between the liquid and container walls and the amount of liquid present in the container. The geometrical configurations have been interpreted in terms of a minimization of the total surface and interfacial energies. Similarly, the configuration observed in our SPAR II experiment, i.e., an aluminum-rich spherical core surrounded by an annular indium-rich region, can be explained on the basis of surface and interfacial energies since the surace energy of the indium-rich liquid is appreciably lower than the surface energy of the aluminum-rich liquid (490 compared to 850 erg/cm^2), and the interfacial energies between the aluminum-rich and indium-rich phases is expected to be low. Moreover, calculations of Bond numbers at the microgravity level show values of 10^{-4} - 10^{-5} and thus demonstrate the importance of surface tension forces compared to acceleration forces.

In order to reach the low energy state described below, some mechanism(s) must be active to transform the structure from the anticipated uniform dispersion of droplets to the configuration ultimately observed. A number of possible mechanisms have been analyzed, some more fully than others. For example, the residual motion expected from the rocket spin-up and despin has been analyzed and found to be well damped at the time the sample is cooled. On the other hand, Marangoni convection has been shown to be a possible contributor to fluid motion; Marangoni numbers of 229 and 500 have been calculated for the Al-40 and Al-70 wt. % In alloys, respectively. Conventional convection in the extreme condition where there are regions of pure aluminum and pure indium present can lead to a fluid-flow velocity of $\sim$ 0.1 cm/sec, a somewhat marginal value.

Another possible mechanism, liquid droplet spreading on a solid surface, is judged to be possible but has not been analyzed at this time. Such spreading mechanisms have been observed in the microgravity environment and in time periods that are short compared with the duration of our experiment.

Two other mechanisms are now being analyzed:

1) heterogeneous nucleation of droplets in the vicinity of the crucible walls, and

2) the possibility that a composition gradient exists in the single phase liquid above the miscibility gap at the start of our experiment.

This latter possibility now appears to be a probability and the ramifications of its existence are presently being studied.

A second rocket experiment is now being designed to avoid some of these potential complications and to ascertain which of the fluid-flow mechanisms is active.

Discussion

Question: How certain are you that the soak period at the beginning of the experiment while still on the ground was long enough to give complete interdiffusion of the two metals?

Answer: That is a good question that we have recently done a lot of work on. When we first contemplated this experiment we knew that diffusion alone would not provide a uniform composition in the liquid phase above the miscibility gap. So we relied on the vibration of the rocket and the spin and the de-spin. We have recently taken another look at that problem and feel that it would certainly be worthwhile in future rocket experiments to increase the soak period. I have done a number of experiments at the present time mainly just depending upon convection currents--what little there might be--without the vibration and without the spin and de-spin, and found that true equilibrium has not occurred in the short time holds that we are talking about. We believe that if we did not have any convection currents induced by the rocket flight, then it would take about an hour and three quarters to get equilibrium within one percent of our anticipated end composition in the rocket sample configuration. So we are contemplating much longer time holds for the next series of flights at least to determine what effect this may have on the resulting structures.

Comment (Charles Shaffer): The soak time that was used was probably not long enough to produce a homogeneous material to start with and that perhaps some of the segregation that was observed in the resulting structure was due to the lack of homogeneity in the starting liquid.

Answer: As I say, that is a decided possibility and that is something we are looking into. I can see the effect more if you had two phases present in which you essentially have an acceleration-driven Stokes flow, so to speak. I think it is a lot more difficult to get the segregation due to the centrifugal action of the spin up and spin down when you have your atomic species essentially distributed on an atomic scale. That is why I still have a question in my mind. I think that has to be analyzed more fully, both analytically and experimentally.

Question: Would it be possible for you to use a sample that has been prepared by taking the two metals above the miscibility gap, stirring them up, and then splat cooling?

Answer: Sure that is right. That would help answer this question as well.

Question: What is the contact angle between the molten Al and the molten In and the alumina crucible?

Answer: We only have qualitative information on that. The In appears to wet the crucible quite well so we believe the contact angle is very low in that condition. With regard to the aluminum, we feel that the contact is very high as evidenced by the fact that aluminum rich spheres remain spheres in contact with the alumina crucible. This is the basis on which we predicted the equilibrium configurations, essentially the low interfacial energy material being on the outside and the high interfacial energy being on the inside.

Comment: Based on diffusion calculations, it would take very long times to reach a uniform distribution of solute.

Answer: Yes, we recognize this. Our diffusion coefficient, as well as we can find a value in the literatures, is about 8×10^{-5} cm^2/s. I have actually a series of slides showing how the composition gradient changes with time and for the configuration that we are using in the rocket experiment, we calculate about an hour and three-quarters. We have also done some experimental work on a somewhat different configuration using differental thermal analysis. We have essentially measured the miscibility gap boundary as a function of hold time above the miscibility gap and have found for that configuration that it takes about eight to nine hours to reach what appears to be an equilibrium value. Based on this calculation, we feel that our calculations and experiments agree quite well and on that basis, the hour and three-quarters that was calculated is given some validity. But this, of course, is based on essentially diffusion alone and our initial expectations were that we would have appreciable convection during the rocket take up and spin up. So this very well may not be the case, it turns out.

Question: Do you discount coalescence as a mechanism for getting the observed flight structures?

Answer: The answer to that question is no, we do not discount it. In fact it is really implicit in our assumptions that we are getting fluid flow. We believe that there would be no difference between the 1-G situation and the 0-G situation in so far as diffusional growth. The difference in 1-G and 0-G at least initially were attributed to the absence of collision-type coalescence processes that would be present in the microgravity environment.

Question: The agglomerated particles in the 1-G situation appeared to imply some diffusional growth mechanism.

Answer: We interpret that as a collision process where we have two particles of different sizes settling at different velocities that hit each other and essentially coalesce into a larger particle. That is the mechanism that we are calling upon in that case.

CONTAINERLESS PROCESSING OF BERYLLIUM

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Cast beryllium is coarse grained and, consequently, brittle. Much hot working is required to refine the grain structure of a cast beryllium ingot before the material can be used at all. This has spurred research to find a suitable grain refining agent for beryllium. One such candidate has been beryllia (BeO). In order to act as a good grain refining agent, however, the beryllia must be retained in the melt in the form of fine, dispersed particles. Beryllia particles in molten beryllium, however, agglomerate and segregate from the melt, terrestrially. This is primarily due to Stokes collisions and velocity gradient collisions. As the Stokes velocity is directly proportional to "g," the acceleration due to gravity, the rate of agglomeration and subsequent segregation of beryllia from the melt ought to be considerably reduced in the weightless environment of space. As some of the fluid motion leading to velocity gradient collisions may arise from gravity-driven natural convection, the rate of agglomeration and segregation of beryllia from the melt ought to be further reduced in the weightless environment of space. In light of these considerations, an experiment was flown on a sounding rocket, in the NASA Electromagnetic Containerless Processing Payload (ECPP), to melt and solidify a specimen of beryllium containing 1.5 percent beryllia by weight in the weightless environment of space.

The NASA ECPP is shown in figure 1. A blow-up of the levitation coil utilized to position, heat, and melt the specimen is shown in that figure. The specimen is kept centered in the levitation coil by an active servo damping system, with position sensing through a pickup coil. The field strength is varied as the specimen moves, to damp out the motion and position the specimen at the center of the coil. The heating, melting, and solidification profile is preset by the use of timers so that the sequence of events is: (1) full power applied; (2) power down; and (3) low power mode. In the low power mode, only enough power is supplied to position the specimen against the feeble accelerations encountered during the weightless period of the sounding rocket flight, so that the specimen may solidify and cool. Table I shows the sequence of events as they occurred during the experiment flight. Although one of the power amplifiers experienced a failure, this occurred after melting and although this reduced the superheat of the melt, the experiment proceeded as planned. The beryllium alloy melted and solidified was Kawecki Beryllco Industries (KBI) HIP-50, which is a high-purity, hot-isostatically-pressed beryllium alloy containing 1.5 percent BeO by weight produced from KBI powders. Due to difficulties in casting and hot working the castings, mentioned above, most beryllium alloys are presently prepared by powder metallurgy techniques. A series of ground-based reference experiments were conducted with spheroidal specimens of HIP-50 alloy, 0.922 centimeter in diameter in the General Electric breadboard facility, which is in essence, a duplicate of the flight apparatus. Then in this first sounding rocket flight, a 0.922 centimeter diameter spheroidal specimen was melted and solidified in the weightless environment of space.

Figure 2 is a macrograph of a ground-based specimen after melting and solidification. The specimen, initially spheroidal, is mounted on a tungsten-rhenium thermocouple. The electromagnetic field of the coil is sufficient to levitate the specimen, however, and after melting it takes a "equatorial bulge" dictated by the electromagnetic field, surface tension, and gravity. Because of the lifting force, good contact was not maintained with the thermocouple. However, temperature-time data was obtained using a disappearing filament pyrometer and the breadboard solid state pyrometer. When power was turned off to

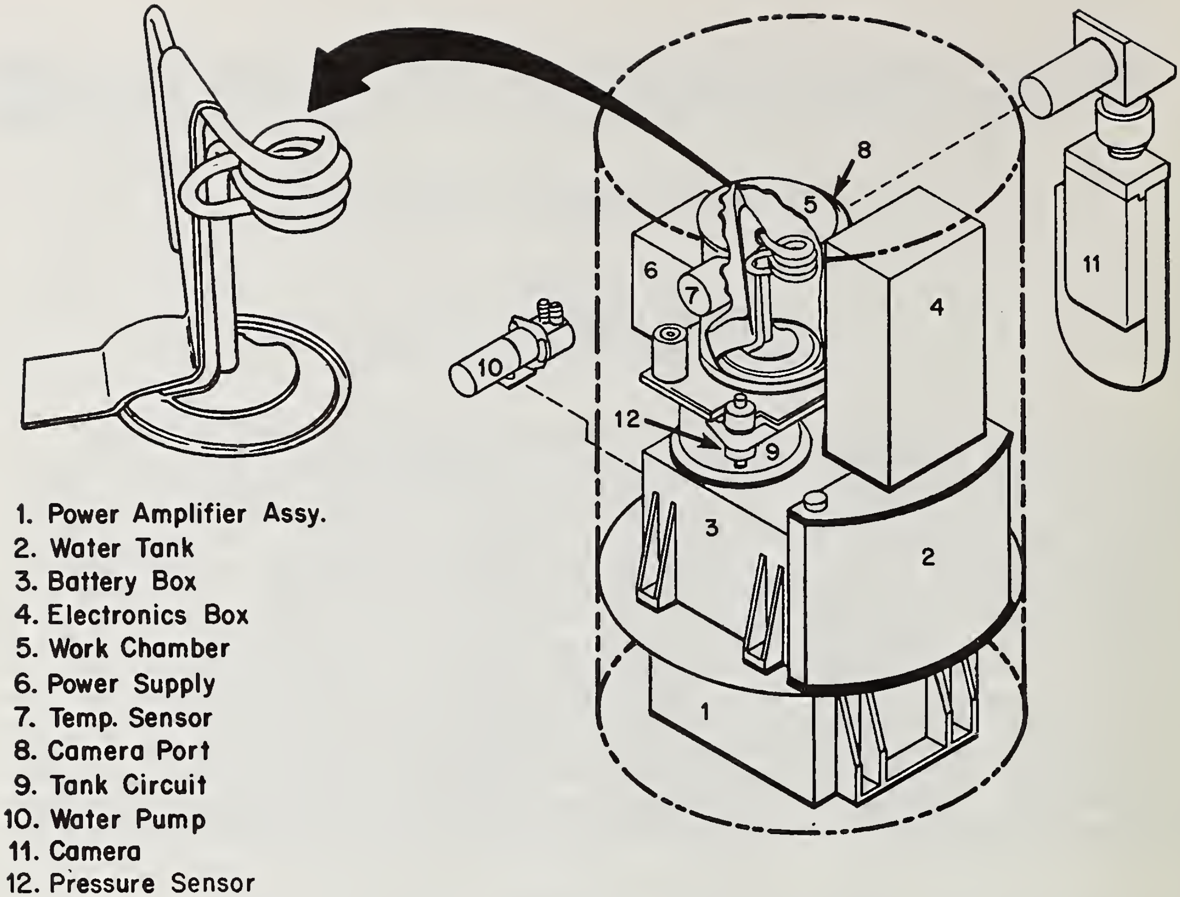

Figure 1. Electromagnetic levitation furnace.

Table 1. Sequence of events.

t	t-50.5	Event
0	0	Launch signal
50.5	0	Power on, specimen oscillations noted
85.9	35.4	First reading from solid state pyrometer
94	43.5	Solid state pyrometer reaches asymptotic reading nearly in saturation
121.3	70.8	Shape oscillation signal, completion of melting
139.4	88.9	Power reduction signal (33%), battery voltage increase
159.7	109.2	Initiation of low powdered positioning mode
169	118.5	Attainment of low powered mode
261	210.5	Loss of telemetry signals

Figure 2. Specimen macrograph - ground based.

Figure 3. Macrograph flight specimen.

let the specimen solidify, it retained the "equatorial bulge" shape due to formation of a stiff oxide layer. Figure 3 is a macrograph of the flight specimen. It has a more pronounced "equatorial bulge" due to the absence of gravity and retained this shape in the power down and low power mode because of the development of a stiff oxide layer.

A detailed study of the distribution of beryllia particles was performed by scanning electron microscopy. Differences between the ground-based reference experiment specimens and the flight specimen were evident. The ground-based specimens showed considerable agglomeration and segregation of beryllia. The flight specimen showed a much more uniform distribution of beryllia particles and no region of the flight specimen was either heavily agglomerated or devoid of beryllia, as were the ground-based reference specimens. Detailed study of the percent oxide in different regions of the ground-based reference specimen and the flight specimen were performed on 1000X and 3000X SEM micrographs by Quantimet Analysis. The normalized results are shown in figures 4 and 5. It is evident that the ground-based specimens have regions devoid of beryllia (<0.1 percent) and regions heavily agglomerated while no such regions are present in the flight specimen.

The grain size in both the ground-based and flight specimens was large (>150 microns average). Thus, even in the flight specimen, where the beryllia distribution was more uniform, the beryllia did not apparently act as a grain refiner. A possible explanation for this is spherodization of the beryllia particles, either during the hot isostatic pressing process or during the molten phase. Consequently, subsequent experiments should seek to start with non-spherodized particles and dwell for a much shorter time in the molten state.

let the specimen solidify, it retained the "equatorial bulge" shape due to formation of a stiff oxide layer. Figure 3 is a macrograph of the flight specimen. It has a more pronounced "equatorial bulge" due to the absence of gravity and retained this shape in the power down and low power mode because of the development of a stiff oxide layer.

A detailed study of the distribution of beryllia particles was performed by scanning electron microscopy. Differences between the ground-based reference experiment specimens and the flight specimen were evident. The ground-based specimens showed considerable agglomeration and segregation of beryllia. The flight specimen showed a much more uniform distribution of beryllia particles and no region of the flight specimen was either heavily agglomerated or devoid of beryllia, as were the ground-based reference specimens. Detailed study of the percent oxide in different regions of the ground-based reference specimen and the flight specimen were performed on 1000X and 3000X SEM micrographs by Quantimet Analysis. The normalized results are shown in figures 4 and 5. It is evident that the ground-based specimens have regions devoid of beryllia (<0.1 percent) and regions heavily agglomerated while no such regions are present in the flight specimen.

The grain size in both the ground-based and flight specimens was large (>150 microns average). Thus, even in the flight specimen, where the beryllia distribution was more uniform, the beryllia did not apparently act as a grain refiner. A possible explanation for this is spherodization of the beryllia particles, either during the hot isostatic pressing process or during the molten phase. Consequently, subsequent experiments should seek to start with non-spherodized particles and dwell for a much shorter time in the molten state.

Comparison of the cooling curve obtained during the flight with theoretical calculations, using known thermodynamic data such as the specific heat, latent heat of fusion, and thermal conductivity of beryllium has shown reasonable agreement in solidification time as calculated and experimentally obtained. The calculated time for solidification was 31 seconds and the observed time was 28 + 5, -0 seconds. Such analysis has led to better understanding of how to interpret temperature-time profiles to obtain thermodynamic data in future experiments.

Insofar as the results of one experiment can be discussed, this experiment has shown that it is possible to obtain more uniform dispersions of beryllia in cast beryllium than have ever been attained to our knowledge terrestrially. A new material has, apparently, thus been prepared, which cannot be prepared terrestrially. Attaining this goal, however, did not result in grain refinement of the berylliym. Consequently, it is necessary to continue this research to understand whether or not beryllia is a grain refining agent for beryllium.

This experiment was jointly performed by the General Electric Company and Kawecki Beryllo Industries. The work was sponsored by NASA, Marshall Space Flight Center, and the contract monitor was Mr. Fred Reeves. Scanning electron microscopy was performed by Dr. V. Damiano of the Franklin Institute Research Laboratories, and Quantimet Analysis by Structure Probe, Inc.

Discussion

Question (Ronald, RCA): Is there any difference in the ductility that was observed because of the distribution of BeO?

Answer: As you know there is a size effect in materials when you test them in tension. The specimens that we produced are of the order of nine-tenths of a centimeter in diameter and are quite coarse grained. If we were to test them against a standard ASTM specimen which is something of the order of two inches long, we would expect to get a very different result. In fact, we might expect to see an improvement in ductility because of the brittle size effect. Now we did do some microhardness testing, but the microhardness is on a single grain, the results are not very different between the initial specimen of beryllium and between the end specimen of beryllium. Now that really does not say much, because there is one fact that we do know. We do know that we have a better dispersion of beryllia in this cast material than had been obtained with cast material previously. We

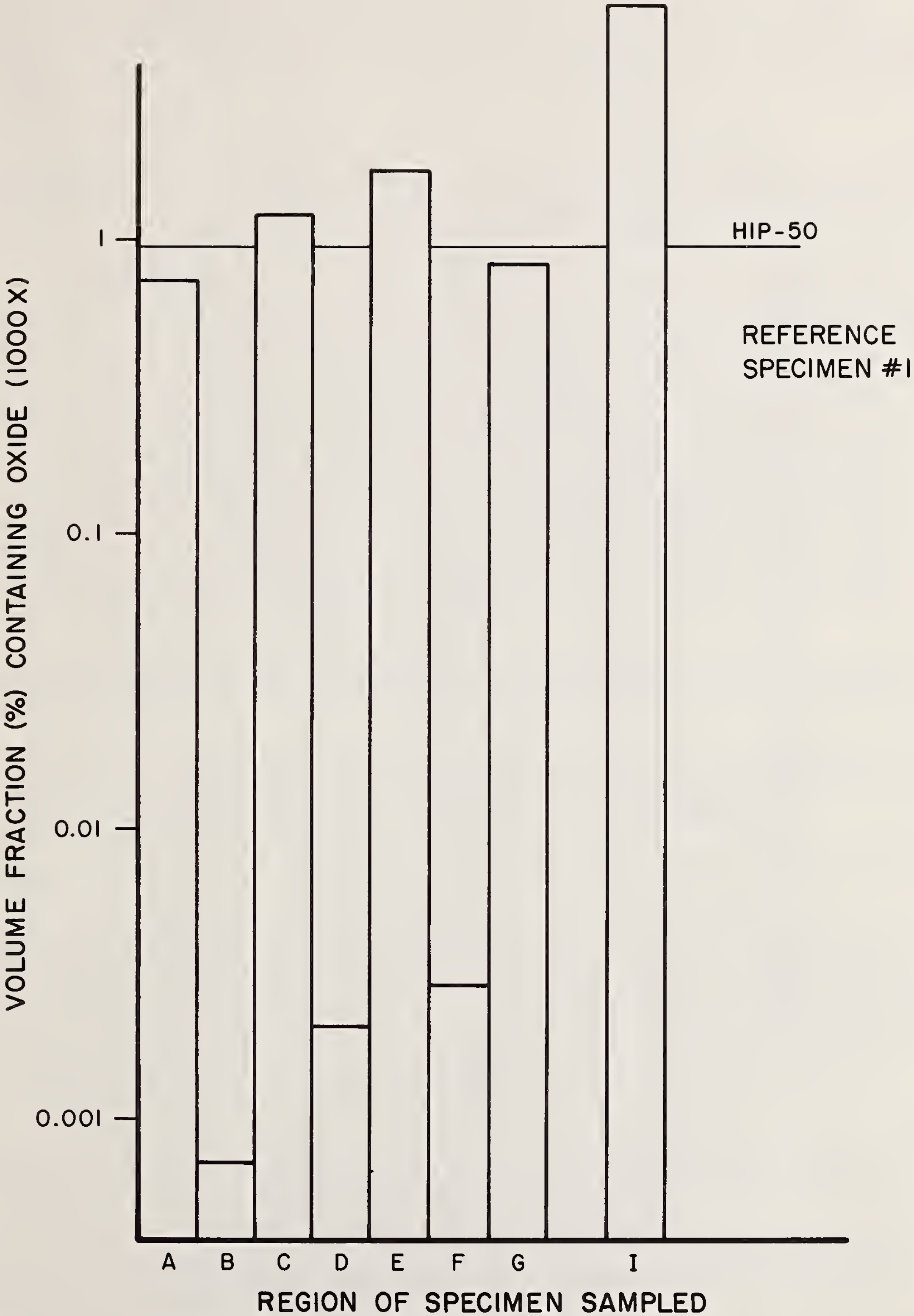

Figure 4. Normalized results.

