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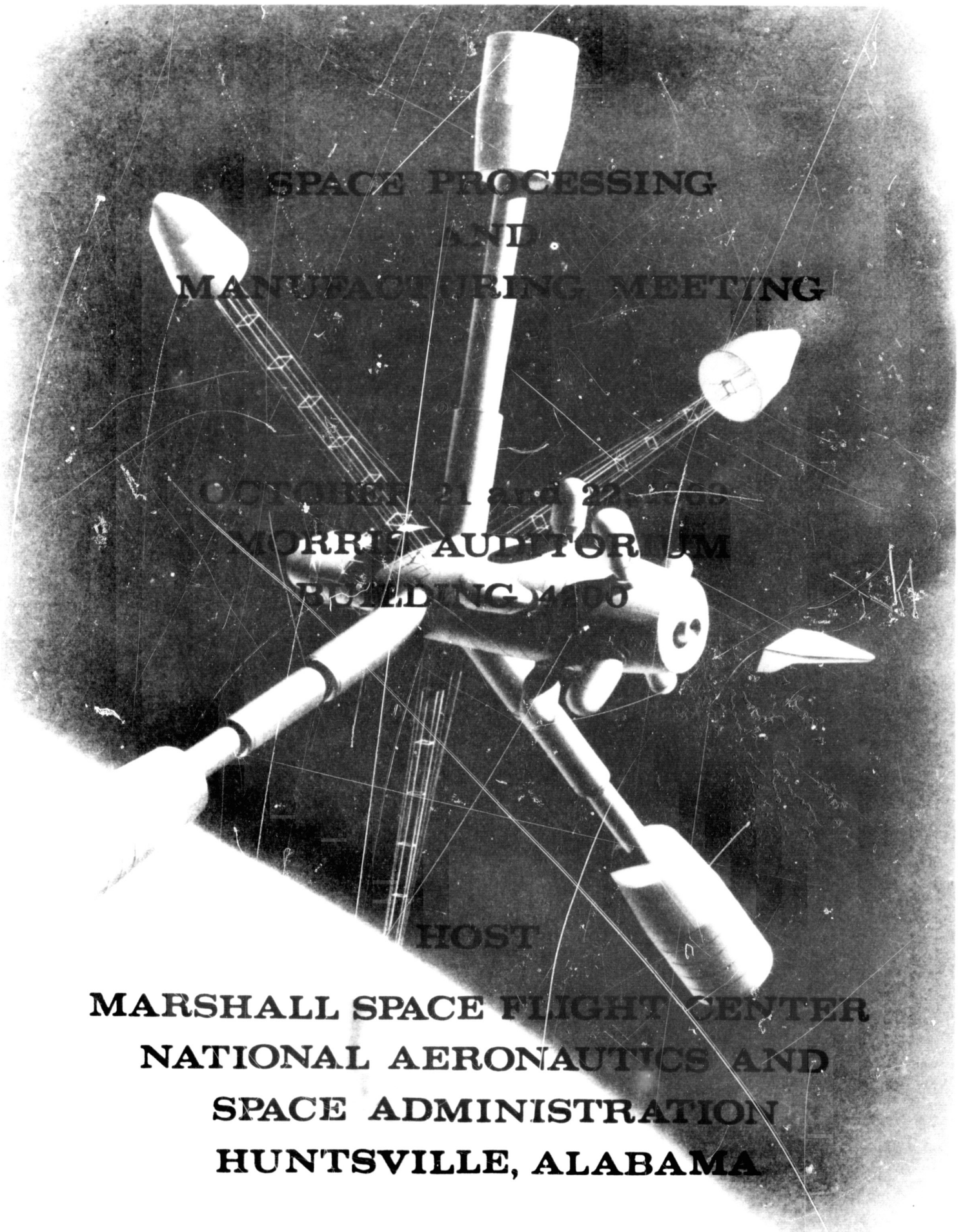
This publication contains the presentations from the Space Processing and Manufacturing meeting held at MSFC, Huntsville, Alabama, October 21 and 22, 1969.

Contents consist of the opening keynote address by Dr. von Braun, Director, Marshall Space Flight Center; thirty-one presentations; and the closing remarks by Dr. M. P. Seibel, Manufacturing Engineering Laboratory, MSFC. In addition, there is a complete listing of the speakers showing their affiliation, mailing addresses, phone numbers, biographical sketches, and a list of attendees.