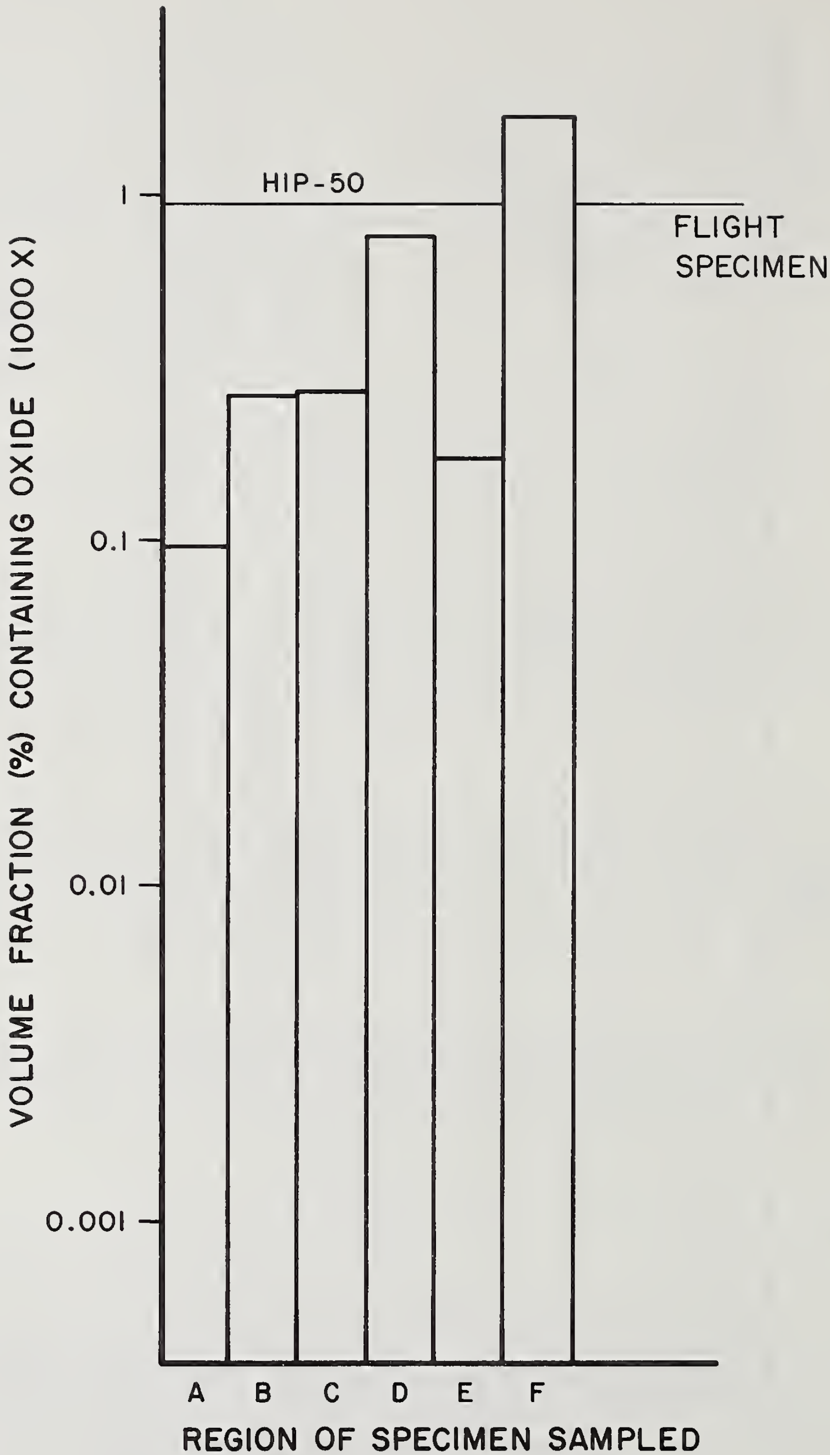

Figure 5. Normalized.

really should not be comparing the powder metallurgy material with the cast beryllium material. The fact that we do have a better dispersion in the material means that we should indeed have better elevated temperature properties. We should have better creep resistance because we have dispersion-hardened it. So I think the next step is perhaps cutting out a single grain and doing some tensile testing of the kind Dr. Pond did at room temperature and at elevated temperatures to see how this material behaves. That would be our next step.

Question (Gelles): What about stirring of the melt by the electromagnetic pulses and the relative amounts on the 1-g samples and on the micro-g samples? The reason I am asking is that we have melted some powder metallurgy beryllium on the ground and have found that the network was retained in our ground-based sample. Do you have an explanation for this?

Answer: The amount of stirring in the ground-based experiment and the flight experiment were identical because the apparatus we used was the same. There was no difference in the field strength, The field strengths that we used in the flight experiment were sufficient to almost levitate the specimen, and that is why it takes the shape that you saw with the ground-based reference specimen. So the amount of stirring that was put in was identical. Pertaining to the retained oxide network, you have to remember that what we were looking at there was a scanning electron micrograph, and that the metallographs that I showed you were at a hundred X. Now comparing the metallographs that you have at 50 X with the metallographs at 100X, one finds that there is enough of a peppery distribution so that there was oxide that was retained in the grains. A very interesting thing was before we went to the ground based reference experiment, we did furnance experiments, and in all cases we found there was indeed some oxide that is retained in the beryllium. There was a definite settling effect that was observed because of the long molten dwell times that occurred during the furnace experiments. The settling effect is not so evident in the ground based reference experiment where the specimen is almost levitated. Instead what you see is an agglomeration and a gross separation.

Comment (Gelles): Let me correct something. We have looked at our specimen in a transmission electron microscope. We have looked at the network at high magnifications as well as low magnifications.

Answer: Right, and you would see some retained oxide, even as we did in the SEM micrographs that we have. Even in the cleared out regions there is some retained oxide. In the non-agglomerated regions. There is a definite oxide network that is retained. In the very grossly agglomerated regions there is almost a solid coverage of oxide.

Question (Glicksman): In your analysis of the solidification behavior, did you solve your Stefan analysis using radiation boundary conditions in addition to convection?

Answer: Yes, the model that I am using is essentially one that is a Goodly, Cater model which takes into account radiation and convection conduction boundary conditions at the surface. Essentially, this is a Stefan problem where we are looking at conduction of the heat through the solid to the boundary where it is then lost, the liquid inside remaining isothermal at the liquid temperatures so that there is no heat flow into the liquid but only away from the liquid. Now, of course, in a highly super cooled situation this would not be the case. You would have initially a gradient flowing into the liquid and away from the liquid which in time would straighten out.

Question: You said essentially that your earth ground-based experiment used field strengths almost identical to the field strengths which you use in the space experiment. So in ground based experiments you also can levitate the samples with the field strengths you apply in space?

Answer: Yes, the specimens were partially levitated. In fact, I have not talked about the thermocouple data because the specimen is being levitated and did not make good contact with the thermocouple.

Question: Even in the flight specimen, there is a large region which has a heavier oxide than in the darker region. How do you explain that?

Answer: We have to remember that, first of all, we have not completely eliminated gravity in the weightless environment of space. We do have some gravity present even though we are in a microgravity regime. Another thing is the velocity gradient collision effect which comes into play. I think what we have shown here is not that we did not have some agglomeration but what we have shown here is that the Stokes settling mechanism is considerably reduced and this seems to be the driving mechanisms terrestrially for obtaining the large amounts of agglomeration. Otherwise, if the velocity collision mechanism was the more important, we would expect to see the same amounts of agglomeration in the weightless environment as we did on the ground-base experiment, and we did not see this.

Question: Did you correlate the positions of the heavily agglomerated regions with what one would expect from the Stokes pattern?

Answer: At the present time, I have not done that.

Question: Stokes settling is not very effective for particles below about a micron. What is the Stokes velocity for the size distribution you have?

Answer: What we find is that there is a distribution of particles that ranges from a third of a micron or less all the way up to two microns or better. We did some calculations on the agglomeration times that would occur as a result of splitting up the distribution into two parts; one with particles on the order of two-five microns in size, the other one with particles on the order of one-half of a micron or less. We find that the agglomeration time is on the order of a minute. Now, as for the correlation of the pattern, these results are, of course, still being analyzed, and I think that is a valid thing to do.

IMPLICATIONS OF METAL FOAM EXPERIMENTS FOR FLUID FLOW EFFECTS ON MATERIALS SYSTEMS PROCESSED IN ZERO GRAVITY

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Experiments to produce metal foams in space indicate that fluid flow of the molten matrix, driven by volume changes in the specimen's gas phase regions, were very influential in determining the structure of the solidified foam. These observations may imply that similar fluid flow phenomena, perhaps driven by phase transformation volume changes are important in determining the solidified structure in other zero-gravity processed materials systems.

Metal foam formation from sputtered deposits was demonstrated in one-gravity experiments and in zero-gravity environments on the SPAR program. Very uniform cell-size foams were produced in one-gravity in one series of experiments, possibly because a very thick oxide scale was allowed to form, thus providing uniform constraints to the samples. Bubble coarsening was observed in these samples with increasing time above the melting point. In other one-gravity experiments and in all zero-gravity experiments, the oxide scales fractured during expansion of the foam, providing nonuniform sample constraint and allowing localized fluid flow. In the thickest samples foamed in zero-gravity, much more bubble coarsening and a larger void volume fraction were observed with increasing time above the melting point. The effects of the oxide scale were still quite pronounced and kinetic information on foam formation behavior was not obtained. This behavior is viewed as an example of a relatively common phenomenon in which zero-gravity segregation in two-phase structures (l + l, l + s, or l + g) does not proceed in the manner predicted. Agglomeration of small second-phase regions into much larger regions, or the occurrence of a large region depleted in the second phase clouds results and precludes obtaining the fine and uniform dispersions usually sought.

These phenomena have been attributed to many mechanisms, most of which imply fluid flow but none of which predict the formation of large regions of segregation, particularly in the interior of the samples. It is suggested that laminar flow occurs in these samples and second-phase agglomeration or depletion occurs along flow lines, i.e., where fluid slip or shear or relative transport occurs. The appearance of solidified microstructures obtained in many recent space and ground-based experiments bears out this suggestion.

If it is assumed that fluid flow is the principal source of nonuniform segregation phenomena in zero gravity, then the driving forces for this fluid flow should be identified so that they may be either eliminated or so that experiments can be designed to produce equivalent flow in all directions, i.e., so that fluid flow is not produced along defined lines and that only massive uniform contraction or expansion is observed.

Some of the sources of fluid flow suggested by others have included: 1) residual forces from launch or rocket despin; 2) low gravity conventional convection; 3) interfacial energy and capillary effects, Marangoni effects; 4) thermal diffusion; 5) thermoacoustic effects; and 6) solute rejection at a solidification front. Another possibility is that fluid flow is driven by the relative volume changes of the two (or more) phases present on solidification. This source, taken together with the assumption of segregation along flow lines, has a signficiant implication for space processing since phase-change driven volume changes do not depend in any way on gravity and are true materials properties. These volume changes, except in the gaseous state, are nearly irresistable (small dependence on pressure) and effectively depend only on temperature. Therefore, these changes would be expected to result in fluid flow if there is any nonuniform constraint on the sample. It is further noted that any density change in a materials system is coincident with a volume change, and the volume change would be expected to produce fluid flow independent of the influence of gravity through density gradients. Flow velocity and the extent of flow would be expected to depend on the phase changes taking place, rate of temperature change (phase transformation), sample constraints, viscosity, wall reactions, etc.

Discussion

Question: What were the differences between low gravity process samples and one-gravity process samples?

Answer: The answer is really that, in general, there were not differences. In the case where there was an extensive adherent oxide film, which was a one-gravity case, there was a uniform constraint provided for the samples. There was no possibility for a localized fluid flow and the foam structure that was obtained was very uniform. In all other cases, one-gravity and zero-gravity, there was a fractured restraining oxide layer that did permit localized fluid flow and did provide the coalescence and behavior that was observed or demonstrated here. So I guess the distinction that came out in this series of experiments really was not one between gravity and zero gravity, it was between restrained or uniformly restrained flow and non-uniformly restrained flow. That really masked any effects of the absence or the presence of gravity. I think the same sort of thing has happened in some other experiments, too.

The Future; Panel Discussions

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As Shirleigh Silverman said yesterday morning, we structured this conference to review the accomplishments made to date in the space processing program, and to look at the future. Yesterday was devoted to the review; today will be devoted to the future.

We have structured the bulk of the day around two panel discussions. The two panels will approach the subject, which is the application of space flight to materials science and technology, in different ways. One panel is organized by materials, while the second is organized by discipline. Thus, while both are discussing the same topic, each will be viewing it from a different perspective, and hence, will very likely see it in a different light.

Now, while we have distinguished participants on each of the panels, our intention is not to have a set of tutorial lectures or a discussion among the panel members. Our intention is to have audience participation, stimulated by the remarks of the panel members. You heard Dr. Naugle yesterday morning; NASA wants to do what the scientific community wants, and we should take this opportunity to make this known, and give NASA our feeling on what this program can accomplish. In that light, let me say a few words about the subject--namely, the application of space flight to materials science and technology. You will notice that the words "space processing" are not in this subject. This was quite deliberate. We do not want to be bound by the different and restrictive interpretations of that term. We want an expression of the different views of this community on how space flight can make a contribution to materials science and technology, whether it be in basic science, applied science, processing, manufacture, or anything else. We will not achieve consensus, nor should we take it as our object to achieve consensus. This may be a task for Dr. Slichter's committee, but not for us. Perhaps, however, we take as a more modest goal that of helping them reach a consensus.

Before we begin the panel discussions, however, we have to recognize that we can only do experiments within the context of the experimental capabilities anticipated on the shuttle. For that reason, we begin with a paper entitled, "Experimental Capabilities on the Shuttle." This will be presented by Robert Adams of MSFC.

MATERIALS PROCESSING IN SPACE EXPERIMENTAL CAPABILITIES IN THE SPACE SHUTTLE/SPACELAB

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1. Introduction

Space processing of materials provides the potential for achieving significant scientific results and the development of specific useful materials and products. In order to ascertain the value of space processing to the materials community, NASA has underway a program to investigate materials processing that will include experiments performed on early flights of the Space Shuttle and Spacelab. To accomplish these investigations, NASA's Office of Applications has requested that MSFC define and proceed towards implementing a program that provides for the early attainment of space processing experimentation objectives. Obviously, implementation of such an ambitious program will require a significant amount of project definition and planning effort. This is especially true when we consider the essential role of the scientific community in not only the definition phase but the design and development phases as well. We cannot successfully attain our objective unless we continually communicate with both the materials and scientific communities to ascertain their needs, respond to their requirements, and to outline the direction of our current plans. This latter factor encompasses the primary objective for today's presentation, namely, delineation of the plans for, and a description of, the experimental capabilities of the Space Shuttle/Spacelab to accomplish materials processing experimentation.

2. Space Processing Planning

Program definition for materials space processing experiments must be responsive to the needs of the scientific community consistent with the capabilities of the Shuttle Transportation System and the guidelines and constraints imposed by agency schedules, budgets, and objectives.

Preliminary scientific requirements have been identified through Space Shuttle Payload Planning Working Groups (1972-73) and through contracts with 40 scientists. In 1975-76, these scientist contracts resulted in the identification of, and preliminary requirements for, 78 "typical" experiments.

In response to these "scientific" requirements, preliminary payload system requirements were developed through various working group meetings and contracted studies undertaken by TRW, Bendix, GE, and McDonnell Douglas Astronautics Company - East during the 1972-1976 time frame. Definition effort has progressed to the point where detailed payload specifications have been delineated (GE and TRW) as well as payload systems support requirements (MDAC-EAST).

Considering the established preliminary payload system requirements, experiment implementation will vary according to the nature of the payload. For example, the Spacelab module (fig. 1) appears to be the best vehicle for investigating biomedical processing and fluids phenomena, because pressurization simplifies fluid system design and the moderate (1-2 KW) power and heat rejection required for these experiments can be accommodated. However, the 3-4 KW of power and heat rejection required by solidification research could be better accommodated on a cargo bay pallet as a secondary objective of a satellite deployment mission (fig. 2).

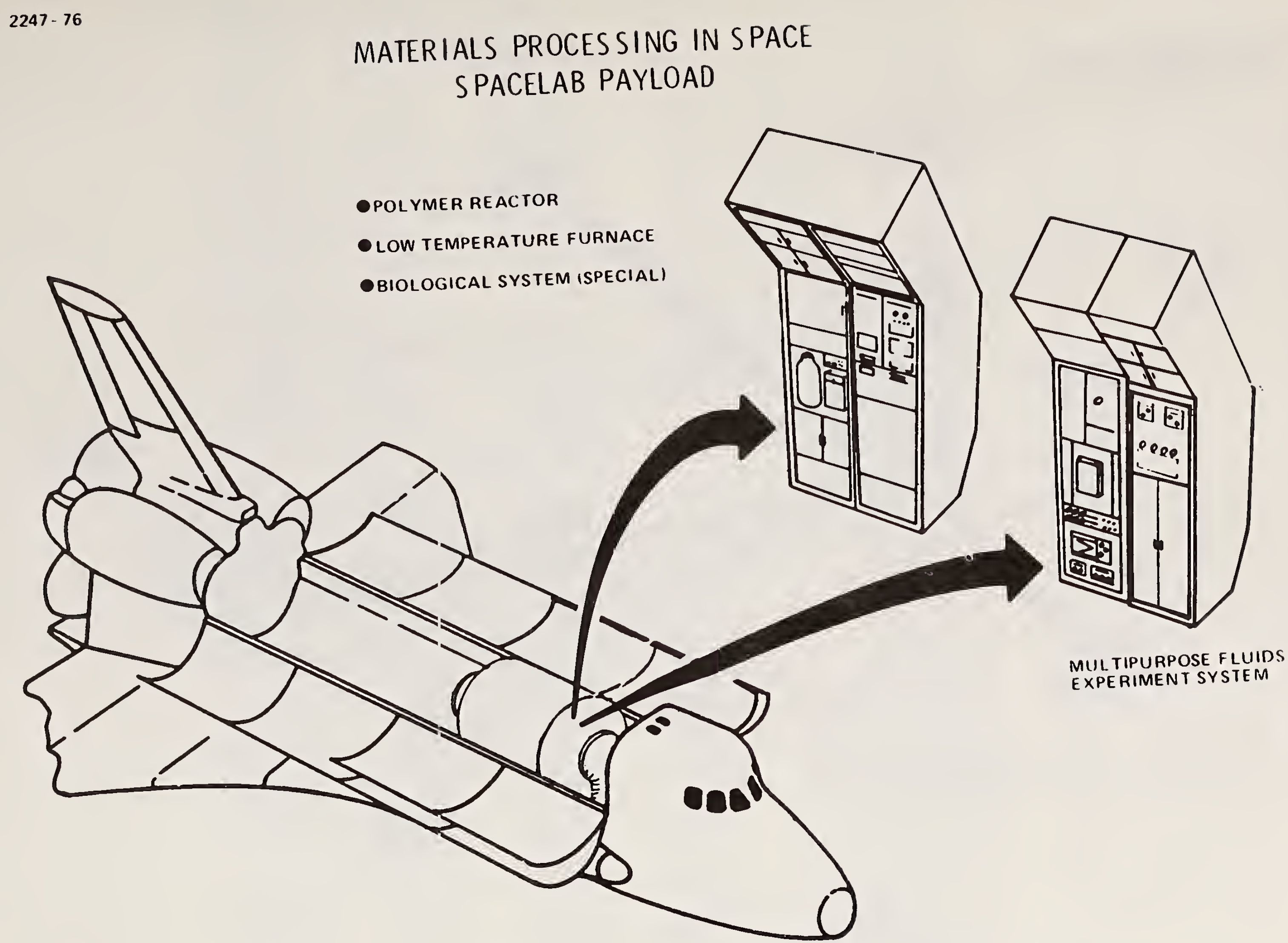

Figure 1. Space Processing Applications Spacelab Payload (Biomedical Processing and Fluid System).