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SPACE PROCESSING AND MANUFACTURING MEETING

OCTOBER 21 and 22, 1969

MORRIS AUDITORIUM

BUILDING 4708

HOST

MARSHALL SPACE FLIGHT CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

HUNTSVILLE, ALABAMA

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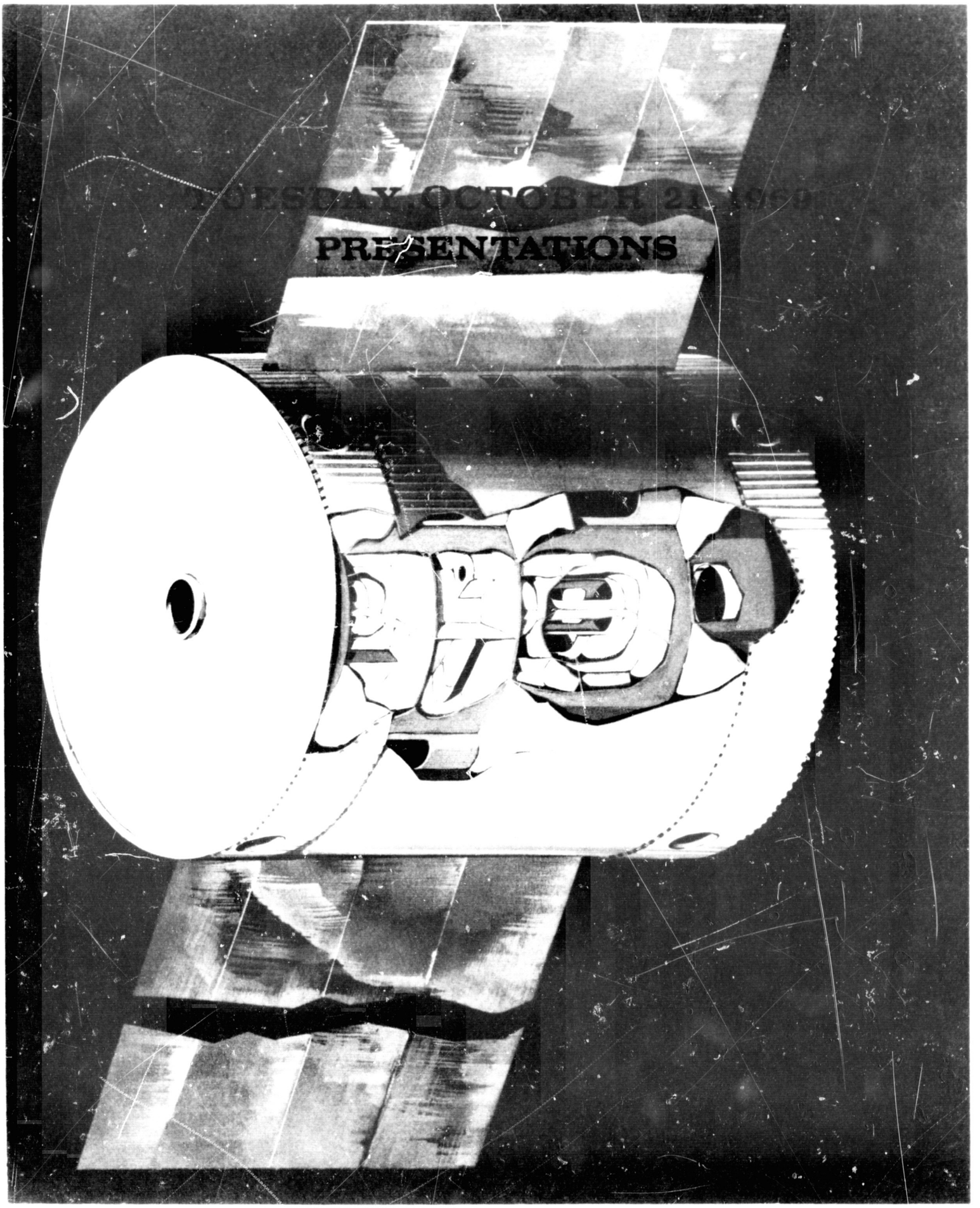
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PRESENTATIONS

OPENING REMARKS

Wernher von Braun

GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA

Good morning! Welcome to the George C. Marshall Space Flight Center. It is a delightful pleasure to welcome you here this morning for our second discussion of one of the most promising space potentials -- one which we think will become a reality in the very near future -- Manufacturing in Space. It seems to be fashionable these days to perform research on manufacturing in space.

We have heard on the radio and television reports of the most recent activities of the Soviet Union in this area, in the series of three manned Soyuz spacecraft orbited a week ago. The news media carried reports that the orbital compartment of Soyuz 6 was converted into a vacuum chamber and one of the Cosmonauts, from a control panel in the command capsule, carried out experiments in welding with low-pressure plasma beams, an electron beam, and a consumable electrode. The results were not disclosed, but the reports certainly indicate that we are not alone in our interest in this field.

Some of you were here for our first exploratory conference on this subject, held in November of last year. Much as happened in space research and exploration since that time. As we now draw near the end of 1969 and the end of the decade of President Kennedy's famous challenge to this nation to go to the moon, we can observe that the individual space tasks undertaken by this nation for the decade of the 60's have been accomplished. In achieving them, we have developed a broad spacefaring capability which opens the door to many new opportunities during the next two decades for further exploration, scientific research, practical applications, and the development of new and more advanced space technology.

As we look ahead into the decades of the 70's and even the 80's the prospects for discovery are, we believe, every bit as exciting as they were at the crude beginning of space exploration more than one decade ago. And the prospects for beneficial returns from space exploration are even brighter, simply because of this broad spacefaring capability that is now ours.

We have developed the ability to place men into earth orbit and on the surface of the moon on a predictable time table. So now we can begin to exploit man's demonstrated ability to live in space and to perform productive tasks in this new environment.

Now you will probably know how your own program, the development of space manufacturing techniques, fits into what is most likely to be the overall NASA program. So rather than spending my time attempting to tell you what you should invent or the ideas which you should originate, I think it will be more useful to give you a simple projection of what we expect to happen in the next few years, and also NASA's long-range projection over the next two decades in the hope that you can then fit your own plans into this overall structure of the space program.

First, we will, of course, continue to explore the moon in Project Apollo, using Saturn V launch vehicles and Apollo spacecraft remaining from the original quota after the early completion of the initial lunar landing. And to this I can make the following general comments.

Back in 1962, about a year after President Kennedy announced a lunar landing in this decade as a national objective, we had, of course, to estimate how much hardware was needed to achieve that goal in this decade. We here at Marshall and our friends in Houston sat down together and finally came up with 12 Apollo/Saturn IB launch vehicles, 15 Saturn V/Apollo launch vehicles for the flights to the moon, and a total of 21 sets of Apollo spacecraft, consisting of command module, service module, and lunar module.

Now you all know that there is still a lot of hardware left over. The reason is simply that we didn't have the boldness, shall we say, to predict back in 1962 that we would fly three men around the moon with the third Saturn V ever to lift off the pad. Our estimate at that time was, rather, that it would take eight to 10 Saturn V's before we would make an attempt to fly around the moon; and with Number 14 we

would finally be able to make a lunar landing, leaving one Saturn V as a backup, namely Number 15.

Things went a lot better than we had anticipated. We had two highly successful unmanned flights of the Saturn V. Then, on the third flight, Frank Borman and his crew made that unforgettable Christmas Eve trip around the moon with Apollo 8. So now, after we have landed Neil Armstrong and Buzz Aldrin on the lunar surface with the sixth vehicle, we have nine Saturn V's left in the inventory.

There are also a lot of Saturn IB's left in the inventory, because we proceeded to fly our Apollo spacecraft earlier on Saturn V than originally anticipated. The same situation applies to the spacecraft. So what should we do? All this equipment has been designed for the specific job of landing men on the moon. It would be prohibitively expensive and time consuming to redesign it for something else. So the obvious decision was to continue lunar exploration.

It was also imperative that we proceed rapidly with the next launches, because our contractor structure in the Apollo program, having completed its limited production job, was shrinking every day. In order to save money, we had to take more and more people off the payroll every year, every month virtually. Clearly, we couldn't fly these complex systems to the moon without a sound backup capability at our contractor plants, not only for supporting the launchings, but to respond to whatever difficulties might arise in flying this fleet.

So it was a question of either doing something right away or mothballing the hardware. If that had happened, all the equipment would have wound up ultimately in a scrap pile, or in the Smithsonian Institution, because there would have been no capability around to fly it.