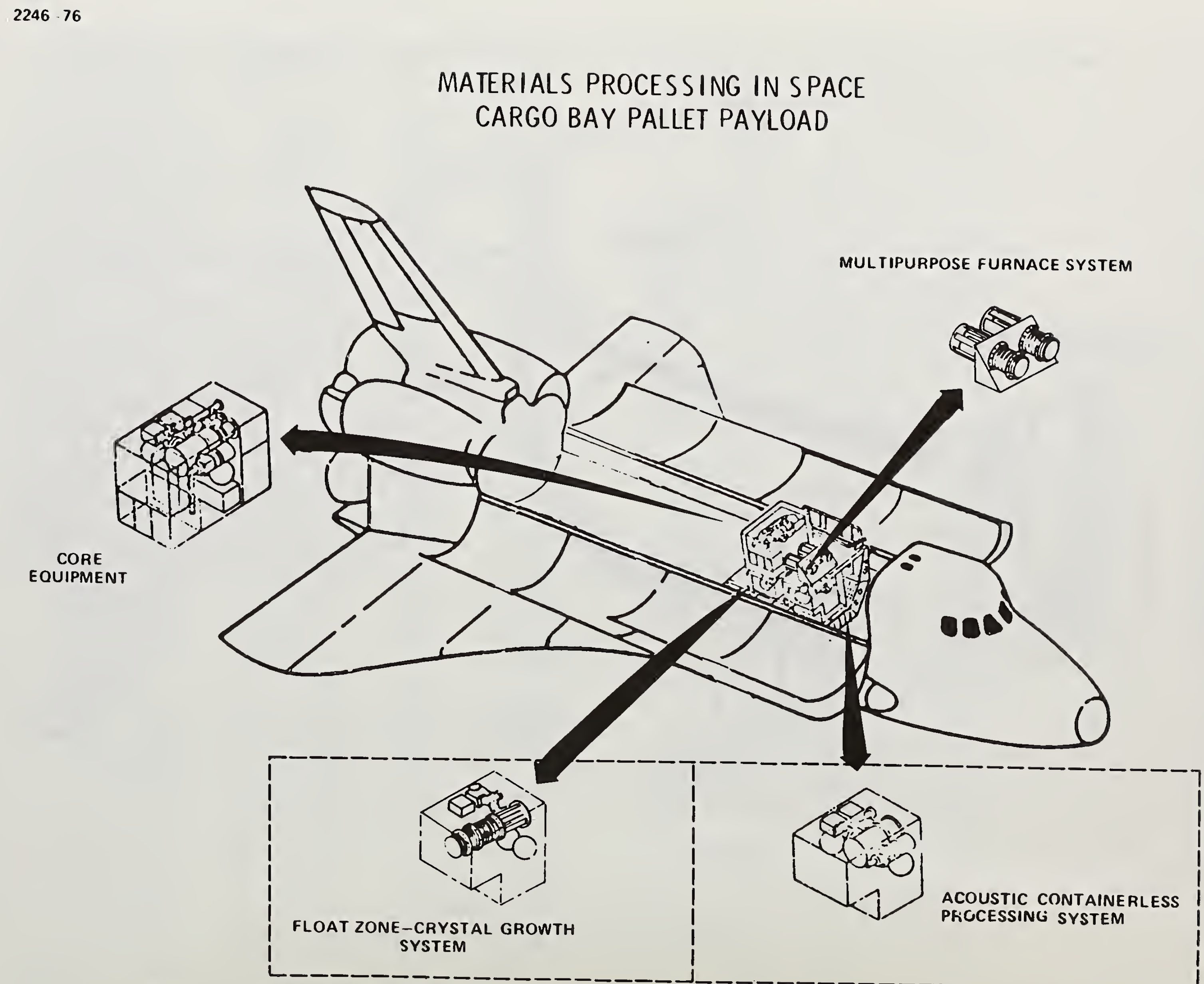

Figure 2. Space Processing Applications Cargo Bay Pallet Payload (Solidification Systems).

In each of the major areas of interest we have established scientific contacts at MSFC that are now in the process of specifying preliminary payload systems requirements or are cognizant over existing experiment systems. These contacts and their areas of expertise are given in Table 1.

Table 1. MSFC Scientific Contacts for Experiment Systems

Continous Flow Electrophoresis ASTP Static Column Electrophoresis	Dr. R. S. Snyder - Ph. No. 453-3535
Multipurpose Fluid Phenomena	Dr. R. L. Kroes - Ph. No. 453-0943
Multipurpose Furnace Float Zone Refining/Crystal Growth Furnace	Dr. M. C. Davidson - Ph. No. 453-3090
Spar Electromagnetic Containerless Process Spar Acoustic Containerless Process	Mr. L. H. Berge - Ph. No. 453-3538

The preliminary payload planning for the incorporation of these experiments has been completed. As previously described, fluid phenomena and electrophoresis experiments will be in the Spacelab. An example of our planning effort to date is presented in Table 2 which lists preliminary description/features and performance parameters of the continuous flow electrophoresis system. The electrophoresis experiments show great promise in extending our ability to separate biological substances which cannot be readily separated by ground processes. We anticipate these experiments will increase our knowledge of the separation phenomena and may be the basis for wide range biomedical processing applications in space. The continuous flow electrophoresis system will be a new development while the static column unit will be the ASTP design with minor modifications.

Solidification research experiments show great potential to develop a large number of unique materials processed in the space environment. These experiments will be pallet mounted and both the multipurpose furnace system and float zone crystal growth system will be new developments. The levitation systems are SPAR hardware, which could possibly be automated.

Scientific experiments in space processing research to be performed during Space Shuttle Mission was solicited by an announcement of opportunity issued in February 1977. The selected "principal" investigators (PIs) will contract with MSFC (SPA/SL Payloads Project Office) to define the final payload system requirements and perform experimentation in their area of expertise.

A prime payload systems contractor, to be selected competitively in FY 78, will design and develop new payload systems meeting the selected scientists' needs and will perform engineering modifications to Government-furnished equipment or designs. In addition, the prime contractor will support PIs with engineering services and integrate their experimental hardware into the Spacelab and Shuttle payload systems.

The Phase I Project Plan reflects two flight opportunities; the Spacelab 3 Mission which would include biomedical applications and fluids research systems and Satellite Deployment Mission # (TBD) that would include solidification systems research. All the experimental systems would be designed for multiple flights and would be refurbished and reflown under follow-on project planning.

Table 2. Continuous Flow Electrophoresis System

- Preliminary Information -

Description/Features

- Transparent Separation Chamber (Column)
- Fluid Management Subsystem (Electrolyte, Buffer, Coolant)
- Sample Handling Subsystem
  - Preparation (Thawing, Centrifuging, Mixing, Rate Freezer)
  - Collection
  - Storage (Incubation, Refrigeration, Freezing)
- Power and Thermal Control Subsystem
- Data Management Subsystem (Includes UV Detector, PH Monitor, Conductivity Meter)

Performance Parameters

° Buffer Flow Rate	0 to 100 ml/min
° Separation Chamber Temperature Control	4 °C to 27 °C (Column Wall) 9 °C to 37 °C (Column Centerline)
° Sample Injection Rate	1 to 10 ml/hr
° Voltage Across Separation Chamber	0 to 670 Volts
° Voltage Gradient Across Separation Chamber	0 to 67.0 volts/cm
° Number of Sample Collection Ports	100
° Sample Storage Temperatures	33 °C to 37 °C (Incubation) 0 °C to 4 °C (Refrigeration) -196 °C to -85 °C (Freezing)
° Sample Storage Volume	.03 M^3 (Incubator) .03 M^3 (Refrigerator) .03 M^3 (Freezer)

3. Summary

The SPA/SL Payloads Project has been established at MSFC and will operate based on science priorities within dollar and schedule limits imposed by agency level decisions. Our planning activities to date have met more than 80 percent of the presently identified scientific needs. Follow-on new starts will be used to meet newly identified needs or expand present capabilities. In this activity the "PI" participation in hardware design and development is the key. This requires commitment and timing of activities by all participants. NASA has given, and will give, this project very high priority in providing the required support. NASA will fund research; design, develop, integrate, and operate research facilities; and via the Space Shuttle, will provide access to space. However, the ultimate achievement of program/project goals rests with the science community.

Discussion

Question (B. Naumann): I am Bob Naumann, Marshall Space Flight Center. Actually, I just wanted to make a comment. The project plan which Bob Adams presented really deals with Space Lab III. Now the Announcement of Opportunity also announced the fact that there would be flight available opportunities on the OFT flight series which commence in 1979. So this would give you at least five early flight opportunities that could be obtained before Space Lab III. Now I do not know how clear that was in the announcement of opportunity, but there was one paragraph that did allude to that. We are undertaking a study of trying to see what can be done by modifying certain SPAR hardware to extend operational time on that and integrate that together in a package, and we have been assured by Bradford Johnson that facilities and resources would be made available on the OFT flights to accommodate such a package provided that there are good experiments to go into it and sufficient justification to do it. In addition to that, Dr. Snyder has the ME-11 experiment that flew on the Apollo-Soyuz which can be contained in the crew cabin. That could also be flown on the early OFT missions and preliminary planning has been made to include that.

Answer (R. Adams): Well, I think that is an excellent point, Bob, it is somewhat difficult for those of you in the audience to understand that NASA does establish a project plan for each new start and the plan that I am responsible for putting together and implementing does not start with the OFT missions. It does, in fact, start with SL3. We clearly recognize in NASA that there certainly should be good cause, adequate cause, to take advantage of the operational flight test missions, the OFT missions, that Bob referenced, with pretty much existing hardware or very minor modification hardware, and Marshall Space Flight Center is attempting to put together an effort in this direction to take advantage of those earlier missions. So thank you, Bob, for clarifying that.

MATERIALS APPLICATIONS OF SPACE FLIGHT - METALS

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Consideration of important applications of space flight to metals, as to any material, is necessarily motivated by the availability of a microgravity field. Therefore, one searches for applications where it would be desirable to eliminate or reduce gravity-caused buoyant forces or flows. There are three categories into which one can group metals-related work that one may reasonably want to perform in space. I will state what these are, giving some examples in each of these and the scientific and technological justification for them. I will then present my personal views as to priorities and to desirable funding procedures.

The first category is that of research designed to yield information, insight, and understanding through the variation of the magnitude of gravity into the physical and chemical phenomena important to the advancing fronts of metals science and technology. For example, in phase transformations, a strong case can be made for investigating critical phenomena at microgravity because at normal gravity density differences interact with gravity-induced pressure gradients to perturb strongly the experimental results. However, the examination of critical phenomena in metal systems does not offer any advantages over the use of systems of simple molecules but does involve additional experimental complications. Hence, the investigation of critical phenomena in metal systems cannot be regarded as a high-priority item.

Continuing with phase transformations, I do not see any scientific merit in the investigation of nucleation phenomena in microgravity for any material. There appears, however, to be a possibility that the study of spinodal decomposition in a carefully chosen binary liquid at microgravity may be scientifically rewarding if it can be shown that normal gravity causes non-negligible Stokes separation. However, metallic binaries are probably not suitable candidate systems since they do not lend themselves to the most appropriate experimental techniques such as light scattering. It is conceivable that the growth of crystals, as well as the inverse processes of vaporization and dissolution, can profitably be studied at microgravity, provided that the processes are in the diffusion-controlled regime and that it is clear that gravity-driven convection sufficiently complicates the phenomena at normal gravity. It would again appear, however, that metallic systems are best left for second-generation experiments. An area of eminent importance to investigate at microgravity is that of how flows, other than gravity-caused buoyancy flow, affect metal crystal growth and phase transformations. Such flows include surface-tension induced convection, thermo-acoustic convection, phase-change convection, and the Soret effect.

Some phenomena that may reasonably be considered for microgravity scientific investigation in their own right, although some also have obvious implications for crystal growth, are the static configurations of liquid metal-gas interfaces and the dynamics of the approach to equilibrium, large-amplitude capillary waves, static and dynamic contact angles, and the Soret effect in liquid binaries of components with a large disparity in density.

Finally, there are some phenomena that may be of scientific profit to investigate at microgravity and that have relevance to the processing of metals on the ground. These include bubble dynamics, such as the collision of bubbles especially of large size, bubble migration under non-buoyancy forces, and dynamics of gas jets into liquids and of liquid jets into gases.

The second category of space-based work on metals is that of the production of "prototype" specimens where there is good reason to believe that the absence of gravity-driven convection can be very helpful in greatly alleviating some difficult-to-avoid disturbances at normal gravity. For example, it is conceivable that in the absence of gravity-driven convective flows, the growth of crystals of great structural perfection and great chemical homogeneity would be much facilitated. If thus successfully grown, such a crystal could be used to measure the "intrinsic" chemical and physical properties of the material and thus serve as the archetype or exemplar for that material. This would be of scientific importance, and the material might also serve as a target for ground-base processing, or in some very rare and remote instance, of space-based processing.

Some composite metallic materials might be considered in this category, since it is clear that normal gravity makes it very difficult to produce composites of great geometrical regularity whenever a liquid phase and constituents having large disparities in density are involved. An example might be a metal with a large volume fraction of monodisperse voids to achieve a low-density structural material. Another example might be a very finely dispersed metal, or semi-conductor, within another metal as the continuous phase, produced from systems exhibiting some immiscibility in the liquid state. The characteristics of interest of such solidified composites might be mechanical properties such as resistance to dislocation motion in some and superplasticity in others, or electrical, superconducting, or magnetic properties. Still another example may be oriented composites, either as-grown eutectics or those produced by liquid-phase sintering. I hasten to point out, however, that although it is justifiable initially to consider as reasonable the space-based production of such prototype materials, it is important to consider carefully the possible disturbing effects of forces other than gravity-driven buoyancy on the desired result.

The third category of space-based work on metals is the development of capabilities that will probably be needed for construction projects in space. Such capabilities would include welding, soldering, brazing, and exothermic brazing.

The experiments and items of the first two categories presented above have been carefully chosen for their apparent justifiability, either scientifically or technically. However, the effect of gravity on ground-based experiments and processing is often of second-order importance and sometimes subtle, and also enough microgravity work has been done that demonstrates that the non-buoyancy forces, masked at normal gravity by buoyancy, can be effective motivators of fluid flow at microgravity. Hence, the importance of careful theoretical analysis and of ground-based experimentation on the phenomenon in question, prior to space-based attempts, cannot be overemphasized. NASA funding in the SPA program should be primarily for ground-based work on phenomena in which the variation of g is deemed to be important scientifically or technologically. Occasionally, there will develop from this work sufficiently compelling reasons for a space-borne experiment which therefore should be funded. In addition, the emphasis for the foreseeable future should be on generating scientific understanding, production of prototype materials, and the development of construction capabilities in space. In the first category, the area of first priority is probably that of the effect of non-buoyancy forces on fluid statics and dynamics.

Space processing of the industrial variety, if economically viable at all, can be expected to develop naturally as a product of the above-mentioned activities.

APPLICATIONS OF SPACE FLIGHT IN MATERIALS SCIENCE AND TECHNOLOGY - CERAMICS AND GLASSES

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This brief discussion of the applications of space flight to studies of ceramics and glasses is based upon the collective thoughts of the members of the USRA Committee on Glasses and Ceramics. The Committee has had extensive contact with many people involved in the space program from Government, industry, and universities, as well as others who have had no direct involvement, and from all of these sources have gleaned a great deal of information. It would be a gross understatement of our belief to merely say that the application of space flights to the furtherance of the science and technology of glasses and ceramics offers unlimited possibilities.

While space environment provides opportunities to examine such factors as high vacuum and unfiltered solar radiation, the primary feature of importance here is considered to be the near absence of gravitational forces. A microgravity environment provides the opportunity to study many basic phenomena which have direct application to the processing of these materials, in addition to obtaining fundamental knowledge which may well lead to the development of new materials and new products. Let us explore some of these possibilities.

Consider first the glass melting process. An unavoidable condition for gravity environment melting is the need for something in which to contain the melt. This leads to any number of effects of contamination, ranging from extremely small to gross. In a gravity-free environment we have the opportunity to melt, on the one hand, in a comtainerless environment and eliminate the impurities, and, on the other hand, to melt in a container and obtain fundamental knowledge concerning the corrosion process. In the absence of a container it should be possible to produce materials having exceptional optical or electrical properties, for example, because often extremely low levels of impurity affect their performance. Not only does purity directly affect performance, but impurities can also lead to nucleation, phase separation, and crystallization. Interaction at the interface of the container wall and melt often leads to unacceptable defects such as bubbles, striae, and crystalline inclusions. Similarly, contact of crystalline ceramics with supporting material can lead to undesirable changes in microstructure.

Melting under microgravity conditions using a container allows corrosion studies to be made in the absence of convection. Basic information concerning diffusion in a convection-free melt should add significantly to our knowledge of mechanisms of pure diffusion. In a gravity environment, the products of reactions at the container wall are swept into the melt by virtue of convection currents set up by density differences, eliminating the possibility of direct observation of the effects of pure diffusion. It would be interesting to study the interaction at the melt, air, ceramic refractory interface under conditions of weightlessness in contrast to those on earth which lead to an undercutting of the refractory at the "metal" line.

The study of the effects of weak forces under conditions where the strong force of gravity is eliminated is intriguing. The role of surface tension and interfacial energies between droplet phases and matrix phases of widely different densities could be explored because surface tension becomes a dominant force under these conditions. The uninhibited effect of surface tension alone or in combination with weak forces due to magnetic, electric or sonic fields could be observed. Wetting and non-wetting phenomena as influenced by surface tension lowering agents in surface layers could be studied without the interference of gravity.

The possibility exists for developing new materials with improved properties for mechanical, thermal, electrical and optical applications. These could include ultra lightweight uniform and homogeneous foams and froths, composites having different density phases, materials with unique composition gradients, or directionally solidified composites. It should be possible, for example, to slip cast high density solids suspended in liquids, a process which is limited in a gravity field. Ceramic crystals could be grown under large thermal gradients without the fluctuations in interface temperature due to convection which influence growth rate.

Other unique processing techniques could be employed. Ion exchange reactions at high temperatures involving glassy materials which would otherwise deform because of a gradual lowering viscosity could be explored using ions of higher charge than the monovalent ions to which the processes are limited to on earth. Greater depths of ion exchange tempering could be achieved in shorter time periods. The process of converting shaped vitreous products to crystalline glass-ceramics could be carried out at higher temperatures where deformation would normally take place. More rapid crystallization rates might be expected with corresponding changes in microstructure which could lead to novel properties.

In summary, processing of glasses and crystalline ceramics under conditions of weightlessness offers the following benefits:

1. freedom from contamination;

2. high temperature processing without the limitations imposed by corrosion or failure of the container or support;

3. freedom from deformation during heat treatment at temperatures where deformation would normally occur;

4. study and control of weak forces such as surface tension, electric, magnetic or sonic fields; and

5. absence of convection eliminating density segregation, minimizing corrosion, and allowing studies of basic phenomena such as diffusion.

Other conditions of a space environment other than weightlessness are worthy of exploration in application to glass and ceramic materials. This includes:

1. large capacity vacuum and the unlimited pumping capacity of the space vacuum;

2. availability of radiation fields such as unfiltered solar energy and other extraterrestrial radiation; and

3. unlimited size of homogenous objects such as the extrusion of unusually long rods, and the formation of thin wall cylinders or large areas of thin plates.

It is evident that glasses and crystalline ceramics will be studied and processed in space. The rationale for this premise is based not only on identifiable potential applications such as: (1) obtaining glasses with unique optical properties unattainable by earth processing; (2) producing high purity of glasses of superior transmission for infrared devices; (3) producing high purity ceramics for electrical applications; and (4) developing special laser glass compositions of higher efficiency and power output because of improved chemical composition, purity and resistance to crystallization, but also because the knowledge obtained from the space processing of these materials will lead to better understanding and more efficient methods of processing glass and ceramics on earth.

It is interesting to note that the USRA Glass and Ceramics Committee has received enthusiastic response from the representatives of diverse glass and ceramic industries it has contacted regarding potential applications of a space environment in their fields. Of particular significance is their interest shown at this stage in performing experiments for the purpose of acquisition of knowledge rather than for improving production.

ELECTRONIC MATERIALS

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To assess the desirability of conducting low "g" experiments related to growth of electronic materials it is helpful to first look at the existing situation in processing technology and to consider the state of our theoretical frameworks for crystal growth and segregation and their contributions to the development and optimization of crystal growth technology.

We enjoy a flourishing multi-billion dollar solid state industry, and we obviously do have the capability to satisfy the basic materials demands of this high technology sector. It must, however, be recognized that virtually none of the materials produced exhibits or even approaches their theoretical properties, nor do the devices made from them operate at or near the expected performance limits. Moreover, the device yield from these materials is generally low and decreases as the complexity of the devices increases.