To determine the validity of this course, we turned to the National Science Academy and asked them formally, "Would it be worthwhile to fly nine more Apollo-type missions to the moon?" The National Academy of Sciences appointed special groups to study the problem very carefully. Their conclusion was: "Yes, it does make sense, provided you do certain things: Number 1, we want you to go to scientifically interesting sites, sites that we, the Science Academy, will designate to you because our experts on the lunar environment think they are of particular scientific interest. Secondly, in order to really enhance the amount of scientific returns from these flights, you must increase the stay-time on the lunar surface."

"Twenty-two hours on the lunar surface, as in the Apollo 11 mission, just isn't long enough. You must increase the stay-time up to something like 72 hours or possibly even 78 hours, with several extravehicular periods and at least two sleep periods in between.

"Thirdly, some of the sites we shall designate to you will be difficult to reach. The terrain will be rough and some will have very poor approach visibility, for example, the bottom of the crater, Corpernicus. So a pinpoint landing capability much better than that demonstrated in Apollo 11 must be available.

"And finally, since we know that some of the sites we want to visit are well nigh impossible to land on, you ought to provide a limited surface mobility so that the astronauts can conceivably land in an adjacent site better suited for landing, and then drive to the science site that we want them to visit. So get us a lunar jeep that can be taken along on the voyage."

These four conditions, then, presented some big "If's". We found that these conditions could be met, provided the descent stage tanks of the lunar module were enlarged. This, of course, would enable us to carry a larger payload down to the lunar surface. This increased capability could be converted into more hover time, meaning better ability to land in rocky terrain or to correct for approach mistakes, thereby, improving the pinpoint landing capability. Or it could be converted into more scientific equipment, the lunar jeep, or more consumables, which would mean longer stay-time.

The increased descent stage tanks for the lunar module meant that the Saturn V had to carry a heavier payload to the moon. Now fortunately, by just flexing its muscle a little bit, the Saturn V could do it. Whereas Apollo 11 has an injection payload of about 102,000 pounds, later missions will have an injection payload of 106,500 pounds.

Because we have other ambitions in space, in addition to lunar exploration, during the last few months NASA has formulated what we call an integrated, balanced space flight program -- not only for the next 10 -- but for the next 20 years. This balanced program will have three major characteristics. One will be maximum reusability of equipment. By that I mean, this business of discarding stages and modules in the Atlantic or in space after a one-time performance just has to go if we

make space flights more economical. We must develop a fleet of space transportation vehicles that hopefully can be reused over and over again.

The most important element in this array of new vehicles, which should be developed during the 70's, will be the reusable earth-to-orbit shuttle. Its design and development will probably become the main thrust of our space program, beginning even this fiscal year. Studies conducted jointly with the aerospace industry clearly indicate some of the space shuttle's main characteristics. First, the engines will burn liquid hydrogen and liquid oxygen, both in the first and the second stages. Secondly, it will clearly not be a single stage vehicle, but a two stage vehicle. All our studies indicate that single stage vehicles are so demanding with respect to the structural factors that a minor mistake in estimating the structural weight may mean that you lose your entire payload. And we are just not far enough in our technology to really predict the structural weights with the necessary accuracy. Finally, we have decided that all schemes that try to throw away only so-called cheap parts such as tanks, or dumb boosters, etc., simply cannot compete with a fully reusable system that recovers everything.

There was a great deal of discussion a half year ago on proposals to make the booster as dumb as possible, to put anything that cost money into the front end and recover it in the spacecraft; but unfortunately, if the booster is dumb enough to be cheap, it becomes absolutely impossible from a weight standpoint.

For example, studies showed that a very simple crude material in a solid-boosted first stage made the whole thing so heavy that the squeeze was immediately on: "Can't we make it a little lighter?" As soon as we start to make it a little lighter, it becomes more sophisticated, consequently far more costly. The same penalties apply to tip tanks and similar approaches. So our reusable space shuttle will be a full-fledged reusable vehicle, with both first and second stages recoverable.

Whether the first stage will be manned or flown back like a target drawn to the launch base remains to be seen. The latter may indeed be the case. The top stage, of course, will be manned. The turn-around time on the ground will be minimized because such vehicles, just like an airliner, can be economical only if you really keep them flying. They lose money while sitting on the ground -- so turn-around

time must be shortened. We will make a very major effort to simplify checkout from the cockpit, utilizing as much as we can of our present sophisticated automatic checkout technique at the Cape, but putting most of the equipment into the craft itself for checkout in orbit prior to return.

Another major element of our space transporation system will be a space station module. I am not talking about the dry Saturn V workshop, a modified S-IVB stage which will be completely outfitted on the ground, then put on top of a Saturn V and flown into orbit fully equipped, even with provisions for an extended period of time. This, of course, will be our first generation space station; but thereafter, we want to develop a space station originally designed for that purpose. The second element in our program will therefore be a space station module, designed in such a way that it can always serve as an element of a space station or as a single unit, for example, as a small space station in geo-synchronous orbit, or for a small base camp on the lunar surface, or even as an interplanetary spacecraft for the long interplanetary trip to the planet Mars.

And thirdly, there will be a smaller vehicle in the program called the "tug", a hydrogen/oxygen powered vehicle that can, for instance, do what the lunar module does: descend to the lunar surface and fly back to lunar orbit, but in such a way that it can be refueled again in lunar orbit to make this trip many times.

And finally, we will have a nuclear-powered shuttle vehicle in the inventory that will use the NERVA engine. It will have the multiple capability of flying, for instance, from earth orbit to a synchronous orbit and back to earth orbit to be refueled there; or it can fly from earth orbit to lunar orbit and back to earth orbit to be refueled there; or it can even be used as a stage in an interplanetary expedition, say, to Mars. This nuclear shuttle will probably be at the end of this program simply because for years to come most of the money for this particular reusable vehicle, the nuclear shuttle, will have to go into engine development itself. These four elements will give us the space capability for years to come.

In addition to reusability, one other factor that all four items will have in common is commonality. Instead of optimizing stages and modules for each particular flight mission in the future, with these four pieces of equipment we can really cover the waterfront. Whether you want to go to the moon or into synchronous orbit, manned

or unmanned, or fly to the planets, or reduce the cost of going to the moon, here are the four elements that can do all that. And, of course, out of commonality and reusability will hopefully come the magic formula for the future for a more economical space program.

This brings me right back to your challenge here for the day, the development of space manufacturing techniques. It is, of course, quite clear that no matter what you are trying to do in space in orbital manufacturing, that it can really become of practical economic significance only if we can drastically slash the transportation costs to orbit. Today it still costs more than $500 to orbit one pound of payload. We have reasons to believe that if the traffic for this re-usable earth-to-orbit shuttle, which will serve as a logistic supply system for the first and second generation space stations, can be increased, it will be able to fly one pound into orbit and back for as little as $50. In fact, if the traffic develops a little better than presently projected, this cost may even come down to something like $30 per pound in orbit.

Now what I told you here today about the projected space program is not what I hope will come to pass, but is actually what President Nixon's Space Task Group has recommended as a national posture for the future. You will remember that the President appointed this Space Task Group in February of this year and instructed it to recommend to him by the first of September what the country's major space objectives should be for the next decade and beyond.

This Space Task Group was headed by Vice President Spiro T. Agnew. Members of the Task Group were: NASA's Administrator, Dr. Thomas O. Paine; then, sitting in for the Secretary of Defense was the Secretary of the Air Force, who was also our former Associate Administrator of NASA, Dr. Robert C. Seamans; and finally the Scientific Adviser to the President, Dr. Lee A. DuBridge. There were also three observers on this Space Task Group: Dr. Glenn T. Seaborg, Chairman of the Atomic Energy Commission; Mr. Robert P. Mayo, Director of the Budget, a very important man, of course; and finally Mr. U. Alexis Johnson, Under Secretary of State for Political Affairs, whose main function there was to appraise the international impact which the space program might have.

This Space Task Group unanimously adopted this integrated and balanced space program that I explained to you which, by the way,

includes a lot of elements that I did not mention, namely, unmanned space exploration and unmanned applications programs in fields such as earth resources, etc., which, however, do not require new modules for development. The Space Task Group has recommended such a balanced program to the President.

You probably have heard that it has also mentioned a manned Mars expedition. The Mars expedition, however, is recommended by the Space Task Group only as a long term objective, not as an immediate program commitment, and it has said specifically that the target date set for this ultimate objective would be a governing factor in the pace that the President wants to establish for space exploration in the future. In other words, they told the President: "This is the balanced program that we recommend. Now the pace at which you wish to pursue this program will depend on what you think you can allot to the space budget after looking into all the competing national objectives. If you think we cannot rapidly increase the funding again to something like the level that we had at the peak of Apollo, then we shall have to stretch out the objectives in time a bit, including, of course, the planetary landing. Or if you want to retain or increase the momentum further, then here is another option: put more money in a little sooner."

The Space Task Group has presented the President with a variety of choices, ranging from the fastest possible program to the slowest possible program. The fastest possible program would not be limited by funding, but only by the rate of technology's advance.

In other words, there is no point in going beyond a certain rate of funding, simply because basic technology wouldn't be available on time to support some of these new objectives. This high level of spending was considered unrealistic, considering the demands of other domestic programs and international commitments.

The slowest possible program would lead to increased unmanned science and applications efforts, but manned space flight would have to be discontinued because of the low level of spending. This would mean surrendering outer space to the Soviets.

Now, in between these two extremes there are three realistic options: one aggresive course, a conservative one, and one somewhere in the middle. It is now up to the President to decide which of these options he will select. The options that the Space Task Group prepared for the President do not vary in content or objective, only in rate -- the rate of speed and rate of funding.

Our earth orbital capability plays a very major part in all these options and for that reason you can count on the availability of orbital laboratories that will accommodate people for an extended period of time. Even with the dry workshop, to be flown on the Saturn V, we are now seriously talking about extending the stay-time of the crew in the third revisit to as much as 120 days. The first visit will be 28 days, the second will be 56 days, and we are presently looking into the implications of stretching the third one to 120 days. Now that's a long time -- that's four months in a row -- and this time period will enable us to do a lot of very interesting things in your field.

And if such a station is now logistically supported with a reusable vehicle which reduces earth-to-orbit costs by a factor of 10, we will really have an interesting environment to do some of the things that you may have in mind.

So, if in the past you perhaps limited your thinking solely to very small and lightweight parts, such as miniaturized electronics or turbine blades, etc., that can possibly be mortgaged for orbital transportation costs, I think the chances of improving this picture to make orbital manufacturing available for even heavier things is quite good.

When will you have this capability? Well, I think even in the Saturn V Workshop we are still looking for more interesting experiments. When we made the decision to move the first workshop, the first rudimentary space station, from a Saturn IB, where a tank used to accommodate liquid hydrogen for the ascent was to be converted into a living room in space only upon arrival in orbit, to a dry workshop, equipped on the ground before launch with all the provisions, all the equipment, and a completely checked-out power supply and data system, launched as a dry payload on a Saturn V, our payload carrying capability increased greatly.

With our increased space capability we can now accommodate much longer stay-times and orbit heavier payloads, so if you want to add more weight and have more ideas for space manufacturing experiments for the dry Workshop, let us know. We shall probably have not only one dry workshop, but two, so if we can't accommodate an experiment for lack of leadtime in Nr. 1, we will very definitely consider it in Nr. 2. So, the climate has never been better for realizing your objectives, and we are really eager to hear your ideas on what we should do with all that new capability in space. Good luck for your conference!

N70-20518

EARTH ORBITAL PAYLOAD PLANNING

William O. Armstrong

OFFICE OF MANNED SPACE FLIGHT
WASHINGTON, D.C.

ABSTRACT

Processing and manufacture of materials in orbit is shown as one of the more promising elements of future earth orbital payloads. Plans for including it in the experiments program of the next decade are outlined and compared with preliminary planning for flight programs in this period. Space vehicles such as the AAP Workshops, the Space Station and the Shuttle are described and related to program planning for processing and manufacture of materials in orbit. Some of the major milestones in the evolution of such a program are also described. Industrial organizations will be responsible for a major part of this effort; therefore, procedures for soliciting and selecting industrial inputs are reviewed and some policy guidelines related to funding and proprietary rights of involved industrial organizations are considered.

INTRODUCTION

The United States declared its determination to lead the world in space technology at the beginning of this decade and has carried it out by a tremendous program of flight technology development in the 1960's. Our success has been demonstrated

by the Apollo lunar landing, the Mariner Mars missions, and many other accomplishments.

To maintain and extend the leadership we have gained, we now need to consolidate the last decade's technological advances by applying them productively, for space flight's long-range future depends on its paying its way by dividends in terms of scientific knowledge, direct economic benefits, and security-related technology. To secure such dividends, we shall need to carry out substantial developmental and experimental efforts in the coming decade.