The existing situation is exemplified in the silicon and gallium arsenide technologies. All melt grown silicon is virtually useless for direct application to I.C. technology, primarily because of deficient dopant segregation. This deficiency must be circumvented by costly epitaxial growth. Bulk gallium arsenide grown by the L.E.C. technique or by the horizontal Bridgman technique meets the low perfection requirements of L.E.D. technology but fails in the more structure and composition sensitive laser structures. Our infrared technology is severely limited by materials deficiencies and a multitude of useful devices cannot be produced because of our inability to grow the required materials with adequate structural and compositional perfection. The situation of our microwave technology is virtually the same. Although irrelevant to the present considerations, it is nevertheless of interest to note that this country has in recent years fallen significantly behind other countries in the advancement of electronic materials processing technology and, as a consequence, Si and GaAs produced elsewhere (specifically in Japan and Germany) are now considered as unambiguously superior to that produced in the U.S.

The study of technological electronic materials indicates the following basic deficiencies:

(a) excessive longitudinal compositional homogenities;

(b) excessive radial segregation effects;

(c) contamination from confinement materials;

(d) excessive nonuniform point and volume defects (microprecipitates); and

(e) structural and compositional deficiencies resulting from interface instability and breakdown in a multitude of binary, ternary, and multi-component systems.

An analysis of these materials deficiencies indicates clearly that all of them can be directly or indirectly attributed to gravity effects. Specifically, density-driven convection, which in high temperature melt systems is unavoidably turbulent, leads to compositional inhomogeneities and together with contamination from confinement materials and the environment (O, C, Si) leads to a multitude of as yet incompletely explored and detected structural defects. It is of interest to note that solid state industry has for a long time taken the attitude that in electronic materials the lack of compositional control on a microscale is inconsequential to device performance and that the costs of materials are negligible considering the price of devices. More recently, however, it is recognized that materials deficiencies do impose serious limitations to device production and performance.

The situation concerning the established theoretical framework on crystal growth is best demonstrated in a study of the open literature: any textbook, still only five years ago, deduced from apparently sound theoretical considerations that dislocation-free crystals can only be obtained by growth at minimum rates and under minimized thermal gradients along the growing crystal (achieved by means of appropriate afterheaters). While this "recipe" was by-and-large unsuccessful, we are today able to grow in Czochralski systems dislocation-free silicon crystals of 10 cm diameter and 150 cm length by using maximized pulling rates and thermal gradients. Significantly, this most important breakthrough in silicon processing technology was made by process engineers who (fortunately) were (most likely) unaware of the established theoretical framework.

It is a fact that crystal growth from the melt on the industrial scale is conducted largely on the basis of empirical procedures and it may well be that the established, inadequate, theoretical framework has, in fact, impeded progress and otpimization of processing technology (if we consider the development of dislocation-free silicon growth as a case in point). The absence of a viable crystal growth theory, applicable to realistic systems, is thus responsible for the high degree of empiricism and "art" still associated with this industrially important activity; it is obviously also responsible for the frequently excessive costs of useful materials and for our inability to optimize processing technology. Finally, it is, in my opinion, responsible for the lack of free flow of scientifically valuable information generated by industry. In summary, the gap between theory and experiment in crystal growth is real, and while there are many factors contributing to the existing situation, it is fair to say that not the least significant factor consists of gravity-induced growth perturbations which can as yet not be quantitatively assessed and incorporated into the theoretical framework.

With regard to the important phenomenon of segregation during solidification, the discrepancy between theory and experimental facts is equally large if not larger. While the basic mass transport equations for segregation under idealized boundary conditions have been established over a quarter of a century ago, we are as yet unable to explain satisfactorily the complex transport phenomena leading to micro- and macrosegregation in real systems. For example, the question of equality between the equilibrium distribution coefficient and the "interface" distribution coefficient is unresolved; the question of orientation dependence of the interface distribution coefficient, first raised in 1953 by Hall, Burton-Prim and Slichter, is still unresolved; the question of the basic difference in the interface distribution coefficient associated with growth on curved and faceted interfaces is still pending; and the dependence of effective segregation on the chemical nature of the system involved remains unexplained.

An analysis of the existing situation points to the fact that, in virtually all growth systems, gravity induced convection effects: (a) prevent us from achieving during growth compositional control and homogeneity on a microscale, and (b) are responsible for the existing gap between theory and experiment. In the final analysis, gravity-induced convection is also responsible for our inability to determine basic physical materials parameters such as diffusion and segregation constants with adequate precision to permit the meaningful application of theory to the experiment.

While gravity effects may, by some scientists (not withstanding experimental evidence to the contrary), be considered as a second order interference in growth and defect formation, their adverse influence on segregation and the development of a realistic segregation theory is today an accepted fact. Considering the existing situation, the questions now are: in what way may experiments, conducted under reduced gravity conditions, contribute to our understanding of crystal growth and segregation; what beneficial impact will space experiments have to processing technology on earth; should we seriously consider the costs involved; are the potential gains from low "g" experiments sufficient justification for their execution; and to what extent must alternate approaches on earth be considered as realistic and less expensive alternatives?

From a scientific point of view, there should be no question about justification or desirability of performing in a reduced "g" environment experiments related to solidification and segregation. Gravity must be considered as a processing parameter which on earth can only be increased to values larger than one. The presently existing situation, in my opinion, may be appropriately compared to the time prior to the development of high and ultra-high vacuum technology. Suffice it to say that the availability of reduced pressure environments in only a few years has added a new dimension to materials science and technology.

The question, will space experiments contribute to our understanding of crystal growth and segregation, is best considered in the light of results obtained from a limited number of experiments conducted under rather primitive conditions on Skylab and during the ASTP mission. Results of these experiments established basic deficiencies of the theory of diffusion-controlled segregation, clarified the thermal conduction process associated with Bridgman-type growth configurations, provided insight into the mechanism of rotational twinning, and indicated the existence of phenomena which were unpredicted and are as yet unexplained. The experimental results, furthermore, provide evidence that, contrary to theoretical expectations, surface tension driven convection effects do not measurably interfere with bulk segregation and that the interactions of melts with their confinement is significantly different from that observed on earth.

From a practical point of view, the justification for conducting experiments related to solidification under reduced gravity conditions is intimately related to the significance and consequences of identifiable deficiencies associated with solidification under one "g" conditions. In this respect, it is evident (from all experimental information available) that gravity-induced turbulent convection is responsible for macrosegregation and for our inability to produce electronic materials of compositional homogeneity on a microscale. Since, at present, it is furthermore impossible even under conditions of laminar convection to quantitatively characterize the diffusion boundary layer at the growth interface, it is not surprising that the identity of the interface distribution coefficient and its functional dependence on systems parameters could as yet not be determined, and necessitated the assumption that it is identical with the equilibrium distribution coefficient. It is my opinion that this assumption is erroneous and is most likely responsible for the existing gap between theory and experiment. In the final analysis, unavoidable convection effects are thus at present also responsible for our inability to optimize the inherently deficient processing technology on earth, since in the absence of a viable theoretical framework it has to be based largely on empirical approaches. In the context of this analysis, it should also be recognized that all approaches to eliminate in growth systems gravity-induced convection, for example, by performing experiments in capillaries or by applying transverse magnetic fields have, in my opinion, failed, at least insofar as the associated segregation behavior was concerned, which in no reported instance is in agreement with the established theoretical framework. On the basis of the preceding considerations and the need for electronic materials with improved structural and compositional properties it appears extremely desirable that appropriate experiments be conducted under reduced gravity. On the other hand, considerations of a large scale processing technology in space must in spite of apparently favorable growth conditions be considered as premature at this time, particularly so in view of a multitude of unpredicted and as yet unexplained experimental results obtained during the Skylab and ASTP missions.

APPLICATIONS OF SPACE FLIGHT IN MATERIALS SCIENCE AND TECHNOLOGY THE FUTURE - BIOLOGICAL MATERIALS APPLICATIONS

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Advances in several areas of the biomedical sciences (biochemistry, cytology, immunology, etc.) are predicated upon isolation of specific biological materials from cells or cells from organisms. Many of the promising cell separation techniques are adversely affected by gravity. Gravitational effects include sedimentation, bouyant convection, segregation of components by density, droplet sedimentation, mixing of fluid in competition with surface tension and density gradients. The conduct of separation processes in space, where low gravity eliminates these effects could offer significant advantages for some separation processes. In biological systems, heterogeneity in size and density is increasingly a problem with increasing particle size. Above about the level of ribosomes, monodispersity begins to disappear and consequently centrifugation ceases to be a very satisfactory technique for separation.

A variety of techniques is employed for the separation of mixtures of biological materials including various chromatographic and partition methods, crystallization, immunoprecipitation and a host of electrokinetic methods. Most of the space-related effort has focused on the electrokinetic methods.

1. Electrokinetic Phenomena

Electrokinetic phenomena involve the motion of charged interfaces or of molecules or particles relative to one another. There are four major phenomena in electrokinesis:

1) Electrophoresis which is the movement or transport of charged materials (solid, liquid, or gaseous) under the influence of an applied electrical field.

2) Electroosmosis which is the movement of liquid with respect to a stationary phase boundary under the influence of an external electrical field. The pressure necessary to counterbalance electroosmotic flow is termed the electroosmotic pressure. Electroosmosis is complementary to electrophoresis and for any system contained in a chamber with charged walls both electrophoresis and electroosmosis will occur on application of an external electrical field.

3) Streaming potential measures the electrokinetic potential which arises from the movement of a liquid with respect to a phase boundary resulting from a mechanical force applied tangentially to the interface--it is the opposite effect to electroosmosis.

4) Sedimentation potential (Dorn effect) measures the electrokinetic potential established by movement of a solid phase under a gravitational field or any other field which will produce movement, sedimentation or flotation with respect to the continuous phase. It is the opposite of electrophoresis.

The most useful experimental electrokinetic approach has been that of electrophoresis which has been widely used for the analysis and separation of complex biological systems as is evidenced by more than ten thousand publications on the subject. The usual aims of electrokinetic experiments lie in obtaining information on the electrical double layer associated with particles or in the analysis and separation of mixtures of materials. Charges on molecules or at the surface of a material in an electrolytic medium are acquired by ionization of functional groups (amino, carboxyl, phosphate, etc.) and/or ion redistribution (adsorption, desorption or exclusion). In some instances, charge is either gained or lost as a result of chemical interactions with a component of the suspending medium.

Electrophoresis involves a tangential motion of one phase with respect to the other phase. It occurs only if the two phases carry free charges of opposite sign. Orientation of dipolar molecules near the phase boundary although creating a potential difference between the two phases cannot give rise to electrophoresis because the charges of the dipole cannot be separated permanently by the applied electrical field. Electrophoresis is therefore concerned with the ionic part of the electrical double layer.

Upon application of the external electrical field, a charged particle or charged molecule accelerates very rapidly until the electrical force is balanced by the frictional forces in the medium after which time it moves at a constant velocity, v.

The velocity, v, of a charged particle for an electrical field strength of 1 volt/cm is known as the electrophoretic mobility, u, and its dimensions are $cm^2\ sec^{-1}V^{-1}$. A number of authors have discussed the theoretical interpretation of electrophoretic mobilities [1-4][1] and therefore only the significant conclusions will be listed here.

a) When the dimensions of a particle of arbitrary shape are large in comparison with the dimensions of the electrical double layer which surrounds the particle, the electrophoretic mobility is independent of orientation, size and shape [5]. The relationship between electrophoretic mobility, u, and zeta potential, ζ, is described by the Helmholtz-von Smoluchowski equation:

$$u = \zeta\varepsilon/4\pi\eta$$

where η and ε are the viscosity and dielectric constant within the electrical double layer. For low surface potentials, the zeta potential is approximately proportional to the surface charge density at the hydrodynamic surface of the particle, a condition generally satisfied by biological cells. The electrophoretic velocities of biological cells depend on specific genetically controlled properties of the bounding membrane. It is because so many of the normal and pathological reactions undergone by cells involve membrane structures that separations based on electrophoretic properties hold such potential in biomedical studies.

b) The concentration of ions of particles is sufficiently low such that their electrophoretic motions are independent of one another.

c) It is assumed that the ions or particles are exposed to a uniform electrical field, all nonlinear terms being neglected; the electrical conductivity of particles is assumed to be zero and the particle is treated as a rigid sphere.

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[1]Figures in brackets indicate the literature references at the end of this paper.

The term electrophoresis covers a wide variety of techniques including static and continuous flow as well as isoelectric focusing and isotachophoresis. The technique may be used analytically using either the microscope approach [4], or laser Doppler light scattering beat frequency spectroscopy [6], for preparative purposes. In what follows, the use of electrophoresis for preparative purposes and the effects a low gravity environment would have on such applications will be discussed.

2. Environment for Electrophoresis

The charged species undergoing electrophoretic separation usually differ in density from the medium in which they are suspended. Moreover, the current flow which occurs during application of the electrical field results in joule heating which gives rise to convection. It can therefore be anticipated that, in principle, the electrophoretic movement will be less disturbed and the resolution of preparative electrophoresis will be greater in a near zero gravity environment than under terrestrial conditions. Weightlessness is the only aspect of a space environment anticipated to improve electrophoretic separations.

In order for electrophoresis in space to be more than a mere demonstration of feasibility, suitable biological candidates for separation have to be identified which can be more effectively fractionated in space than can be done on the ground. The criteria for effective fractionation should include both product quality and required quantity. Several electrophoretic demonstrations or experiments have been conducted in space [7,8], but these have not resolved clearly the two central questions, namely:

1. Is electrophoresis in space more effective compared with the best similar or dissimilar procedures conducted on the ground?

2. What biological separation problems will benefit to a significant degree from electrophoresis in space?

In order to answer the first question, a set of evaluation criteria have to be developed. Each biological system considered for electrophoretic separation will have somewhat different evaluation criteria dependent upon the nature of the system and the purpose of the separation. The criteria should be based on measurable parameters such as quantity, resolution, viability, retention of cell function, speed of separation, etc. It is thus desirable to first develop standard materials with well defined electrophoretic properties to be used for evaluation of electrophoretic equipment both on the ground and in space. Based upon a knowledge of these standards, minimum performance specifications for electrophoretic equipment can be provided. There are, of course, some experimental data bearing on the first question. Electrophoresis experiments at 0 g aboard Apollo 14, Apollo 16, Skylab, and Apollo-Soyuz were, for various reasons, not satisfactorily executed but they provided evidence that particle electrophoresis at 0 g is indeed free of disturbances introduced by convection, sedimentation, and droplet sedimentation [7,8].

A full analysis of the second question requires further considerable ground-based research. The information available on the electrokinetic properties of mammalian cells is still relatively scant, and, as a consequence, the list of biological materials which might be amenable to electrophoretic separation is greater than is currently appreciated. It is recommended, therefore, that attention be given initially to the improved fractionation or separation of whole mammalian cells. These cells are large enough for sedimentation and droplet sedimentation to be a significant problem, and research to date suggests that electrophoresis is one method of separation whose potential has not been fully explored.

A major objective of an electrophoretic separation in a space program is thus the development of electrophoretic equipment for the routine separation of biological systems in space with the best possible resolution and recovery of the separated fractions in adequate amount for the purposes intended. A large sample throughput with at least the same resolution as is achievable under terrestrial conditions is only likely to justify the expense and difficulty of conducting a separation in space if the quantity of product of appropriate purity is increased by more than an order of magnitude.

3. User Requirements for Biological Cell Separations

Approaches to solution of the convection and sedimentation problems experienced in preparative electrophoresis under terrestrial conditions have included density stabilization and use of high viscosity suspending media such as gels to minimize convection and neutrally buoyant media and density gradients in the case of cells to minimize sedimentation. In many media, cells undergo volume and shape changes and pinocytosis. Moreover, the polymeric additives used in density gradient systems often produce cellular aggregation. All of these effects can compromise the success of these separation procedures. In addition, the concentration of cells which can be used is severely limited on earth by droplet sedimentation.

There are two classes of use for cells fractionated out of a mixture.

1. Cloning, injection, culturing, and histological examination; normally 10^4 to 10^7 cells required.

2. Isolation of a cellular component present in small quantities (e.g. enzyme, hormone): often 10^7 to 10^8 cells will suffice, but 10^9 cells may be desirable.

Thus, for the second class of use preparative electrophoresis should be able to supply 10^8 to 10^9 cells in purified form in order to satisfy typical research needs. This implies that often 10^9 to 10^{10} cells must be processed. This is 10-1000 times the number of cells a single continuous flow electrophoresis machine can provide in a reasonable period of time at present throughput rates. Depending on the resolution required, it is feasible that preparative electrophoresis carried out in space could provide this rate of production. Since the period of time over which the separation may be carried out is frequently limited by cell viability considerations to 4 to 10 hours, it is not necessarily possible to match this total throughput by multiplication of the number of machines (due to sample handling and distribution times) or by consecutive runs (if all cells come from a single animal, for instance).

4. Separation of Very Large Biological Cells

There are a number of very large cells with interesting membrane properties of importance to the biomedical research community whose electrokinetic properties have never been examined adequately by even analytical particle electrophoresis because of their extremely high sedimentation rates; e.g., megakaryocytes, fertilized eggs of widely studied organisms such as sea urchins and nerve cells where surface charge is believed to be important in controlling ion fluxes during action potentials. There are difficulties also with other relatively large cells including liver and kidney cells as well as endothelial cells. Some cells could be examined in media of greater density or in density gradients, but in many instances these have been shown to have undesirable effects. Endothelial cells have an extremely active pinocytotic process and develop ultrastructural changes indicative of damage in the media usually used for density gradients. Such cells could be investigated in the space shuttle environment.

Aside from the problems of electrophoretic cell separation, even greater difficulties are posed by studies of the kinetics of cell aggregation, the behavior of cellular aggregates, cell sorting phenomena and cell contact relationships. A microgravity environment would appear to be a fruitful one in which to examine some of these phenomena.

5. Some Suggestions for a Space Electrophoresis Program

1. Theoretical and experimental studies should be conducted to establish the probable limits of performance of ground-based electrokinetic equipment in comparison with that envisioned for space. For a viable electrophoresis in space program, the electrophoretic separations carried out in space would have to be more effective than any type of separation process (including non-electrophoretic ones) conducted on the ground. Preparation of detailed instrument performance specifications for new apparatus must be undertaken based upon user requirements. The need for electrokinetically well characterized standard particles to measure the effectiveness with which new separation techniques meet the performance specifications is apparent.

2. A survey of biological materials as candidates for separation in space must be conducted in order to determine the most suitable candidates for space separations and to ascertain the required precision of the separation, yield, time constraints, etc. (NASA is now supporting under contract the development of an Automated Analytical Electrophoresis Apparatus to be available in June 1978 for preliminary screening of various cell and particle preparations.)

3. A logical program of development in both analytical and preparative electrophoresis should be pursued, and the present commercial product/process oriented program should be abandoned until a firmer technological basis is developed. The ultimate prospects for electrokinetic methodology should be examined by thorough ground-based experimental and theoretical studies using a step by step approach which lends itself to a systematic examination of all alternate options.

4. Space flight experiments should not be considered until thorough ground-based research has established the requirement for the weightless environment (has established the existence of questions and problems that can only be solved in the microgravity environment of space).

5. Since space flight experiments by their nature take in excess of one year to develop, the best separation technologies on earth should be strongly supported to assure that the space experiments, when finally accomplished, will constitute a real advance in the field and not a simple repetition of earth-based technology.

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CRITICAL PHENOMENA AND CONDENSATION

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1. Second Order Phase Transitions

Second order phase transitions were classified as such by Ehrenfest as a result of the observations made in helium. They were called that way because the second derivatives of the chemical potential is discontinuous which means that the entropy and density are continuous but have a kink. (The first order transitions are characterized by a discontinuity in the first derivatives of the chemical potential.) Nowadays, we prefer to do geometry in the space of the field variables: the second order phase transition is the end point of a line of first order transitions or the edge of a surface of first order points.

This description can be used on a class of systems. Examples are:

(1) ferromagnetism where the ordering parameter (OP) is the magnetization;

(2) pure fluids, OP is the density difference between liquid and vapor;

(3) binary alloys, OP is sublattice population;

(4) antiferromagnets, OP is the staggered magnetization;

(5) liquid mixtures, OP is the concentration difference above and below the meniscus; and

(6) ferroelectric, OP is the electric polarization.

All have in common that upon lowering of the temperature they spontaneously "burst" into an ordered state, a state which is no longer a one-dimensional representation of the symmetry group, but is one of the components of a multidimensional representation. At the moment of bifurcation, there is a certain arbitrariness as to which choice is made. This is usually done by very small, let us say "stray" forces. In the magnetic case this is, so to speak, the magnetic field of the earth. The second order seems to suggest that they are of secondary importance. This is not the case. On the contrary, the line of thought is that they are of primary importance and, if properly understood the first order transitions will automatically become transparent as an aftermath.

2. Thermodynamics

In each class of physical systems mentioned, there is a thermodynamical variable, the OP, that takes spontaneously a non-zero value. It does so despite symmetry considerations. This quantity we call, for the sake of simplicity, the magnetization or density difference, since it represents the most commonly occurring case. Each of these quantities has a thermodynamically conjugated variable: with the magnetization we have the magnetic field and with the density difference goes the pressure. The equation of state is always expressed using the two members of such a pair and the temperature T. In terms of thermodynamics, the critical point is characterized by the disappearance of the first and second derivatives of the order parameter with the field parameter; i.e., infinite susceptibility (compressibility).

Slightly deeper than the thermodynamic description lies the theory of Landau who constructed a free energy-density which fitted the general conditions, but which does not fit the shape of the isotherms. Its theoretical equivalent is the Mean Field Theory, which does the same: it gives a qualitative picture without too much success in realizing the quantitative aspects, and it ignores all fluctuation phenomena.

Before going over to improvements, let me mention that Landau, or rather Ginsburg, added a term that introduced the gradient dependence, which plays an important role as soon as one deals with inhomogeneous situations. It is of importance for later to realize that these equations do not take any surface or wall forces into account.

3. Power Laws and Renormalization Theory

Next came the realistic observation that none of the curves around the critical point seem to behave like polynominals, but that they do fit a set of power laws with irrational numbers. Historically, it is of interest to remark that this had been discovered already in 1900 by Verschaffelt, but his results were completely forgotten.

I will not display the power law equations since they are well known and often repeated (see general references).

It came as a surprise in 1973, I think, that it turned out to be possible to construct a theory which is able to calculate these exponents. Leading up to this theory was the notion by Kadanof that one could introduce renormalized coupling parameters for "fused" spins in such a way that the result near the critical point was non-analytic, while the steps that were leading up to it were analytic.

First, I would like to point out the broad picture: the leading thought is that one can find universal equations of state using the critical point as reference point. The situation bears some resemblance to the theory of complex functions. If you know the parameters that characterize the singularity, you know the complete behavior of the function. This has a strong appeal to both the scientist and the engineer.

The theory is not yet perfect, the range of the power laws may be restricted, and there is no good link to the behavior of T = 0 which is already theoretically established. Last, but not least, wall and impurity effects are usually ignored. Some of these incompletenesses fall into place; for instance, it seems to be possible to give the range of the validity by determining the next term in the non-analytic series (a weaker singularity) and its amplitude.

Based on the firm belief that closeness to T_c might clear up most questions, one has to ask what prevents the investigators from getting there. The answer can, to a large extent, be given in one word: gravity!

4. In The Chains of Gravity

Near the critical point, even the smallest change in pressure results in large differences in density due to the flatness of the isotherm. Hence, the barometric height effect, usually of no importance in any fist size experiment, becomes the limiting factor. Even by going to effective sample sizes of only one millimeter in height, one still has the trouble that the quantity observed, the density difference, is actually only the density difference averaged over a millimeter. This is not accurate enough to determine the shape of the curve for $|(T - T_c)/T_c|$ less than about 10^{-4}. (A more precise way to express this limitation is described in Moldover, Hocken, Gammon, and Sengers, NBS Technical Note 925, October 1976).

The correlation length, actually the pair correlation length, can be, in principle, detected by light, x rays, or neutrons. (I would like to mention inter alia that the last are rather expensive so that it would be that if an equivalent optical method exists, one may be cheaper off by doing a measurement in space.) Since it is a necessary condition that the wavelength is short compared to the range of the correlation, one would be inclined to favor neutrons and x rays. However, a second condition is that the wavelength should be long compared to the range of the interatomic forces and this is true for neutrons and x rays only in a range where the correlation length is still rather short. Too far above T_c one detects the so-called short range order, which is not very interesting. Hence, light scattering is the front-running candidate after all, but in order to have correlation lengths in the right range, one has to go so close to the critical temperature that density differences are completely washed out by gravity effects, as explained above when I was talking about the equation of state. There is little doubt that the ultimate light scattering experiment can only be done in a meaningful way in a space laboratory.

Will everything go fine if gravity is drastically reduced? The answer is three-fold. On one hand it may; on the other hand, it may not; and finally, I think we may tumble into some unexpected surprises because the situation depicted so far may have been oversimplified by not ignoring all surface and wall effects.

5. Chemical Potential Differences

In order to understand what will happen in gravity-free condensation, it is instructive to compare the situation with the magnetic process. In the figure, I have double-labeled the axes. If the system is cooled from a temperature above the critical temperature and if the field is kept exactly zero, which is of course impossible in reality, it may either magnetize "all up" or magnetize "all down." In reality, there is always some small field and so the condensation will be biased. However, the stray field may not be homogeneous, and most likely is not. This means that certain portions will magnetize up,

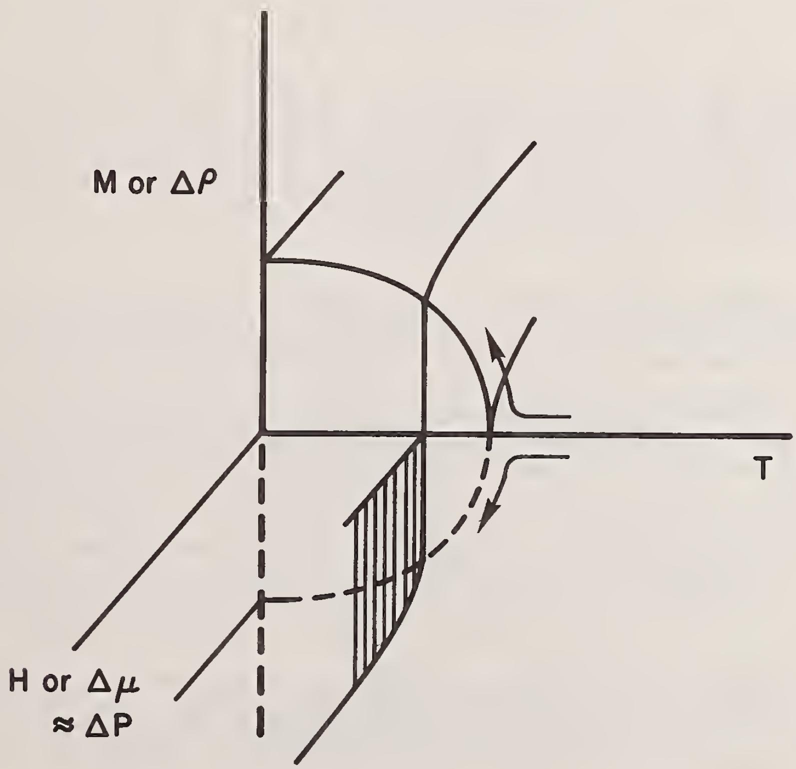

Figure 1. Gravity-free condensation possibilities.

other portions will magnetize down; and if there is no surface energy associated with the domain walls, this inhomogeneous state will have the same energy as either one of the homogeneous states. Now let us return to the condensation language. The magnetization is replaced by the difference in density between the liquid and the vapor, and the field variable is replaced by the chemical potential difference. While physicists have spent a lot of time and attention to field-free spaces, they have had a rather laissez faire attitude versus the making of chemical potential differences. [I may point out that the request to the NASA is basically the request for the opportunity to create the first pure Chemical Potential Difference Generator.] The chemical potential is steered by the pressure, but since the pressure is not homogeneous in a gravity field, our control is limited. We can control the pressure pretty well. Zero magnetic field corresponds to critical pressure, but we are still stuck with a gradient. Hence, the lower part of the magneti will have spin-down; that is, a liquid, and the upper part will have spin-up that is a vapor, as soon as the temperature is lowered below T_c. If the pressure or the chemical potential is really homogeneously zero, we have a change that the system follows either the upper line (remains completely in the vapor state) or the lower line (complete liquification). It is also possible that one may obtain an inhomogeneous situation with arbitrary domains in space that contain liquid and the remaining space filled with vapor. All this is possible with equal probability as long as we ignore surface forces.

6. Surface Forces

Gravity is but one of many forces of our system. If we take it away, we may find that other forces emerge. The candidates are: surface tension forces, dynamical oscillations of suspended blobs, electrostatic forces, forces due to temperature changes, and also the remaining gradients of the gravity. I will assume that the surface tension forces will dominate all others; or more precisely, that we deal with experimental conditions in which they are the main emerging forces after gravity has been removed. These forces, or rather energies are comparable with the Bloch wall energies in the magnetic model (I mean comparable in the figurative sense).

If it requires additional energy to form surfaces, the system is biased and the system will follow the vapor part of the coexisting curve upon cooling and will not condense at all! If, on the other hand, we put in a slightly positive chemical potential difference in the same way as we could have used a slight biasing magnetic field in the positive z-direction, the system will go for the all-liquid state. I presume that this monster-droplet will form with a silent bang and then will hang there. This is rather different from magnetic spins which are tied down to a lattice and, hence, do not have to deal with wall forces. The picture I conjured up may not be right because we now have to deal with the wall forces, contrary to the magnet.

Rather than to go on speculating what the influence of wall forces may be, let me mention the liquid mixture experiments. A large number of miscible liquids separate upon lowering of the temperature. Some do it when the temperature goes up, some even do it in both ascending and descending temperatures. These critical points have been studied enthusiastically in recent years, among others by Sandra Greer at the National Bureau of Standards. There is a certain "gravitological" aspect to these experiments, since one can diminish the effect of the vapor-liquid density difference by choosing two liquids that have densities that are almost the same. This is, so to speak, the poor man's (or rather woman's) space flight. These systems are extremely attractive since they can be made with a much larger variety of parameters. Not only does one have a certain control about the resulting density differences, but it is possible to use ternary systems which are comparable to metamagnets. A metamagnet is a system that has two types of coupling, antiferromagnetic and ferromagnetic. In passing, I would like to mention that improved understanding of these systems could very well lead to better theories of alloying of metals.

The critical wetting theory of Cahn (J. Chem. Phys., April 1977) shows that in ternary systems one may have, under proper circumstances, a layer of the third liquid between the meniscus of the separated one and two components. Gravity pulls this layer flat, at least as long as we stay away from the walls of the container.

7. Spontaneously Created Spacial Inhomogeneities

In the last section, I would like to make some speculations about the possibility of spontaneously-created spacial inhomogeneous systems in a gravity-free environment. Spontaneously created inhomogeneous states are found in bubble domains and in superconductors. The common feature is that certain systems can lower their free energy by forming additional internal surfaces. In a sandwich-type superconductor, the energy is lowered despite the fact that there are normal regions because the additional area of "meniscus" with lower free energy outweighs the increase of free energy in the normal regions.

Cahn discovered that under the proper circumstances the free energy near the wall may be lower than in the bulk. If this is also the case in a three-component mixture, it may result in the spontaneous creation of as much wall area as possible. This could take place in the form of surfaces that are parallel to each other (striation) at a distance not too close together; otherwise, the free energy goes up again. It may be possible to make computations to see if such states exist and to see how one could make a detection system that can observe the situation adequately.

Discussion

Question (Jan Sengers): What experiment would you do on a space flight?

Answer: The most interesting experiment is to do the light scattering extremely close to the critical point. I do not know how you actually perform this experiment, but one must get as close to the critical point as possible. The reason that one wants to get so extremely close is that one wants to really see if these power laws behave to the very end.

Comment (Wang): Some people are doing this, looking at second order phase transitions very close to the helium lambda point using liquid helium as the system. Bell Labs has done 10^{-7} K and some people at Stanford are thinking of trying 10^{-9} K. They were essentially trying to verify the universality of this critical phenomena.

Answer: True.

Comment (A. Sengers): Tacking on to that remark; the reason for doing these studies in fluids is that these fluids we are talking about here are not supposed to be in the same universality class as helium. These fluids are supposed to be Ising model and superfluid helium is not. Secondly, 10^{-7} K in liquid helium translates to 10^{-5} K in fluids and we are already in that region with the experiments we are doing here at NBS. Thus, we can come close because we have the advantage of working at 200 K, not 2 K.

Answer (Meijer): First of all, universality is the same as the Protestant church; it splits constantly into subdivisions. Secondly, it is crazy to send up a liquification system if you first can do a much simpler experiment.

Comment (Oriani): At some time in the past, I have worried about negative surface tension and I convinced myself that the only possibility was in a multicomponent system. But you seem to have the concept of a negative surface tension for a one component system because you have this for the liquid-vapor transition.

Answer: No. I do not mean negative; I mean less than the bulk material.

Question: You alluded to a direct effect of gravity on surface tension. I wonder if you could point in the direction you have in mind?

Answer: I can give you several papers. The point is a calculation to show that if gravity is taken away, the thickness of this surface layer is a little larger. The effect is so small it is not worth the effort to look at it.

THERMODYNAMICS AND PURIFICATION

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I thought at first I would try to give you a little bit of background on what we have been doing on a levitation type experiment in an earthly laboratory, and then talk about some of the possible extensions of this to space systems. We and a number of other people have, for a number of years, been levitating in a set of induction coils which are wound first one way and then the other, connected to some RF source levitating small samples of material on the order of a gram or so. I realize that at Westinghouse and at G.E. and at many other laboratories, people have levitated pounds of materials in similar kinds of systems. We do not have enough kilowatts to put to our levitation experiments to do these large-scale experiments, but for the purpose of thermodynamic measurements in which we are interested, one-gram samples are sufficient. When we have, through input of the RF field and through the balancing of the two reversed solenoids influencing the metallic sample, attained a steady state temperature which we can observe pyrometrically with an optical parameter, either a one or two color pyrometer, we then cut off the field, drop the sample into a very traditional kind of calorimetric receiving block correcting for radiation losses and convection losses to the gaseous atmosphere. As we drop the sample, we can determine the total enthalpy content. These kinds of studies have been done now for some 15 or 20 metals, mainly transition metals, by persons in the Rice University laboratories, at the Sandia Corporation in Albuquerque by Russian scientists, and by scientists at General Electric doing quantitative calorimetry.

The results of these kinds of measurements are rather interesting and, for the first time, have provided enthalpy increments H_t-H_{298} say as a function of temperature and one can do this for a solid and get a series of points, and then for a liquid and get another series of points, and the discontinuity in these two lines, of course, is at the melting point. Then, from a quantitative measure of the discontinuity, one can evaluate the heat of fusion and from the slopes of these lines, of course, one gets Cp for the solid or the liquid metal.

Now dull as it may seem, the fact is that no one had ever measured experimentally the Cp's of liquid metals like platinum, or titanium vanadium, or niobium, or zirconium, etc., previous to this levitation kind of experiment. And these heats of fusion have turned out to be of the order of 50 - 100 percent different than previous estimates, and, furthermore, the Cp of liquid metals has turned out to be quite different than apparently theoreticians have expected. Because when you make the plot of Cp versus temperature for the traditional metal system assuming no low transitions or anything, one comes to the melting point. Now the question is, where is the Cp of the liquid metal going to be? Will it be higher or will it be lower? Assuming one or the other, will it have an increasing change with temperature? Will it be flat with temperature? Might it even decrease with temperature? I think more people would have voted for an increasing kind of curve like this. There are some examples of both other kinds, but the fact is that out of the levitation studies, almost everything follows the flat with temperature curve and the Cp of liquid zirconium, for instance, is flat over a range of 1,000 degrees within one or two percent. This is pretty similar to the behavior of emissivities over ranges of temperature for liquid metals, of Hall coefficients, electrical conductivities which are slowly varying, and a number of other properties, electronic in nature. So this kind of background information does exist for a large number of systems.

Now, in addition to just dropping the sample into a calorimeter, one has here a potential system for chemical systhesis, and because I am a chemist interested in systhesis we have done experiments leaving the calorimeter out where we put in a reactive gas--one may introduce oxygen or nitrogen or a halide or methane and thereby convert your metal to a suboxide, a normal oxide, a higher oxide, various halides, or make carbides, or borides, or nitrides. So, there are synthetic interesting possibilities using the levitation device available in almost anybody's laboratory that has a good RF induction heater.

The interest, of course, in extending these experiments into a space environment has to do with why this is necessary. One of the disadvantages of the experiment we have shown here is that in order to levitate even one gram samples, you have to put so much energy into the sample you superheat it, you take it way above the melting point in most cases. We cool the sample by a gas flow down to the temperature where we want to do our experiments and then carry out the experiment. In other words, one has two conflicting kinds of parameters, one the levitation and one the heating. And the way the experiment is done on earth, you get both and you cannot avoid and you cannot separate the two in this kind of experiment in RF induction levitation. So that a space system would offer the advantage of levitation with the input of energy and then you would have pretty free temperature control. Therefore, so one of the big advantages I would see in a space levitation experiment from a chemist's viewpoint would be the possibility of the elimination of this particular problem.

Now I have got four or five transparancies to look at. In the sense of chemical systhesis, the subvalent species, SiO, GeO, and AlO are all well known. They have all been made on earth. Controversies running over some thirty or forty years of the literature have still failed to answer whether or not crystalline SiO can be prepared. No one has yet prepared a macro sample of calcium monofluoride. There are arguments even about solid aluminum monofluoride, solid SiF_2 is a polymeric material much like teflon perhaps and seemingly can be prepared. There are then higher valent state species of the chromium hexafluoride, of course the UF_6 is well known. But, probably a third category should be added to this and this is new species unpredicted. That is, carrying out the chemistry without a container, because one will eliminate the possible influence of minor impurities introduced by the container, it is possible and realistic to anticipate new systhesis being practical.

Now, in the other range of discussion, one can ask what materials should be studied and this is a list of the kinds of materials I would propose for study. One would like to look at the very highest melting materials, tantalum, tungsten, zirconium carbide, tantalum carbide. Dr. Frost at the General Electric laboratory has levitated and melted tungsten. We have levitated and melted tantalum. We have been levitating but have not yet melted ZrC and I do not think anybody has melted or levitated in a levitation experiment, tantalum carbide. Of course, all of these things can be melted in literally exploding wire types of experiments where you load them up with enough electric current until they finally heat up and do melt. But the possibility of getting these very high melting materials in a system where the impurities are minimized and where one can then do thermodynamic measurements would be of interest.

Another interfering factor in many of our experiments in the Rice Laboratory has been the problem of volatility. Elements like silicon, maganese, chromium, or beryllium are so volatile at the melting points that the vapor species coming off tend to condense out on the copper coils. These are water-cooled copper coils and when the sample vaporized, one gets condensation of the metal and shorting of the coils and very exciting laboratory events for a few seconds while everybody madly sets records for getting out of the room fast. However, if you could levitate without this coil and then heat by some other indirect means, radiation heating, or by pulse heating with a laser or perhaps electron beam heating, then one would have alternative approaches. Then, poor conducting systems are, of course, not even practical. We cannot levitate things like boron, silicon, and even graphite does not levitate too well. You can heat graphite up to 2500 degrees or so, but to levitate and heat it is more difficult at 450 kilocycles.

Now, one has a range of frequency and a range of power and we have not the facilities to explore all of those ranges but if you could be in a space environment then this problem would be totally eliminated. Poor conductors could be studied, and even more exciting I think from the viewpoint of possible interest in chemistry, nonconductors would levitate - things like sulfate, carbonates, silicates, borates, etc., or the non-metallic elements, sulfur, selenium, tellurium. Now, a lot of these materials have been studied. If you read the literature, people have been looking at behavior of sulfates since the 1700's, and I presume the alchemists even back long before that knew what we now call the sulfates. However, it was not until about ten years ago that people recognized one of the major problems in turbine systems in many of the MHD experiments and certain fuel cell applications was the volatility as molecular species of things of K_2SO_4, Li_2CO_3. Sulfates do not decompose to alkali-metal oxides and SO_3 or SO_2. Carbonates do not decompose to alkali oxides and CO_2. There is a volatile molecular Li_2CO_3. There is a volatile molecule, K_2SO_4 and one needs more information about such species. Again this information can be obtained. We have done experiments in our laboratory, and low pressure, high vacuum mass spectrometry situations at the Bureau of Standards here, by Dr. Hastie, and at Dr. Jonel's laboratory, high pressure sampling of vapor species in flames is being done. I talked to Dr. Binele on the phone a couple of days ago and he was telling me about his four-stage vacuum system - starting with a 12-inch pump and working down as he finally gets the high pressure sample into the mass spectrometer for study. It is a very expensive experiment when it is done on earth. It may be very expensive when it is done in space, but the versatility of the space experiment may be much greater. So these kinds of various kinds of studies of non-conductors in space environments will be important.

To summarize some of the kinds of measurements then, one would like to measure enthalpies, enthalpy increments, particularly, specific heats and heats of fusion. One would like to measure vapor pressures, identifying species in high pressure ranges especially. And then there are some what people often think of as trivial questions like what are the densities? Nobody knows the density of liquid molybdenum or liquid titanium, and things of this kind. So, there is a whole range of studies of importance in long-term metallurgical and other applications just to establish densities--emissivities, conductivities, and other properties of that kind. Finally, if one goes to multi-element systems, phase diagrams will be of some interest. Now in terms of apparatus, what kind of things does one need? One interesting obvious point is, of course, that you cannot use a drop calorimeter in space because the blob does not drop. And so we have been considering, under NASA activity for the past few months, alternate designs of calorimeters, and there are various views. One is that calorimeter might come out and gulp the sample. Another one would be that you might literally electromagnetically eject the sample into the receiving block. But, a third, and we really feel perhaps most exciting alternative, is to use some kind of a heating or cooling method in essence to maintain the sample at a more or less steady state temperature, and then put in pulses of energy to raise it a certain amount or shut off the power a certain amount and watch the sample cool.