POTENTIAL FOR MATERIALS PROCESSING

Lately it has been pointed out that the weightless conditions in an orbiting spacecraft offer some unique advantages for work on materials and processes that can yield valuable returns in all three of the areas mentioned above. Part of this idea's appeal comes from prospects for producing materials in new forms, but much of it also comes from the fact that some processes carried out in zero "g" may add enough value to their raw materials to enable space operations to show a profit. Interest in these prospects has been lively; a number of potentially useful processes have been identified, and Government and industry teams are currently evaluating them.

Some of these processes are listed in Figure 1; since other papers at this meeting will discuss them in detail, only a few comments will be in order here. Most of these proposals concern processes in metallurgy: either the familiar kind that deals with metals or the sophisticated new metallurgy of semiconductors and other electronic materials. The chemical field has been explored much less, and so far the only definite proposals seem to be to exploit the advantages of weightlessness in physical methods of chemical separation that are important in biological processing.

It seems clear that this is only a beginning, and we feel confident that many other areas of interest for industrial application have yet to be identified. If the field develops as most other technologies have, we can expect that the most valuable and far-reaching ideas will be uncovered after research efforts are well under way, and by active workers in the program. The major purpose of this meeting is to arouse your interest and solicit your participation in exploring this promising new area of science and technology.

SPACE FLIGHT PROGRAM PLANNING

We have talked briefly about the significance of a program for materials processing in space. This leads to a natural question from any of you interested in this kind of activity; what flight programs and mission capabilities are being planned over the next decade suitable for this type of research? As you fully realize, our future space effort is highly dependent on the national interest and availability of funds to carry on this exploration. However, we in NASA are optimistic and are planning a very aggressive program of space activities in the seventies.

A schedule of earth orbital missions in the manned program as developed in the plan for an "Integrated Space Program for the 70's" is shown in Figure 2. The current plan for the Apollo Applications Program (AAP) calls for launching a ground configured Workshop (shown in Figure 3) unmanned on a Saturn V vehicle in mid-1972. The orbit will be at 270 mile altitude and moderate inclination angle. This is followed by a series of three manned logistic launches to permit occupancy of the Station for periods of nominally one month, two months, and two months respectively. The exact sequencing and time phasing of these launches have not been fully established but intermittent periods of dormancy are planned.

The Station is designed to accommodate a crew of three and, as shown by Figure 3, the crew is quartered in the basic Workshop. Sufficient expendables are launched with the Workshop

to accommodate the entire mission sequence. A docking adaptor is provided for docking the CSM with the Workshop during periods of manned operation.

The mission is intended to extend the period of astronaut exposure to zero "g", verify his compatibility with this environment, evaluate the suitability of the design of his surroundings and carry out a number of significant scientific and technological investigations. Major experiment areas are

medical evaluations,
habitability & crew performance studies, and
ATM solar astronomy.

Included in the experiment complement of the Workshop are the M-512, Materials Processing, investigations described later in the paper.

Current planning considers following the first Workshop with a second one launched in early 1974. This Workshop would be the same basic configuration as the first but with new and improved payloads. Planning calls for at least four manned logistic missions spaced at 90-day intervals to support the program. The second Workshop is planned to be continuously manned with a crew complement of three and will be designed for an operating life of 12-18 months. It would operate at an altitude between 210 and 270 miles at an inclination up to 55°.

Payloads for this program will emphasize the experimental facility approach with the idea that NASA will provide basic research laboratories available to participating scientists and engineers to carry out investigations of interest and value to the various disciplines.

Major payload elements for the Workshop may include:

A follow-on ATM Astronomy Module
An Earth Resources Package

A Modest Hi-Energy Physics Lab.
A Life Sciences Payload

An improved facility for materials processes research is also planned for this program.

Work will also have been initiated to develop a Space Station for launch in 1975. This would be the initial vehicle which serves as the basic building block for assembly of a space base available for use by the end of the decade. A fully operational space base would be capable of supporting up to 100 men of various disciplines, including scientists, engineers, and technicians.

The Space Station (conceptually illustrated on Figure 4) considered for this period is significantly more advanced than the Saturn Workshop. Our goal is to establish a multi-purpose, general use station capable of satisfying operational objectives in a variety of disciplines. It is intended for long life (5-10 years) and will be designed for in-orbit check-out and maintenance. Flexibility and adaptability will be attained through a modular approach as illustrated on Figure 5. Modules would be developed as living quarters, command and control stations, basic subsystem modules and experiment modules. In this way we hope to obtain a level of versatility, adaptability and safety suitable for the type program planned for the late 70's. With this design concept, it is expected that the Space Station modules would be adaptable for build-up of an earth orbiting space base, a geosynchronous station, a lunar orbiting station and ultimately a spacecraft suitable for interplanetary travel.

A major part of the earth orbiting program in the late 70's will be devoted to scientific, technological and applications experimentation. The experiment modules planned for the station are designed uniquely to support investigations in various disciplines. These modules may be segments of the basic station as illustrated in Figure 6, or free flying as shown in Figure 7.

If we are to maximize the benefits afforded by a space station, however, it is essential to reduce costs associated with transporting payloads to orbit. Recognizing these needs, the Space Agency has set as a paramount goal for the 70's the development of a cheap transportation system to orbit—the Space Shuttle. Today it costs from $500 to $1500 a pound to launch payloads to orbit. With a space shuttle it is hoped to cut these costs by at least an order of magnitude. To achieve this cost reduction, the shuttle would be designed for reusability much as today's modern jet liners are.

A number of alternatives are currently under investigation and several aerospace organizations are studying the problem. Based upon these studies, the more promising configurations would be carried into a Phase B evaluation. An example of such a vehicle is shown in Figure 8. It consists of two stages—fully reusable. The operational concept of such a system is shown in Figure 9. The initial stage would launch the spacecraft and, upon depletion of fuel would return to base. The second stage would continue on to orbit and deliver its payload. Once in orbit, it would rendezvous with the Space Station, off-load its payload and pick up return cargo. The shuttle would then separate from the Space Station, de-orbit and return to base where it would be readied for a subsequent mission.

Our planning calls for development of such a system for flight by 1975 (Figure 2). As flight experience is achieved, scheduled operation would increase as shown in Figure 2 until, by the end of the decade, flight frequencies approaching 100 per year would be attained.

PROGRAM DEVELOPMENT FOR SPACE PROCESSING OF MATERIALS

We can now begin to define a program for space processing of materials utilizing this capability, based on the earth orbital planning outlined above. Since we are only beginning in this new

field of endeavor, our program must allow for an orderly evolution from basic research through exploratory investigations of potentially promising processes to eventual commercial production of economically feasible products. The flight program also must be coupled with a substantial effort in ground-based research and experimentation, particularly in the early phases, and should involve the support of Government and university groups, as well as industrial organizations.

Within NASA, close coordination has been established between Manned Space Flight and the Advanced Research & Technology Office, and we are jointly sponsoring effort directed toward a common program in this area.

Although no detailed program plan has been developed as yet, Figure 10 outlines a general approach we are considering. As indicated on this chart, a number of contracted and in-house studies are already under way to develop better understanding of processes affected by gravity and to determine the interests of industrial organizations in space processing of materials for commercial application. This work is outlined in more detail in the next chart (Figure 11). As shown on this figure, our effort encompasses a broad range of activity including: 1) theoretical research; 2) investigations of specific processes sensitive to a weightless environment; 3) surveys of industrial organization to establish their needs; and 4) studies leading to design of a flight facility for investigations in space.

Preliminary experiments in the materials processing area are planned for the first Workshop. Much of our current effort is directed to the definition and development of these experiments for flight. Our present activity is quite limited, however, and the facility available in which to carry out these studies is modest. A schematic of the Workshop processing unit is shown in Figure 12. It consists basically of a chamber to provide a safe and evacuated space in which to conduct our studies. In addition, it is equipped with a control panel, a power supply, and a number of experiment packages to study various processes in

flight. Figure 13 lists the various experiments planned for the missions. Papers to be presented later in the conference will discuss both the facility and the planned experiments in more detail. A number of papers also will review in depth many of the supporting studies noted earlier.

These flight experiments and supporting studies should provide a substantive base from which to progress into a more ambitious effort on the second Workshop. It is unlikely, however, that we will have reached a point where commercial application is a reality. Rather, we think it will be necessary to continue our exploratory effort through more ground-based studies of promising processes and development of flight experiments to verify concepts. This is how we have structured our program approach as shown in Figure 10. We would expect to handle more complex processes than on the first Workshop and allow verification of certain techniques proposed by industrial organizations which may have commercial application. The flight facility envisioned for this phase would be improved and more versatile than our initial chamber. It probably will consist of several elements for positioning, heating and processing materials, for growing crystals, and for blending of composites. Hopefully, it will be capable of accommodating experiments developed late in the program and carried up to the Workshop on resupply missions.

By the mid-70 time period when the Space Station becomes available, we should have progressed so that we can identify processes that are commerically attractive. A major share of the responsibility for determining and developing these experiments and processing equipment should be assumed by industry.

NASA plans to provide a capability for carrying out investigations of industrial processes both within the confines of the basic station and later in a detachable module. It is doubtful if either the funding or the technology will be available to provide an independent module for operation at the beginning of the Space Station program. Rather, it is expected that a more advanced

facility, evolving from our previous chambers, will still be of value and provide the necessary continuity to bridge the gap between the second Workshop and a separate module. Thus, in our program approach we have included a third generation space processing laboratory, integral to the Station for continuing materials processing studies. Since the Space Station will be functional for five to ten years, this laboratory should maintain its utility for an extended period of time. It need not become outmoded when the Space Manufacturing module becomes available and should be designed with sufficient flexibility to allow updating and expansion in orbit. Space processing equipment could then be developed and delivered well downstream of program initiation for use with this expanded facility (shown by the hatched bars on Figure 10).

By the late 70's we should have acquired sufficient experience to justify deployment of an independent module for space manufacturing. It would be capable of supporting commercial production of economically feasible products growing out of earlier investigations. A concept for such a module is shown in Figure 14. It could be operated either attached to the mother ship or separate in a free flying mode when environmental conditions for certain processes dictate. This module might be thought of as our initial plant or factory in space, utilized by industry for profitable operation. Initially it would be Government-owned and operated, leasing space to industrial organizations for their special needs. Ultimately it, or facilities like it, could be privately-owned and operated much as COMSAT is today.

INDUSTRIAL PARTICIPATION

I have briefly reviewed some of our future planning for earth orbital missions and outlined a program approach in the area of materials processing. This gives rise to a rather obvious question of interest to you. What is the mechanism by which industry becomes involved in such a program and submits ideas for investigation?

Precedent does exist in NASA for soliciting participation in the science area. Where opportunity exists for flying various classes of experiments on a planned space mission, the Agency issues what is called an "Announcement of Flight Opportunity" (AFO). The AFO is issued by the responsible Program Office as an open invitation to any qualified participant wishing to submit a proposed investigation for flight.

As briefly outlined in Figure 15, the AFO describes the type of mission being planned and defines the characteristics of the space vehicle on which the investigations would be flown. Sufficient detail would be included so that a potential investigator could determine whether or not there is general compatibility between the planned mission and the research contemplated.

Since a variety of science, applications and technology disciplines will be studied in the earth orbital program, the AFO would identify the category or class of investigations being solicited. For example, since future lunar missions afford an opportunity to conduct research in lunar orbit, an AFO was issued to the scientific community requesting specific proposals for lunar orbital science experiments.

Major milestones leading to experiment development and flight are identified. Dates for such major events as submission of proposals, anticipated time for experiment selection, delivery of flight hardware, and planned flight period would be specified.

Finally, instructions for preparing and submitting proposals would be included. A specific form has been developed by NASA for this purpose. (Experiment Proposal, NASA Form #1346) The form is not described in this paper, but interested organizations can obtain copies of this form from the forms distribution offices at NASA Headquarters or MSFC.

Manned Space Flight is expected to adopt the AFO approach for soliciting proposals for materials processing investigation on future missions. If approval is obtained for a second

Workshop mission, an announcement of flight opportunity would be issued to interested organizations some time next year.

Assuming an organization submits a proposed experiment for flight, one would then logically ask, "What procedure is used by NASA in the selection of proposed experiments for flight?" Figure 16 schematically diagrams the major steps followed in this selection process. As shown here, the activity is initiated by issuance of an AFO. Upon receipt of a proposed investigation, the Program Office would transmit it to a Field Center (MSC, MSFC, etc.) for evaluation both in terms of technical content and applicability to the experiment program. Similar reviews also would be carried out by competent people within the Program Office. Upon completion of these reviews, recommendations for either selection or rejection of the proposal would be made to the Program Office. It is the responsibility of the Program Office to decide from among the experiments.