So by heating and cooling curves much like the ΔH, ΔT, determinations of the low temperature calorimeter, we think that some more useful information about high temperature heat capacities could be obtained that gives you a technique that is at least consistent with space areas. The density experiments mainly need to be done by photographing levitated samples against a cross-hatched area of properly calibrated emissivities as a function of wavelength. So that is a pretty complicated problem. The trouble in determining the emissivity of a liquid metal is that you could determine the emissivity at the melting point where you simultaneously know the temperature and measure the emissivity, but above the melting point, you have no reference. If the emissivity has changed, you may have difficulties establishing the true temperature. So it is a nontrivial question what the variability of emissivity with temperature is. Then, as I said earlier, there is the high pressure mass spectrometry sampling of vaporizing materials. Well, these are the kinds of things that could be done. They would represent useful and currently nonavailable types of information about thermodynamic and other high temperature properties of materials.

Discussion

Question (Sekerka): You mentioned measuring densities of liquids, and I wondered why you felt you wanted to do that in space for these high melting point metals. Given in a skull melting rig of some sort, you can melt a metal contained in its own self and determine its density by floating a little piece of solid in it.

Answer: I think the main limitations on experiments done in that kind of environment is simply the more likely possibility of contamination.

Question: In skull melting?

Answer: You are talking about the material on itself. You cannot have both a solid and a liquid simultaneously in contact at equilibrium and do a density experiment.

Question: Well, I will admit that there will be a little temperature variation in the liquid, but I would be willing to correct for that theoretically.

Answer: But I want to do the density over a range of 1000 degrees and you cannot have solids floating in liquids that are a 1000 degrees different in temperature. I agree we can do densities in our experiments--all we do is photograph through our coil. But, we do have a limited range of temperature and we do have to worry about this combination of levitation heating. Whether the result is worth the effort is another kind of question. One thing I did not mention, perhaps I should, is that when one lets these levitated liquid metals cool, you can supercool--we have supercooled molybdenum about 300 degrees below the melting point, and you can drop these supercooled samples into the calorimeter. So, we have experimentally measured the Cp or the enthalpy increments for supercooled liquids quite a bit below the melting point. In the space environment one would hope that the supercooling might be extended even more. At least, the possible nucleation parameters might be minimized so that learning more about supercooled liquids would be another possible interesting point.

Question (Taylor Wang, JPL): You can also levitate acoustically, can you not at high temperatures?

Answer: Yes, with proper design, I suppose one could levitate small samples.

FUTURE RESEARCH APPLICATIONS IN CRYSTAL GROWTH

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The most significant attribute of an orbiting spacecraft to future research applications in crystal growth is persistent weightlessness. Microgravity levels in the 10^{-5} to 10^{-7} g range are expected in the Shuttle/Space Lab "during working hours." If achieved, then a truly unique environment will become available for crystal growth experimentation over time periods long enough to embrace most processes of interest.

The main characteristics of a microgravity environment with long-term persistence are:

- independent control of heating and levitation,
- suppression of gravity-driven convection flow,
- exaggeration of surface molecular forces relative to body forces,
- diffusional control of heat and mass transfer,
- elimination of conventional containment, and
- modification of stability criteria.

These characteristics, taken individually or in combination, may have important impact on a given crystal growth process; however, the large costs incurred in obtaining a usable orbital environment will demand prudent choice and extreme selectivity of the processes so studied.

The guiding precept of the commentary which follows is that the most significant benefits of the low-gravity environment to crystal growth science and technology are as yet unknown. Any attempt made *a priori* to establish a list of "must do" experiments is little more than enlightened guesswork. Nonetheless, much can be planned to prepare for efficient use of the available capacity of the Shuttle/Space Lab for materials science and technology experiments.

At present, we benefit greatly from the perspective provided by the earlier studies on crystal growth and solidification conducted during space flight, specifically, those carried out aboard Apollo 16 and 17, and aboard Skylab and Apollo-Soyuz. A considerable body of in-house NASA reports and a lesser number of archival papers now exist to help guide future work in this area. A study of this literature shows clearly that novel effects and the generation of new techniques and materials are doubtless in the offing. Before we "turn the corner," so to speak, and realize these benefits, considerable preparation is needed. To be specific, a carefully planned series of investigations is needed to elucidate the influence of reduced gravity on the basic processes and phenomena involved in crystal growth. Included among these, to mention a few are:

- fluid dynamics,
- heat transfer,
- surface tension effects,

- mass transport,
- interface stability,
- "containerless" control, and
- nucleation.

Obviously, each topic listed above is so broad that one must select sub-areas germane to crystal growth. For example, within the topics of fluid dynamics and heat and mass transfer, we are especially interested in convective heat and mass transport, since these phenomena are involved in virtually every terrestrial crystal growth process; moreover, we expect (and indeed there is good evidence for) substantial modification of convective transport at reduced g values. Similarly, as body forces are reduced, then weaker forces such as surface tension and surface contact forces become relatively more important for fluid phases. To control the position of and velocity fields within fluid phases at microgravity levels, one must employ methods never before used which effectively control the weaker surface forces encountered. Thus, it becomes clear that before we can expect great progress in terms of improved materials obtained from a novel crystal growth environment, we must invest considerably in preliminary studies to control and use that environment. It remains a distinct possibility that after adequate study we will conclude that only limited aspects of crystal growth benefit enough from the attributes available in an orbiting laboratory to justify the cost.

The situation overall seems much brighter. Serious investigations on the fundamental phenomena associated with crystal growth will enrich our understanding of terrestrially-based processes and broaden our knowledge in materials science. The ability to reduce g-forces to low levels will permit measurements on high-temperature physico-chemical properties never before possible. The insights gained into controlling convection during solution growth, growth from the melt, chemical vapor deposition, and physical vapor deposition will all add to our ability to conduct these processes better on earth as well as in orbit. Finally, with proper investment in a ground-based research program to support and augment the flight program, we will enhance the chances for "breakthroughs" and exciting developments not projected from any linear extrapolation based on today's knowledge and understanding of crystal growth.

COMMENTS ON SOLIDIFICATION IN SPACE

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The remarks that I would like to make may be subdivided into three categories, namely, thermodynamics, kinetics, and technology. I think it will become clear later why such a peculiar subdivision is warranted.

At the outset, however, it is important to stress that whatever we do in space ought to be something for which the space environment is unique or, alternatively, the most efficient and/or effective now available.

Although we have heard of various possible advantages of the space environment, e.g., high vacuum and radiation levels, I shall focus on the micro-gravity aspect of this environment because I believe that the other possible advantages can be duplicated on earth. We should, therefore, look for phenomena where the presence or absence of a gravitational field can really make a difference.

If, for example, I examine the thermodynamics of solidification and ask how the presence or absence of a gravitational field might lead to a considerable difference, I am led along the following lines. Since the writings of J. Willard Gibbs, it has been well known that the effective chemical potential of a chemical component in a gravitational field is its value in the absence of gravity augmented by an amount equal to the product of the molecular weight, the gravitational acceleration, and the height above some arbitrary reference level. From this, one can calculate the sort of compositional separation that would obtain at equilibrium in a column of a given height simply because of the fact that it is in a gravitational field. For a binary solution at room temperature, there will be significant compositional separation for a column whose height is the order of several miles, consistent with our knowledge that the earth's atmosphere is of a scale sufficient for such separation phenomena to be important. For samples of ordinary laboratory scale, the effect is negligible except possibly as one approaches absolute zero (the relevant length is proportional to the gravitational constant and inversely proportional to the absolute temperature for small changes in composition).

Insofar as the thermodynamics of phase changes are concerned, the "gravitational enhancement" of the chemical potential is the same for a given chemical species irrespective of phase; therefore, if you calculate the relevant changes in free energies between transforming phases, they are the same whether or not one is in a gravitational field. Therefore, there is no "direct" effect of gravity on the thermodynamics of phase changes.

One consequently wonders how the presence or absence of a gravitational field could influence a solidification event. My answer would be "indirectly" via two phenomena, both of which are related to density differences. Once one overcomes, via the manipulation of usual thermodynamic variables such as temperature and pressure, the entropy of mixing and achieves separation of phases--be it via a miscibility gap in a liquid or via the formation of a partially solidified melt--one gets sedimentation of the heavier phases and buoyancy of the lighter ones. The possible absence of such sedimentation might conceivably lead to the ability to produce uniformly dispersed composite materials; however, I believe that one can produce such materials on earth (possibly better) by rapid cooling or by mixture of partially solidified materials and/or powders. The remaining phenomenon is the alteration of fluid flow that is driven by density differences. Fluid flow in carefully controlled space experiments will undoubtedly be reduced in magnitude but will become more obscure in the sense that it will now be driven by small perhaps unforeseeable forces.

This, nevertheless, suggests that we might be able to check some fundamental aspects of solidification theory, given that we can often solve the diffusion equation in the absence of fluid flow and predict compositional profiles capable of comparison with experiment.

A question that remains at this point is whether or not such experiments will lead to information which cannot be obtained easier and better on earth. To shed light on this question, consider the simpler experiment of the determination of the shape of a liquid zone "floating" in the space between circular cylinders in various gravitational fields. When you "scale" that problem, the important parameter is the so-called "Bond number" which is a dimensionless parameter equal to the product of the density, the acceleration due to gravity, the square of the cylinder radius, and the inverse of the surface tension. Of course, one can alter the Bond number by manipulation of any one of the parameters that it contains. For instance, if one does experiments at very small radius, he gets the same results that he gets for a larger radius and reduced gravity; there is, therefore, no need to perform such an experiment in the space environment. Similarly, other experiments that involve the manipulation of only a few relevant dimensionless groups can often be designed to correspond to an effective reduction in gravity. However, in a complicated phenomenon such as the solidification of a binary alloy, there are too many important dimensionless groups to allow for a simple scaling that is compatible with experimental apparatus. For instance, one has a liquid and a solid, conduction and convecting, latent heat evolution, selective incorporation of solute and interaction with heating and containment facilities, all occurring simultaneously. From such complicated phenomena, it is possible that one might want to go to a micro-gravity environment to conduct a few critical experiments.

A typical example of such an experiment would be one designed to test recent theories of the growth of cellular (non-planar, steady-state) interfaces. These theories are only applicable to the case where convection can be neglected. Therefore, they can only be tested in an environment wherein gravity driven correction can be suppressed and such is the environment of space. Of course, the presence of Marangoni convection in space might obscure such a test. Therefore, for this or any other potential space experiment, there should be extensive ground-based preliminary research before flight is decided upon.

The remaining general category is technology. Although I cannot yet conceive of any examples where space manufacturing is justified at the present time, there is a class of experiments in solidification whose justification for performance is manifest; this is the class of fusion joining experiments. It is my conjecture that, eventually, one will want to perform welding, brazing, or soldering in space either to repair some existing structure or to build in space some structure that you do not want to transport _in situ_. Along these lines, I would only remark that the usual phrase "to lay down a weld" becomes rather devoid of meaning when "down", itself, ceases to be defined. It seems to me, therefore, that a number of fusion-joining experiments could be justifiably performed in space for their technological value alone.

TRANSPORT PROPERTIES IN FLUIDS

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One of the features of space flight that can be exploited to allow improved measurements of material properties is the drastic reduction expected in density-driven convection in microgravity environments. On earth, convection resulting from density gradients frequently is the dominant mechanism for transport and mixing in fluids. As a result, it prevents the accurate measurement of other transport mechanisms which may be important, but not dominant in experiments done on earth. In a space laboratory, convection resulting from density gradients can be minimized, thus allowing measurement of other transport effects.

Two examples of transport properties are: mass transport, in particular, diffusion in liquids; and heat transport, in particular, thermal conductivity. In measurements of both diffusion and thermal conductivity, the measurement requires the establishment of a gradient (of composition or temperature) and then a determination of the flux (of material or heat energy) resulting from this gradient. While this is occurring, one wants to avoid fluxes arising from other extraneous effects, such as convection.

In the case of diffusion in liquids, it is well-known that special precautions must be taken to avoid convection on earth since one is necessarily dealing with constituents having different masses. Horizontal density gradients cause fluid flow. Thus, they must be avoided, which can be very difficult at high temperatures. There is also the possibility of convection arising from vertical density gradients if these gradients are destabilizing and sufficiently large. What can be done is to arrange to have the denser material at the bottom of the liquid column in which diffusion measurements are being made and to carry out the measurement in thin capillary tubes in order to inhibit convection. Nevertheless, in some cases, it appears that even these precautions are not sufficient. In corrosive liquids, contamination from the walls can affect most of the liquid volume in small-bore capillary tubes.

Convection, especially, may occur where the measurement requires combined composition and temperature gradients, as in thermomigration experiments. To maintain stability against convection in a temperature gradient, the colder and, hence, denser part of the liquid should be at the bottom. On the other hand, liquid alloy diffusion as influenced by the temperature gradient can cause an equilibrium composition gradient to be created in the liquid alloy. For example, if the heat of transport of an alloying element in the liquid is larger than that of the solvent material, diffusion will tend to make the impurity collect in the cold end of the liquid column at the bottom of the column. This condition leads to a stable configuration against convection if the impurity is more dense than the solvent. However, if the impurity is less dense than the solvent, an unstable condition may be created, leading to convection. Such density-gradient-driven convection makes measurement of an equilibrium Soret concentration gradient impossible.

An interesting feature here is that it is not just the linear sum of the density differences caused by the temperature gradient and concentration gradient that must be in a direction to be stabilizing. Instead, the interaction between these two gradients is more complex. For example, a region of liquid which contains an enhanced concentration of light-element constituents may still be more dense than the rest of the liquid if the temperature gradient causes this region to be sufficiently colder than the rest of the liquid. Then, a stable configuration would exist with this region at the bottom of the liquid column. However, if this portion of the liquid were perturbed to rise somewhat in the melt as part of a fluctuation, the stable configuration could be disturbed. Since heat diffuses much faster than matter, this element of liquid could quickly heat up while still retaining its light-element constituents. This would reduce the density of the region below that of its surroundings, leading to a further upward motion and creating density-gradient-driven convection.

Additional complications arise when diffusion in liquid alloys takes place in an electric field. Here the difference in the effective charges of the various constituents plays the same role in setting up an equilibrium concentration gradient as does the heat of transport in the case of the temperature gradient. In ternary alloys, application of electric fields or temperature gradients could make one heavy constituent collect at one end of the liquid column and a second heavy constituent at the other, leaving the lightest constituent predominantly in the middle. In this situation, convection would be very likely to occur in at least part of the column if the experiment were performed in normal gravity.

During unidirectional solidification of a liquid column on earth, similar convection effects can arise. For the temperature gradient to be stabilizing against convection, the liquid is normally frozen first at the bottom and solidification then proceeds up the column, so that the coolest and, hence, densest part of the liquid is toward the bottom. If the light constituent in an alloy melt is preferentially rejected back into the liquid at the solidifying interface, the resulting concentration gradient would tend to be destabilizing. In this case again, it is not sufficient to have the sum of the density differences from the concentration and temperature gradients be stabilizing against density-driven convection. Instead, a more stringent condition must be met in which the coupling of the two gradients must be considered. Otherwise, a fluctuation as described above can cause convection to occur in the liquid.

In the absence of convection, steady state diffusion profiles are formed ahead of the solidifying interface in the liquid. Diffusion coefficients and Soret coefficients, which give the effect of the temperature gradient on diffusion, may be determined from the profiles near the interface. When convection arises, formation of steady state diffusion profiles is prevented. In a space laboratory, density-gradient-driven convection problems found on earth should be much reduced. This will allow better measurement of diffusion and other significant transport effects.

At present, ground-based work is being initiated at the National Bureau of Standards to study convection during plane-front unidirectional solidification in off-eutectic alloys and effects on diffusion profiles in these alloys. Here, the light constituent will be rejected into the liquid for alloys having compositions on one side of the eutectic composition but not for those on the other side. Two other experiments in which liquid diffusion profiles were measured have previously been carried out in space by other investigators. In one, self-diffusion of radioactive zinc in a temperature gradient was measured, and in the other gold tracer diffusing in lead was used to determine convection patterns. Diffusion experiments in liquid metals also are expected to be part of the European space processing program.

Discussion

Question: (Grodzka): During the coffee break we were talking about diffusion and the advantage low g might offer for measuring materials properties. It was suggested that perhaps there is a place in the program for a laboratory in order to get good data, materials properties, and things that cannot be measured too well on the ground such as Soret coefficients and other diffusion coefficients.

Answer: Yes, I certainly agree with that. I think that one thing one should look at is the possibility that one can make measurements in space that cannot be made here on earth. These measurements could be used either for further applications work in space or for applications here on earth. Because if you get rid of gravity effects you can measure quantities much more accurately, quantities that might be masked in measurements made on earth by convection effects.

Question: (Wachtman): Do you consider the measurement of thermal transport--diffusivity on thermal conductivity--in the absence of gravity-driven convection an interesting possibility?

Answer: Yes, I did not talk about it at any length, but I think that is another example of a transport property where you definitely want to get rid of extraneous fluxes. I believe there are situations where you cannot really do that in earth-bound experiments.

FLUID AND COMBUSTION DYNAMICS

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Combustion phenomena which occur at normal gravitational conditions (g = 1) are frequently influenced, or dominated, by gravitationally induced natural convection processes. It is not surprising, then, that g ≈ 0 combustion studies, typically carried out in drop towers, provide observations [1-6][1] that are substantially different from those generally observed at g = 1.

Some combustion experiments at reduced gravitational conditions have been carried out during the past several decades. They have been frequently motivated by the needs for fire safety information for space flight--and constrained by the physical times available (less than 10 seconds, generally) for experimentation.

More recently [6,7], we have come to understand that the most compelling bases for g = 0 combustion studies derive from unsatisfied scientific and societal needs for combustion information that earth-based laboratories have not provided. The central question in combustion embraces an understanding of single and multiphase combustible reactants; steady, unsteady, and oscillatory combustion; flame structure and stability; flame initiation and extinction; and composition and pressure limit phenomena. g = 1 experiments aimed at addressing these questions frequently sustain natural convective energy and mass transport processes which tend to obscure or transform the underlying g = 0 phenomena. g = 1 combustion theory is confronted with frequently intractable representations which must include the complexities of the multiply-coupled transport processes (natural convection-conduction-radiation) with details of chemical kinetics and flow.

Thus, we may be confronted with intractable g = 1 theory, to be applied to three dimensional g = 1 combustion phenomena. The following are the most common approaches to dealing with such difficulties:

(a) The theorist ignores all gravitational effects. Theory is then less intractable. It may or may not represent adequately the g = 1 observations.

(b) The theorist assumes that natural convection is the only operative transport process and that chemical kinetic rates are infinitely fast. Again, theory may or may not represent adequately the g = 1 observations.

(c) The experimentalist attempts to select those experiments (e.g., upwards or downwards flame propagation--but not sidewise) which provide an axis of symmetry for free convective effects. This is not possible, frequently (e.g., flame spread over a pool of combustible liquid, or an array of cellulosic particulates, etc.).

(d) The experimentalist attempts to select those experiments for which free convective effects are dominant over all other transport processes, and for which the "flame sheet approximation" (i.e., infinitely fast chemical kinetics) is acceptable. This is not possible, frequently, particularly for ignition limits and flame propagation limits.

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1 Figures in brackets indicate literature references at the end of this paper.

(e) The experimentalist hopes to attack all problems of compelling theoretical importance. This is not possible, frequently. Consider for example the issues raised in attempting, at g = 1, to create a uniform, quiescent, stationary cloud of combustible particulates. Then to observe one or more of the phenomena of:

(i) autoignition,

(ii) ignition and the transformation to quasi-steady flame propagation, and

(iii) the transformation of quasi-steady flame propagation to extinction.

Such clouds cannot be created and maintained at g = 1. In effect, not all problems of compelling theoretical interest have been found to be "doable" at g = 1.

I believe it correct to assert that we often employ substantially truncated combustion theory in the interpretation of an unfortunately limited range of (g = 1) experiments. It may be argued that limited or not, g = 1 combustion observations are the reality we live with and that g = 1 is the reality we must represent and understand. This may be. But nothing in the latter argument provides guidance as to the best approach to such understanding.