In most cases, experiments selected will go through a period of definition and assessment for flight compatibility prior to submission of the proposal to the Manned Space Flight Experiments Board (MSFEB) for review and approval for flight. It is the function of this Board to give final approval for flight of selected experiments. Approved experiments would then be assigned to a Flight Program Office (AAP, Apollo, etc.) for development and implementation.

A final question of interest to you relates to NASA policy for funding development and flight of materials processing proposals and the rights of the proposing organization to treat acquired data in a privileged or proprietary manner. This question is currently under review by our legal, procurement, and industrial relations staffs. No formal policy has been established yet; however, our objective is to encourage private utilization of our space capability. To this end we would adopt a policy as liberal as is practically consistent with public interest in accommodating industrial involvement.

In a real sense, it may not be practical to establish a fixed policy because of wide variance in each situation. Therefore, Government-industry relations will probably be established on a case by case basis, and the needs of industry will have considerable influence on what agreements are reached. So far, our review of Government-industry relations in space manufacturing has concentrated on developing preliminary guidelines on the basis of the existing precedents. Only general guidelines are possible at this stage, because of differing circumstances. However, to illustrate how our objective might be approached in some specific cases, we have selected four categories of possible industry-Government relations for discussion in this paper. These are outlined in Figure 17, which lists the important characteristics in each case and shows what policies and precedents could be applied.

The first category is representative of most experiment activity currently undertaken by NASA. Proposals are solicited for technical work in accordance with a work statement expressing ideas that originated within the Government or from a source having no proprietary rights in such ideas. A contract is let to the best-qualified bidder in a competitive selection, and all experiment definition, hardware design, and flight experimentation is funded by NASA. For this situation, policy has been established which grants the investigating organization undisturbed access to all data derived from the experiment for a specified period. Terms for such access are negotiated in the contract with the investigating organization. At the end of this period, results must be published for general distribution, and use and rights to all data and inventions are retained by the Government.

The second category considers a case where a private organization has conceived a promising idea and performed a certain amount of research on it, using private funds. Believing that the idea would be appropriate for space experimentation, the company submits an unsolicited proposal for NASA for support; justification is established for a sole-source procurement, and NASA grants a contract to the company for experiment develop-

ment, flight, and reduction of data.

In this case the company enters on its contract with a certain amount of equity in the basic idea, and its unique competence for further development is recognized by the sole-source procurement. Whatever proprietary rights were generated by its prior research will remain secure under any NASA contract because the National Aeronautics and Space Act does not require public ownership of background rights. Whenever such proprietary rights are to be obtained by NASA, they must be acquired by specific negotiation. With respect to rights in data and inventions resulting from the work done under contract, however, the sole-source contractor will be in much the same position as the winner of a competitive procurement. Private patent rights can only result if the Administrator of NASA finds it in the public interest to waive ownership, and in that event the Government retains a royalty-free, nonexclusive license to practice the invention.

In the third category we consider the case of a cooperative agreement involving substantial private investment. A private company conceives a promising idea for space manufacturing and desires to retain the fullest possible rights in development information and any resulting patents. It therefore proposes to develop a flight experiment and build the necessary apparatus, using its own funds, with NASA having the responsibility for integration and flight of the apparatus.

It seems probable that arrangements striking a satisfactory balance between public and private rights can be made for this class of activity. It should certainly be possible to make arrangements whereby the industrial participant would perform no work for NASA except tasks relating to vehicle integration and the like, where the proprietary idea would not be involved. On the other hand, NASA would always have some legitimate interest in scientific aspects of the experiment itself, which could not be ignored in an acceptable cooperative agreement. This interest would have to be covered by an arrangement to

publish a reasonably full description of the experiment and its results. The technical depth of disclosure could be negotiated, however, and therefore we expect that publication could be accomplished without unduly compromising the company's proprietary rights.

Our last category is an example of the kind of arrangement that might be made for actual manufacturing of a fully developed product. We suppose that the manufacturer has developed the product wholly with his own funds, so that he has an uncompromised proprietary interest in it, and that he intends to market it commercially. He seeks to lease space in a NASA space station for his operations and to use the services of NASA launch and reentry vehicles for transportation on a pay as you go basis.

Our legal staff is of the opinion that authority for such an arrangement exists in the Space Act, and there are other precedents for private use of NASA facilities in the Unitary Wind Tunnel Act and the Communication Satellite Corporation arrangement. In this case the Government is fully compensated for its services and has no vested interest in the industrial undertaking. Therefore, we would assume in this case that all data, inventions and products would belong exclusively to the private concern.

In concluding, I would like to reiterate that no formal policy exists for developing agreements for industrial exploitation of space. However, our interest is to encourage participation to the maximum extent possible. I would emphasize that formulation of policy in this area will be strongly influenced by the views of industry and the propositions they suggest in response to the opportunities that space manufacturing affords.

PROMISING MATERIAL PROCESSES IN A WEIGHTLESS ENVIRONMENT

- GROWTH OF LARGE DISLOCATION FREE SINGLE CRYSTALS
- LEVITATION CASTING OF MATERIALS
- BLENDING OF DISSIMILAR MATERIALS
- FOAM CASTING
- 'G' SENSITIVE CHEMICAL PROCESSES
- SURFACE TENSION CASTING