In recent years, a number of combustion areas of experimentation have been identified as promising to provide important insights into the underlying combustion processes for the case where g = 0. It can be argued that g = 0 combustion experimentation, adequately represented and theoretically understood can be used [6] as a basis for better understanding the complexities of combustion where $g > 0$. The Space Shuttle Laboratory could provide the laboratory conditions for such experimentation. A list of some pivotal areas for combustion observations (which may be provided by a Space Shuttle Laboratory and which have not been obtainable otherwise) includes:

(a) single (and two phase) premixed flame propagation and extinction limits over a range of apparatus size and pressures;

(b) noncoherent flame propagation and extinction;

(c) autoignition for large (and/or high pressure) single-phase (or two-phase) premixed combustible systems;

(d) upper pressure limit combustion phenomena and ignition, propagation and extinction phenomena in the neighborhood of upper pressure limits;

(e) oscillatory combustion associated with the hydrocarbon-oxygen and with the carbon monoxide-oxygen systems;

(f) two-phase flame spread and extinction phenomena involving large liquid-gas or solid-gas interfaces;

(g) radiative ignition of solids and liquids;

(h) pool burning;

(i) smoldering of solid combustibles and the associated transition to flaming (or extinction);

(j) laminar gas jet combustion;

(k) coupling (or damping) of convectively-induced turbulence involved in various combustion phenomena; and

(l) transient responses of combustible systems to time variations in gravitational field strengths.

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THE FUTURE FLUID FLOW RESEARCH APPLICATIONS

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The behavior of fluids in a reduced-gravity environment can be different from that under normal gravity conditions. In particular, it can be expected that buoyancy induced flows and sedimentation phenomena would be diminished. These offer attractive benefits for materials processing and crystal growth in space. There are also associated undesirable effects.

The reduction of the gravity level may be a mixed blessing because forces that are normally suppressed can become important. Therefore, there exists other driving mechanisms for convection at reduced gravity such as surface tension, g-jitter, phase changes, and electric and magnetic fields.

It is, of course, essential to understand the physical mechanisms for materials processing techniques in order to utilize all design options to reduce or minimize deleterious effects. Unfortunately, this knowledge is not available even for most ground-based processes. Therefore, a serious research effort in fluid dynamics is required to deal with such complex phenomena that occur in the processing of materials such as convection due to combinations of temperature and concentration gradients with different orientations and convection due to a g-jitter (which is inherent to space vehicle experiments).

Perhaps the most unique aspect of the reduced-gravity environment is that it offers the possibility of containerless processing of materials so that container contamination can be eliminated. There are also other advantages of containerless handling of liquids and molten metals. It, therefore, appears that containerless processes have great potential for new and significant developments in the space environment.

To achieve the indicated technological breakthroughs the containerless technique and processes must be designed and implemented from as much knowledge as possible. Therefore, it is essential to understand that the behavior of liquids and molten metals with free surfaces will be significantly different in a space environment than on Earth. Because the related surface tension phenomena cannot be simulated in ground-based experiments, space flight research on these phenomena is required. There is, as a consequence, very little known concerning the convection induced by thermocapillarity.

A preliminary assessment of which crystal growth techniques would be most affected by the space environment indicated that essentially melt growths would be most different, primarily because of surface tension. Thus, such techniques should receive the greatest emphasis.

The little fluids research done to date that was stimulated by the space program has indicated that it is not convection, per se, that is detrimental to regular crystal growth, but rather the uncontrolled or inappropriate use of convection. In principle, it should be possible to use convection to augment transfer rates, controlling it in such a way that the mass flux rate over the growing crystal is uniform in space and time within prescribed bounds. Such control options are available from related fluid dynamics experience. In other words, space flight is not the only option for control of convection.

Panel Discussion

Question (Gilbert Morris): I have a question for our last speaker. Would you please care to identify some of the hormones and enzymes which are candidate materials? I think this is an extremely interesting subject.

Answer (G. Seaman): One, I think, which I would like to mention first of all is one which in fact has been in the program already. This is the enzyme urokinase which one obtains from fetal kidney cells. This was one of the experiments performed on the Apollo Soyuz NAO-11 batch electrophoresis experiment where embryonic kidney cells were separated into fractions, frozen, brought back to earth, sliced up, and the separated fractions cultured at Abbott Labs in order to identify which fractions were producing urokinase. Urokinase is an enzyme involved in the lysis of thrombi or clots and in terms of treatment of thrombotic disorders, the demands for the enzyme at the moment exceed the production by probably a couple of orders of magnitude. At one time, it was isolated from urine but there were considerable problems with that since it is present in extremely low concentrations in urine; so thousands and thousands of gallons of urine were needed, and it is always sort of difficult to work out ways of getting that. One can go through this sort of general series of examples. Another possible one would be insulin from pancreatic cells. One of the sort of difficulties here is that these are all interesting and worthwhile areas, but the majority of people working in cell biology are unaware of perhaps some of the possibilities which might exist for increasing the yields of these materials.

Question (Joel Levy, Operations Research, Inc.): The question is really to the whole panel but perhaps especially for Dr. Oriani and Prof. Rindone. While we all admit that there are a great deal of basic processes to be solved, one of the problems which NASA is beginning to wrestle with is the question of space industrialization and one of the cornerstones of any movement towards development of industrialization capability in space would be space processing or materials processing. I wonder how the members of the panel feel about the timeliness of such considerations at this time?

Answer (Oriani): Let me have a try at it. I think it is timely to consider such things now. However, the time scale of such events, I think, is fairly long. I certainly cannot estimate it, all I want to say is that we must begin much farther back than attempts to industrialize. We must begin with investigating the phenomena which we can feel fairly confident are, in fact, significantly affected by the magnitude of gravity, otherwise there is no sense in going out there. Wherever one has an equally intensive effort to accomplish a goal, it would be much cheaper to do it on earth than in heaven. Nevertheless, I think it is important to begin to consider these things, and I think it is justifiable that we be here to consider these problems but we must begin with research and scientific insight first.

Professor Rindone, did you want to comment on that?

Answer (Rindone): Well I think it is timely, too. I think it is time that we learned something about the technology of the materials that we are thinking about making in space by actually making them in space and seeing what happens, and I think we have got to do this very soon and then get on to some of these new processes. I am sure, I know industry is very much interested in this because we have talked to people who are not interested in making products right now, but they are more or less interested in understanding some of the processes that they are involved in, and they feel we can do it in space.

Question (Mike Foster, IBM): I was very interested in Gus Witt's comments about transmutation-doped silicon and the progress that seems to be made in Europe. It is certainly a very interesting and intriguing thing and people have been thinking about this for a long time, but there are real problems in trying to commercialize on this sort of thing.

I think a typical single crystal silicon ingot in the industry state-of-the-art is perhaps now 3 inches in diameter and maybe 33 inches long. I am sure the neutron inhomogeneity in a typical pile over 33 inches is greater than the inhomogeneities in getting from the Czochralski of pulling the silicon crystal. The neutron cross section for silicon is, I do not remember, it must be quite low, I suppose it is not over a tenth of a barn. Neutron flux in a typical reactor where it is homogeneous will be about 10^{11}. You go up 10^{12}, you lose quite a bit in homogeneity. You go up 10^{13}, it is very hairy. To put a single crystal silicon of 3 feet or 30 inches long in the reactor, I think perhaps you will have two orders of magnitude of flux variation over the length of that crystal. To get the homogeneous region of 10^{11} to 10^{12}, you have to go where the flux is very low and that is where it is homogeneous. Now, to pick up an order of magnitude in flux, you lose homogeneity so you stay in the low flux region which means that instead of irradiating for perhaps 3 days, you radiate for 30 days. Now, if somebody is selling silicon which they have radiated for 30 days, I think the state is paying for the reactor. Something is being given free. So, I think it is an extremely interesting concept totally aside from radiation damages, which is one of the problems. But this has been looked at here. I do not recall whether it was here at the Bureau or whether it was at the Naval Research Lab, but people are looking at this and it is a very clever way of homogeneously doping small pieces of silicon. But, believe me, if you are going to dope an ingot 3 feet long, I do not think you would do it in a nuclear reactor and expect the homogeneity that you can get now, Gus.

Answer (Witt): I expected you to have some comments along this line. Let me say to the extent that I recall results from Wacker, I believe the radial resistivity variation was less than 2 percent in phosphorous-doped silicon. That means in principle that the capture cross section of silicon is not large. Therefore, the nonuniformity in doping levels is drastically decreased. As far as longitudinal nonuniformity, it is evident that we are not talking two orders of magnitude compositional changes; otherwise, it would not be construed as a viable process. The question is, I think, the core region in the reactor, the size of it, and to my knowledge in Europe, maybe John Carruthers knows more about it, but to my knowledge there is one reactor in Italy, and one I believe in Ireland. The Germans do not do it at the moment. Most of the material goes, I believe, to Italy, and Dow in this country also does the irradiation, but I am not aware of major longitudinal segregation effects, certainly not radial segregation effects. If you want to test device performance, you normally look at a radially uniform slice and forget the rest of it.

Question: Yes, but what about the radiation timing if you are in the center of the reactor. I recall the doping level at about the low 10^{17} will be 100 hours at least. I think the radiation time is something you have to get a handle on.

Answer (Witt): Sure, Mike. I would not know at this time. They are also talking InSb irradiation; they are talking also other systems. John, do you have any input on the radiation times?

Answer (Carruthers): I think this material is not really cost effective below a resistivity of approximately 10 ohm centimeters, which is really saying the same thing that Mike has said--that there is a cost problem but at these low doping levels and for the times involved, the axial uniformity is somewhat better than suggested by Mike. It is certainly not as good as the radial nor do we expect it to be. But the phosphorous-doped silicon is the only material that can be used in large area varactors. For instance, the high power devices that Siemens is using and marketing for AC to DC high voltage conversion and, of course, DC power transmission is a very, very important area and it is one that is not addressed to any large degree in this country.

Question (Mort Jones, Texas Instruments): I feel compelled to comment on some of Gus' remarks. Not that I think you said anything wrong, Gus, but I think you might have left some rather misleading impressions.

In talking about the Wacker silicon, he mentioned that this led to better devices and hence, industry is willing to pay ten times more for the material. Now, it is certainly true that for some very specialized devices where homogeneity is extremely important, the devices are better, but I do not think that one could make a general comment that better silicon means better devices. For example, I would maintain that your SR52 calculator or your Texas Instruments digital watch will not operate any better if the integrated circuit is made from Wacker silicon. Another comment along those lines is that we have a rule we live by in industry that some people in academia may not be familiar with called "design to cost." In its simplest sense, this means that one must look at the cost performance tradeoffs and this is almost always a highly nonlinear relationship. One does not make a Cadillac when a Volkswagen will do. So certainly better silicon or better other electronic materials will, in some cases, make better devices, but I believe it will be a small fraction of the devices made. Another comment along these lines, certainly the yields of semiconductor devices are far from 100 percent, rarely as low as the 1 percent you mentioned.

Answer (Witt): I would dispute that. It is a question of how you calculate your yield.

Answer (Jones): But, I would say 5 percent is probably a better number. Much of that is not lost because, well 30 percent of it is probably lost by saw kerf not due to the quality of the material, in fact I would maintain that the quality of the material is one of the least important causes of loss.

Answer (Witt): I appreciate your comments. Let me try to justify my comment first. What was missing for a long period of time was a confirmation of the fact that if you do have compositionally homogeneous material, then the performance of the material in the devices will be improved. We have been talking for years about segregation effects, microsegregation, transient segregation, facet effects. Industry generally, production industry, took it as an academic exercise removed from the realities of life. To me, it was a confirmation of the basic theoretical concept that if you do have internal strain fields, electrical perturbations, charged perturbations, they must affect the performance of the device. So, I do not want to imply with that statement that we should go to homogeneous silicon for $2000. Industry would never go into that anyway--that is out of the question. But, what I wanted to demonstrate was that the material that we routinely produce is far from being where it could be if we had control over the solidification process.

Question (Jack Wachtman, NBS): I would like to ask Dr. Rindone and Dr. Oriani and anyone from the audience that would like to get into it, to elaborate on the question of nucleation and crystallization. Whether use of the space environment is or is not promising for a study in that field? We seem to have a difference in viewpoint. Perhaps there is a basis for that difference in the behavior of the two classes of materials.

Answer (Rindone): Well, I think that is largely the main difference. We are talking about glasses which are metastable materials; and consequently, the glassy state tends to revert to the crystalline state at the slightest provocation. And, so nucleation phenomena in glass formation is extremely important, particularly if you were looking for unusual glasses which are borderline. The presence of heterogeneous nuclei which would occur at the surface in contact with the container, for example, would certainly and we know for a fact in many cases, do prevent the formation of glasses. There are experiments which are being performed now by levitation means whereby it is possible to produce glasses in systems, calcium gallate systems, for example, where there is no contact with the environment or at least very little contact, that one can produce glasses which you normally could not otherwise.

Answer (Oriani): My remarks were addressed to the idea of studying nucleation per se at zero microgravity instead of at 1 g. What Dr. Rindone is talking about is avoiding nucleation and I have to agree. You avoid contamination and to some extent you avoid unwanted nucleation. But, the point I wanted to make is that to study nucleation per se is a fruitless endeavor at zero g compared to 1 g. The basic reason for this is that the thermodynamics of systems are not modified by going from zero g to one g or vice versa, or any value of g for that matter. Therefore, the driving force remains identically the same at micro g as it does at one g. Furthermore, the nucleation event that is of importance is something that happens in a very, very small space--a composition and density variation which extends at most to 10^{-6} centimeter and that is already a large estimate. So, if you consider what you are trying to avoid by going to zero g, namely the avoidance of Stokes settling so as to know exactly what the composition environment is of the thing which has nucleated, the Stokes settling is only of the order of 2×10^{-8} centimeter per second for something which has a density change of 1 gm per cubic centimeter and has 10^{-6} centimeter diameter which is really a very large thing for nucleation. So, I submit that the important stuff has already occurred in less than a second, so why worry about settling out at 2×10^{-7} centimeters.

Answer (John Carruthers): Just an additional comment, I guess. Do you not feel that the elimination of the containers would assist in providing better experimental data on the nucleation from the liquid to the solid? I think a lot of the original Turnbull experiments were done with small liquid drops which had to be isolated by an organic medium in order to provide a reproducible surface. Those, of course, were of necessity very small drops. Similar nucleation experiments should be done with larger drops and the space environment would allow this by virtue of the containerless aspects.

Answer (Oriani): Well, again, you wish to avoid unwanted nucleation to perhaps study other nucleation, presumably homogeneous nucleation. That is a viable proposition but one has to be very wary. In my own experimental work in hydrocarbon liquids nucleation, I found that it is very easy to nucleate on the free surface, whereas it does not happen in the interior. So, a free surface can be a happy nucleating place even though you have avoided a crucible. There may be cases where, in fact, you might get homogeneous nucleation even though you have a free surface, but I think it would be very rare.

Question (Bill Walton): Professor Rindone, one of the arguments I have heard discussed a few times in glass ceramic work is the fact that the growth and the nucleation of the crystal after it has formed from the glass are at different temperatures and you really cannot optimize these in one g because of slump problems. If you were in low g environment you would have a chance of coming up with a glass ceramic that would have better properties than you would have in the 1 g. Would you comment on that?

Answer (Rindone): Well, I think that is entirely possible--it depends on the system. The ideal glass ceramic, of course, is one where you have a wide separation in a nucleation temperature and the growth temperature so that you can control or tailor the growth in the manner you wish. So, if you have a material in which nucleation occurs at a relatively low temperature and you want to enhance the growth at some higher temperature, then certainly the weightlessness will be a very important factor because then you are not limited in the temperature that you can go to without deforming the substance.

Answer (Oriani): My negative comment on nucleation should not be extended to be negative about studying the growth problem.

Question (Philomena Grodzka, Lockheed, Huntsville): I would like to comment on Dr. Seaman's remarks and that is, which is more important, identifying the material or the technique. Now for biologicals there are a few new techniques on the scene today that have not been adequately explored for their potential in the biological area. In particular, I refer to field flow fractionation and also the Clusius Dikle technique. I wonder if you might like to comment.

Answer (Seaman): I wonder if you could comment on what the advantages of a microgravity environment would be for field flow fractionation. I am not clear on that.

Answer (Grodzka): I will speak to the technique I am more familiar with--the Clusius-Dikle. That is, by decreasing the level of gravity one can go over to larger cell widths and thereby be able to control your convection in a manner that is beneficial. Here, on the ground you are restricted to such very narrow cell widths that you lose control over your convective pattern. So, by lowering the gravity you increase your control over the convection and also the additional benefit of allowing you to handle larger sample sizes. However, both these techniques have not adequately been explored for what their applications might be in the biological area.

Do you have comments Professor Seaman or do you want to pass?

Answer (Seaman): I think it is like a game of bridge, I will pass.

Question (Grodzka): Someone else might want to bid. Jerry Wouch, do you want to?

Question (Jerry Wouch, General Electric): I would like to address a question to Dr. Seaman also. Some years ago when I was doing a survey on float zone refining I realized that a lot of biological materials are prepared by float zone refining, a case in point something like potassium antimony tartrate where they are trying to reduce the amount of lead impurities in using that as a biological support material. Would you care to comment upon the applicability of this process for space processing experiments?

Answer (Seamans): Yes, I would. In fact, I have in my hand the final report of a NASA contract conducted by Dr. Brooks in which he examined the possibilities of this technique for biological materials and if I may quote very briefly the half dozen points he has in here, if that is appropriate, it will take me under two minutes. Dr. Brooks makes seven points for why this method is unsuitable for biological materials. The first one concerns the freezing and subsequent revival of biological cells. He points out there are no procedures known which allow survival of all the cells of any one type subjected to the freeze/thaw procedure. Some types of cells cannot be frozen under any conditions with subsequent retention of viability. Secondly, successful preservation of those cell types which have been found to be capable of surviving the freeze/thaw cycle depends on the presence of prior protective agents. These are, for example, dimethyl sulfoxide, glycerol, and so forth, as well as on the strict adherence to an empirically determined temperature time profile. It is not at all clear that the conditions necessary for cryopreservation and for thermodynamically determined partition at the freezing front are compatible. Thirdly, for freezing front separation to occur, the advancing solidification front must be smooth and free of dendrites. Aqueous salt solutions do not, in general, freeze with a smooth boundary. Additives, therefore, would have to be developed which would eliminate dendrite formation. These additives would have to be compatible with biological cells over a wide temperature range. The fourth point is that very large electric fields generally are found at the solid/liquid interface of freezing aqueous salt solutions due to differences in ion activities in the two phases. It is unlikely that differential partition would occur in the presence of large electrostatic fields since in liquid two phase systems, a phase boundary potential difference of 2 millivolts is sufficient to completely eliminate differential partition effects. Fifth, using conventional geometries, the capacity of a freezing front separation device will be rather low since once the interface is covered by a monolayer of cells, no further interaction between suspended cells and the solid/liquid interface would occur and all cells would be pushed regardless of surface properties. The sixth point is many biological cell separation problems require fractionation of the parent population into a number of subpopulations, each characterized by a set of unique properties. Since freezing front separation can only divide a soluble into two fractions, it is inherently unsuited to problems of this kind. Finally, point seven is that it has not been demonstrated that the difference between the free energy of the cell frozen solution interface and that of a cell solution interface varies sufficiently among various classes of cells to allow separation to be made on this basis. A great deal of work would have to be done to prove this point. So, it goes on and I guess I could add a few additional ones of my own which would include the problems with the changes in composition of the system so that even if we were to have a suitably iso-osmotic system during the freezing process, there would be a change in composition close to the interface where the separation is occurring. So, I think those were the essential comments from his study.

Question (Wouch): Yes, and this would apply to systems that are essentially either living or at some time had aspects of life. What I am talking about is the fact that many biological materials are not cellular at all but are materials, potassium antimony tartrate, are merely materials that have to be zone refined because when they are used as stable binders or as materials for medicinals, there are trace impurities in them that produce very deleterious side effects. And, the amounts of these impurities may be extremely small.

Answer (Seamans): Yes, but are not in fact the majority of the problems solved on the ground. I mean, for example, I have used zone refining and have not felt a need to think about a microgravity environment for most of the materials I have considered. In which group of materials do you think there is a significant problem with other than the organelles, viruses, cells and so on?

Answer (Wouch): Well, the advantages of float zone refining would be the same as the advantages of float zone refining in semiconductors and metals. You can get a larger zone length and you can grow a rod of the materials so if you are producing something--I keep going back to a material like potassium antimony tartarate where apparently that is used as a medicinal and the amount of lead impurities in that has to be reduced to an extremely low level. Now, if you are thinking of zone refining as a production process, as a viable production process, it is obvious that you would want to grow larger diameters of rods and perhaps to get better refining with a less number of passes.

Answer (Witt): I would like to make one comment with regard to float zone refining. I think it is an erroneous basic assumption of yours if you think in the absence of gravity, under low gravity conditions, absence of convection, you have more efficient float zone refining process. The contrary is the case, you have a rapid build up of the boundary layer concentration gradient at your interface and the efficiency of segregation decreases. In other words, segregation decreases, the concentration goes up faster and the purification process is inferior. In other words, float zoning will be much more effective if you have convection than without convection.

Question (Scriven, University of Minnesota): I feel like an almost neutral but not quite neutral cloud, or perhaps a ground fog, and I would like to address the lightening rod, Gus. Gus, to what extent would the Japanese and German research and invention to which you referred have been materially accelerated by experimental studies in microgravity and with what effectiveness in comparison with ground based studies either alone or in conjunction with?

Answer (Witt): I think your question is a very fine one. Let me give you a relatively brief answer, it is in the light of my being provocative. If you want to find out what is going on in silicon processing in industry, for example, if you go the TI System, you are confronted with a door with an armed guard in front of it and you have absolutely no access. That means that the developments of individual corporations in optimizing the growth process are kept certainly away from any discussion. You will never see a TI man talking about the latest in segregation effects on crystal growth or pedestal growth technology. If we had low gravity space experiments, we would be able to study clearer the theoretical background of radial-segregation and we could, obviously, avoid the conditions if at all possible which lead to radial-segregation. Thus, everybody would get the same footing.

Question: I understand the point, but the example you give is germane. That is to say your student has managed in the laboratory, working with a small specimen to reduce, and I presume, to understand the radial-segregation process. The question here is in the last part of my original question--with what effectiveness might one have linked in microgravity experimentation along with, in this case, the ground based study to which you refer.

Answer (Witt): I think you made one statement that I did not make. You presume that the student or either John or myself understand what is going on with radial-segregation in the system where he could reduce it to 2 percent, and that is a wrong presumption on your part. We think we do, but we cannot call that an understanding of the basic phenomenon because if you dope it with another material the situation is entirely different.

Question (Dr. Jackowitz, Merck): Dr. Seaman, a question in conventional biological terms. Do I understand that your conclusion is that at the present time there are no biological materials problems--separation problems--which, in fact, have been identified as requiring microgravity?

Answer (Seamans): This is a question very much to the point. I do not like to act like an attorney, but I think it depends on what one means by "require." I think that there are a number of candidates which have been identified where the probable purity, yield and so forth, could be significantly enhanced by conducting the process in space. What I do not think is clear is how well these procedures would compete with terrestrial activities, because we are certainly, in the case of electrophoresis, dealing with something which is normally done under terrestrial conditions and in the majority of the cases you can certainly obtain a small amount of product. As I mentioned earlier, you can presumably obtain more product by multiplying the number of machines or by devising various techniques to overcome the problem of gravity.

Question (Bob Sekerka, Carnegie-Mellon): I have a question of Gus Witt and I guess it is a two part question, Gus, although the parts are certainly related. I believe you made the statement that convection in crystal growth was the main barrier to a further understanding and that perhaps by going into a microgravity environment one might gain such better understanding. Now, I would be the first to admit that if you could eliminate convection that it is a lot easier just to solve the straight diffusion equations than, say, convective diffusion equation. But, of course, that is not quite what one is faced with even if you go to a microgravity environment or even a zero gravity environment. You are still going to have convection, smaller in magnitude, but much less well characterized than you might have in 1 g and so I would submit that that is very important and one ought to perhaps say that well characterized convection in 1 g might be a lot better for fundamental studies than poorly characterized convection in micro-g. Part 2 to that is that you and, I guess, Harry Gatos have very nicely demonstrated, I believe, in indium antimonide that if you grow a crystal on the earth which displays heavy segregation in bands caused by temperature oscillations related to convection effects, if you grow such a crystal on earth, remelt it partially, and regrow it in space, that you will have an absence of such bands. Now there are two interpretations to that experiment. One is that you can do something in space that you could not do on earth. That is, the space grown crystal is better than the earth grown crystal. I guess the other interpretation is that particular space grown crystal is better than that particular earth grown crystal which you remelted. So, I would ask you and, perhaps, John Carruthers whether or not one can duplicate that bandless crystal on earth, whether he can, and whether in fact one has? I am sorry that is not very well stated. You can not say you can unless you have. If you have not been able to do it, do you think you can do it?

Answer (Witt): I think the two questions are closely related to each other and I will treat them as such. We have been able to analyze the germanium experiment on ASTP beyond the level of the submitted final report and I believe some of you must have seen this appendix to our final report where we make a basic quantitative segregation analysis. Now the evidence that we have, very briefly, indicates that if convection was present it was laminar; there certainly was no evidence in the growth region of 2 cm that we have analyzed of turbulent convection. If laminar convection was present in the system to the extent that we can take the existing theory and apply it, and I will come to that point in moment, we have all the evidence that we could ask for, that if convection was present it did not effect the boundary layer build up and therefore was ineffective in any way modulating the segregation behavior in the system. However, we did find out not surprisingly, although we did not think about it before, that while we have no convection effect, we do have a curved interface, and as a result of a curved growth interface you must get radial-segregation. Since the thermal configuration of the system was basically deficient, we got two transition regions in which we had, from heat leveler to heat stabilizer to a third segment in the multi-purpose furnace, clear interface morphological changes which are readily attributable to the structural elements in the furnace. We can quantitatively determine the growth interface morphological changes and also quantitatively the segregation changes. But these segregation changes are redistributions in the radial direction and do not constitute any interference of any convective effect with the boundary layer build up or propagation. So to the extent that we can apply the theory, we have the evidence that convection, if present, did not interfer with the basic segregation process. In other words, the momentum boundary layer was outside the diffusion boundary layer. Let me come to the other question; namely, can we reproduce the behavior in space. Well, a last comment to the first, namely our analysis, we are talking now a normal freeze equation analysis. Unfortunately, the theoretical treatment was made, as we are all aware, for a step function growth from zero to a finite growth rate at zero time. This is an unrealistic configuration which cannot be realized in any growth system, so the first thing we did--fortunately we had some help from the Bell people--is work on analytical expressions for that. You yourself were helpful in parts and I still have your four pages of double integrals to try to come to a solution. However, an unambiguous application of the theory is not possible for two reasons. The theory is not designed to treat transient growth rates and the two basic constants required to test the theory, namely the distribution constant and the diffusion constant, are uncertain. Thus, a check of the absence of convection within the framework of existing theory and physical parameters has been made and indicates complete absence of convection. In comparison, ground based growth and segregation experiments performed under stabilizing vertical gradients but in the presence of unavoidable radial gradients indicate clearly the evidence for laminar convection and interference with diffusion boundary layer build up. In other words, the initial transient in space grown material is just about the theoretical behavior. The initial region in the ground based experiment is not. It is very flat, and you would reach steady state at the distance of about 2 meters if you extrapolated.

Question (Sekerka): Gus, not having gotten the answer that I expected, I think I did not ask the question accurately. Let me try to rephrase part of it with respect to, for example, a study of radial segregation. I think what you have just shown is that there is a tremendous amount of radial segregation in a space grown crystal; therefore, that is not the place to study radial segregation, but one might better study it in the normal Czochralski situation where by virtue of the rotation you have created a flat and uniform boundary layer. For the second part, when I asked you whether or not you were able to reproduce on earth what you grew in space, I meant that in terms of crystal quality, not in terms of whether or not you could produce anything like the convectionless growth. Can one grow a crystal of the same quality on earth as you did in space?

Question (Witt): In terms of crystallographic perfection?

Answer (Sekerka): In terms of the absence of banding caused by convection effects.

Answer (Witt): You cannot do it on earth. I do not know of any means nor have we ever been able to achieve it. You cannot avoid the presence of laminar convection on earth. Banding you can suppress to about a 1 percent level, you cannot eliminate, the application of transverse magnetic fields reduces turbulent convection to laminar convection and does not stop fluid flow.

I still have just one more comment. On the radial segregation, your comment is very appropriate, but your comment indicates one thing that we never were aware. We have not even thought about the radius of curvature in any way leading to compositional radial gradients on the diffusion control. It is obvious.

Question (Sekerka): I admit by hindsight it is obvious. It is a question of how hard one would have had to think to know that was going to happen.

Answer (Witt): But the point is, Bob, our evidence has shown that one of the things we have to do is achieve interface morphology control through heat transfer manipulations. If you do not have that, forget it.

Comment (Carruthers): Yes, addressing the first question, I think it is clear from the results of the ASTP experiments that we are going to require flat interfaces and that is going to require some additional control over the heat flow in the systems in the absence of thermal convection. By the way, if we intend to do any more eutectic experiments, I believe that we also will require an absolutely flat interface. It will not be acceptable, in my opinion, to do more eutectic growth experiments without that extra caveat. I think perhaps Gus and I would differ on your second question: I think in principle, yes, it must indeed be possible, if we work at it, to grow a crystal with a uniform composition on earth. Let me just state, however, this has to be in principle. If we work with InSb, grown vertically with stabilizing vertical temperature gradients; and then admit that the thermal convection is in the laminar or so-called laminar region and try to damp that down with a transverse magnetic field, it is my opinion that it is, in principle, possible to achieve a completely diffusion controlled segregation profile. However, the problem is InSb is not a material that is commonly used in the semiconductor industry. It is a prototype material used for studies of this type. If we try to do this for silicon, we immediately run into problems or even with germanium which is an intermediate melting material. The problem addresses backwards to the metal crystal growth business where, for instance, soft mold techniques had to be developed in order to grow crystals vertically using the vertical Bridgman technique in order to avoid the problems of: (a) container interaction, and (b) the influence of the container on the deformation and, therefore, crystallographic perfection of the grown crystal. I think it would be safe to say at this point that if one tried to grow silicon in this way or even germanium, that one would end up with powder rather than a single crystal simply because of the container interactions adversely affecting their crystallographic quality. So there are other factors involved here and we focused in on a certain select set of materials. I think that perhaps Gus and I might differ here. I would stress the feasibility of doing things like this without the container present and I think perhaps that may be an important difference.

Comment (Jim Patten, Battelle Northwest): This is more in the nature of a general comment addressed to Dr. Oriani's discussion. Just an observation that many very interesting crystalline non-metallic materials are binary or higher systems and as such they have a two phase solidification behavior; that is, they go through a liquid plus solid region on cooling. So that Dr. Oriani's very perceptive comments about the fundamental considerations in metallic systems and the priorities should really apply directly to those crystalline non-metallic systems also and probably should receive the same kinds of attention.

Question (Lacey, NASA, Marshall): I would like to address my question to Dr. Oriani. I think he is made some very astute comments in terms of model systems, particularly in some of the two phase systems such as immiscible systems, and examining critical phenomena at the microgravity. I would agree that nucleation in such processes are not expected to be influenced by gravity, but there are influences once you nucleate and then you start growing by diffusional processes. You have Ostwald ripening which is very difficult to normally observe on the ground once sedimentation effects start taking place. To me, it is very difficult when you are talking about doing critical experiments in zero gravity to completely separate the nucleation processes from these diffusional processes after you have nucleated and the kinetic processes such as coalescence. I am wondering if you would like to comment on that?

Answer (Oriani): Well I could not agree with you more. The nucleation is a very difficult thing to study, because it is so difficult to divorce it from subsequent growth. But that is true on earth and also true at micro-g. So nothing is aided by micro-g insofar as a study of nucleation itself is concerned. I also agree with you very much that the study of subsequent growth, if you choose the system carefully, could be aided by micro-g environment to avoid the settling out effect you are talking about. I indicated before that my negative comment about study of nucleation at micro-g should not be extended to any negativity on my part about the study of growth.

Question (Lacey): May I have a second part to that question? Recently, we have been performing studies in the laboratory and in a drop tube at the Marshall Center, and I have been persuaded of the opinion that in certain reactions, particularly dealing with peritectic compounds where many of these processes are studied on the earth by using skull melting techniques in order to avoid interactions with the containers of the system, you tend to develop severe gradients across the sample. For the peritectic reaction when you first start nucleating the solid phase, the most likely place that the nucleation occurs is at the cold interface of the chilled block that you are dealing with. Consequently, I feel that gravity plays an important process here. First of all, it feeds the process by a Marangoni type convection, I think, particularly in the refractory type metals. Would you agree that nucleation, homogeneous versus heterogeneous nucleation, in these kinds of systems is influenced by the ground-based techniques, not precisely by gravity, but by the ground-based techniques that we presently use to study such processes?

Answer (Oriani): Well I am not quite sure of the nature of the experiment you are talking about. I would like to answer a bit generally that certainly if you are forced to do a skulling type experiment, that nucleation on the colder interface is bound to be much more probable to the extent that excessive gravity forces you to that stratagem of the skull type of container. Yes, excessive gravity is harmful to that particular study. Nevertheless, I maintain that going to microgravity will enable you only to avoid that particular interface, perhaps by a leviation technique which is easier in microgravity, but it will supply for you a free surface which may or may not cause heterogeneous nucleation. Again, the growth problem is certainly affected by gravity; there is no question about that.

Comment (Lacey): Fine, thank you. I think we are in perfect agreement.

Comment (Jack Lagoski, MIT): I would like to make a comment concerning the electronic materials. The comment is briefly related to the fact that number one certainly does not mean all, and as I think, this number one will not be enough in the future. This number one is, of course, silicon. But, if you look at the physics on this type of materials, what is typical for electronic materials, they are semiconductors. And, what is so fascinating in semiconductors from a scientific point of view is they are sensitive; their properties are sensitive to all possible factors, to temperature, electric-field, magnetic-field, pressure. hydrostatic pressure, anything you like, anything you can imagine. So, if we are dealing with semiconductors, certainly, work does not end with today's electronics. There is no question that in the future we will need these other properties of semiconductors. If you can think of optical communication, certainly silicon is not number one in the future, and we will have to think of this. Also, there is one thing very irritating about these fascinating semiconductors and about semiconductors compounds in that their fascinating properties are studied on more than other materials which are grown up to date; and, there is another point that experiments, some of their experiments, for instance, on InSb or on compound semiconductors, has already demonstrated that in low gravity something can be done to improve the qualities of these materials. Any type of material processing in space, I think has to be directed to what kinds of materials will be important in the future and what kinds of materials will allow us to extend the application beyond what it is possible to do with silicon. Furthermore, this broad range of semiconductors which are not only electronic materials, but which I believe belongs to this group represented by Gus here on the panel, are also active in some other fields. They are also very important catalysts, some of them, and space offers here not only zero gravity but some other possibilities of studies on these materials. One comment--since it happens that I am from Poland--I would like to pass along the information that four months ago an intensive program of space material process was initiated by the Soviet Union and all socialistic countries are engaged in this program. It was done very rapidly, certain committees were formed in all academies of sciences of socialistic countries. Other eastern European countries had to participate also financially, and already some programs were submitted. I am glad to hear that according to information which I have that considerable parts of this program are directed to semiconducting compounds. Of course, it is clear that this crystal growth of compound semiconductors is much more complex; however, as I believe in the future it may be very important.

Does any member of the panel wish to comment on that comment?

Answer (Witt): I agree with your statements. Your information I believe is extremely interesting with regard to the recent developments in the Soviet Union with regard to space processing. I have tried to get some of the results of the sky lab in ASTP experiments to no avail, nothing was available to me. I do not know if we have gotten any of theirs, but they certainly have our results because we are part of the open literature. But I agree with you that there are many other materials. I think a typical candidate in my opinion would be ultimately, if we are talking specific materials, gallium arsenide to be very very specific. If I look at the complications in silicon, the complications in gallium arsenide are much, much higher. We have the uncertainties dealing with stoichiometry, but we also have the increase of thermohydrodynamic perturbations due to the high pressure; pressure problems go up in the case of indium phosphide where we are dealing with about 30 atmospheres where convective effects become even more a problem. I agree, catalysts are equally important.

Question (Wachtman, NBS): Guy, I would like to address a two part question to you. You mentioned the advantages of studying corrosion in a diffusion control rather than a convection controlled regime in the context of corrosion of refractories in glass melting furnaces. Those are relatively viscous melts and one might think if it has value, that is might have even more value in other types of high temperature corrosion where the melts might be liquid metals or slags of lower viscosity, and there would be a greater input from convection or even to corrosion in general. My first question is; do you see the value as being much broader than just in the context of glass? The second part of the question though is: has your committee considered any detailed experiments as to how you would geometrically do this, what other types of flows in the absence of gravity driven convection might arise, and what types of information you would get out that would be pertinent to the earth based corrosion situation?

Answer (Rindone): Well, to answer your first question, obviously, there are many unconventional melts that are very fluid at high temperatures. At the temperatures required to melt them, the convection effects are much more serious than in a commercial soda lime glass for example, where if you bring in alumina, you develop a very viscous coating on the refractory and this, of course, retards the action. So the effects there are not that important. But there are many new systems being explored, as you know. If you heard the speech of the President in the last few days, the glass industry is one of the industries that consumes a lot of energy and we are going to have to go to new systems or new methods whereby we can decrease the energy. Many systems that can be made into glasses are extremely corrosive, but yet they are extremely good systems from the point of view of properties and durability. So, if we can study these systems where the corrosion problem is horrendous, I think maybe we stand a chance to determine what we can do. Now, as far as whether the committee has designed any experiments for doing this at the present time, no.

Question (Phil Klein, Naval Research Lab): The panelists appear to think that the principle benefit from working in space is the microgravity. Nevertheless, the benefits of abundant solar radiation and passable vacuum were pointed out yesterday to us, and we all know about them. Is there any benefit in the minds of any of the panelists in making some adjunct use of solar availability or high vacuum availability in the microgravity experiments, or should one do the best he can to do good microgravity experiments and let the other things come along later? This is my question.

Answer (Oriani): Well, I guess I am as guilty as anyone on the panel in having omitted these other advantages, and I omitted them on purpose. The reason is, you see, that my feeling at the present time is that those features can be duplicated on earth. Admittedly, a 10^{-14} torr kind of pressure is difficult to achieve on earth in large volumes, but one can do it if one works as hard as one would have to, to put up a wake shield facility which will cost at least $20 M, not to mention the cost of the shuttle flight itself. The same thing goes for the solar radiation, so that the only advantage I can see is where both are brought together, microgravity and 10^{-14} torr of pressure. If one could come up with something that really needs that kind of combination, I would be very happy to hear about it and I would like to sponsor that sort of thing myself.

Comment (Witt): If I can just make one comment; I agree with what was just said. There is just one aspect that I took implicit in all considerations, namely the possibility of containerless processing. I do not say that containerless processing is not of interest to the country, I think it is a major asset of space environment, but what I am thinking about is in having containerless processing, you still need melt shaping facilities. They may be partial confinement I personally do not believe that acoustic positioning or any electromagnetic positioning devices will yield the result that we want. My feeling is that we are introducing here body forces which may introduce effects which are undesirable and negate much of the effectiveness of your low gravity environment. But, I may be wrong.

Answer (Passaglia): Acoustics would not be a body force.

Comment (Witt): Well, if you take, for example, electromagnetic positioning, it certainly generates a body force. I think the result of the one experiment where they did acoustic levitation were negative. In other words, the sample, the liquid drop, apparently just moved through the node where it was supposed to be positioned.

Answer (Carruthers): About the vacuum capability, I think it is not clear at this point that the vacuum achievable although the absolute pressures are comparable, that we are talking about the same type of dynamic vacuum at all. The low pressure gas dynamics are considerably different behind a wakeshield traveling at 18,000 mph than they are on earth in a typical sort of standard vacuum system.

Comment (Oriani): The pumping capacity in space is certainly superior.

Answer (Carruthers): Yes, you see what I have in mind here, in addition to that fact, is that the gas pressure dynamics being different could possibly give some enhanced interest to studies of surface physics and chemistry which are concerned with, say, a one knock-on process where, since the space craft is traveling faster than the average velocity of the gas molecules at that orbital level, we can now, in fact, characterize the surface with molecules which can be assured to have only one collision with the surface, and then that is it, there are no multiple collision processes. So, it is possible that if we do some thinking about this that there may be some interesting surface physics and chemistry that we can do in this environment. I am not saying that there is; I am just pleading for some time and thought on that.

Question (Steve Tel, Operations Research): This morning, everyone has been talking about the primary advantage of space processing as being microgravity and to continue on with the last topic, I would like to bring up another area that I would like the panel to consider. That is, the removal of possible harmful processes from the closed environment of the earth. For example, in recombinant DNA experiments in Cambridge, the city has found it socially undesirable to do it on earth. Are there other areas such as this where space processing may offer some advantages?

Answer (Witt): I am not qualified to answer your question, but I would like to just project for a moment. If anything happens on that spacecraft and it somehow goes the wrong way over New York or Boston, I want to be somewhere else.

Comment (Rindone): Well, there are a number of very toxic materials that can be prepared in space under these conditions, as you say, where you have adequate venting which is very difficult to control on earth. I can think of a beryllium fluoride type of glasses, for example, and many materials of this type which have extremely important and good mechanical properties. Also, in the laser glasses, there are many corrosive type glasses which could well be explored up there.

Comment (Oriani): Well, I do not feel competent to discuss the antiseptic qualities of the spacecraft to carry out such things, but I would like to point out the opposite side of the coin--that one should also worry about the pollution aspects of some space processing work, where one may be spewing out large quantities in the near environment, that is 250 km out, which may, in fact, if in large enough quantities, modify that environment around the earth. I know people have worried about this sort of thing too.

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