FIGURE 1

INTEGRATED SPACE FLIGHT MISSION PLANNING

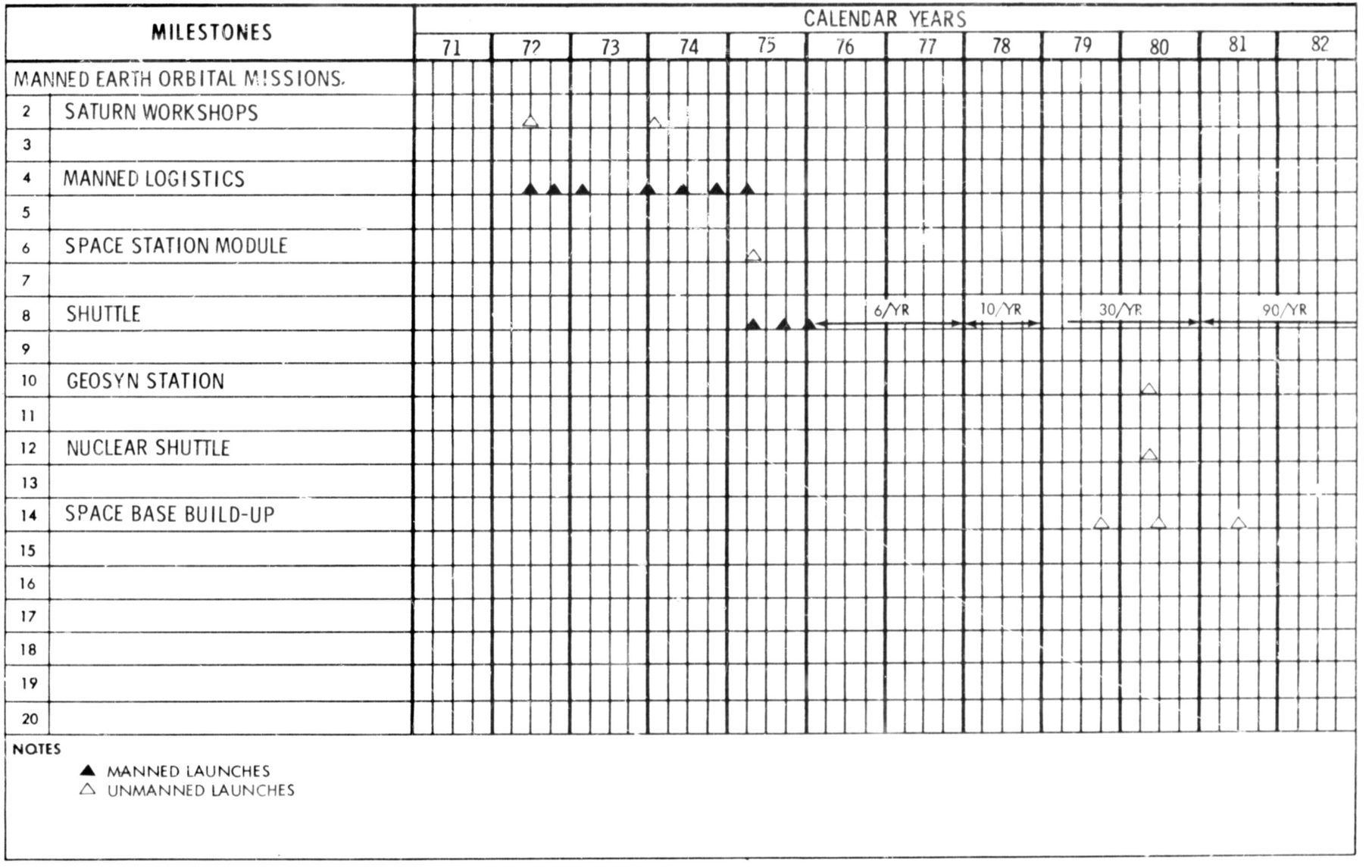


FIGURE 2

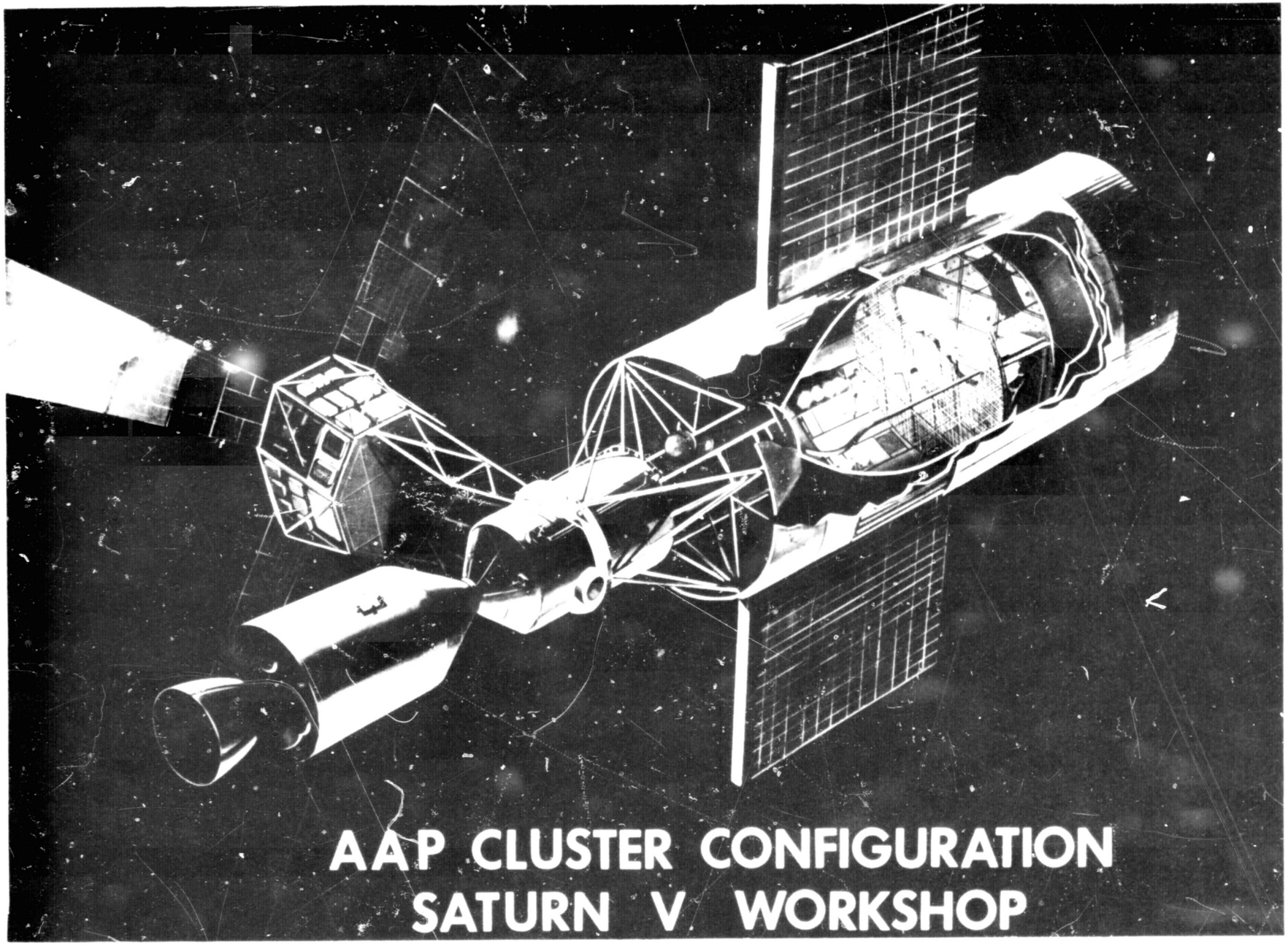


FIGURE 3

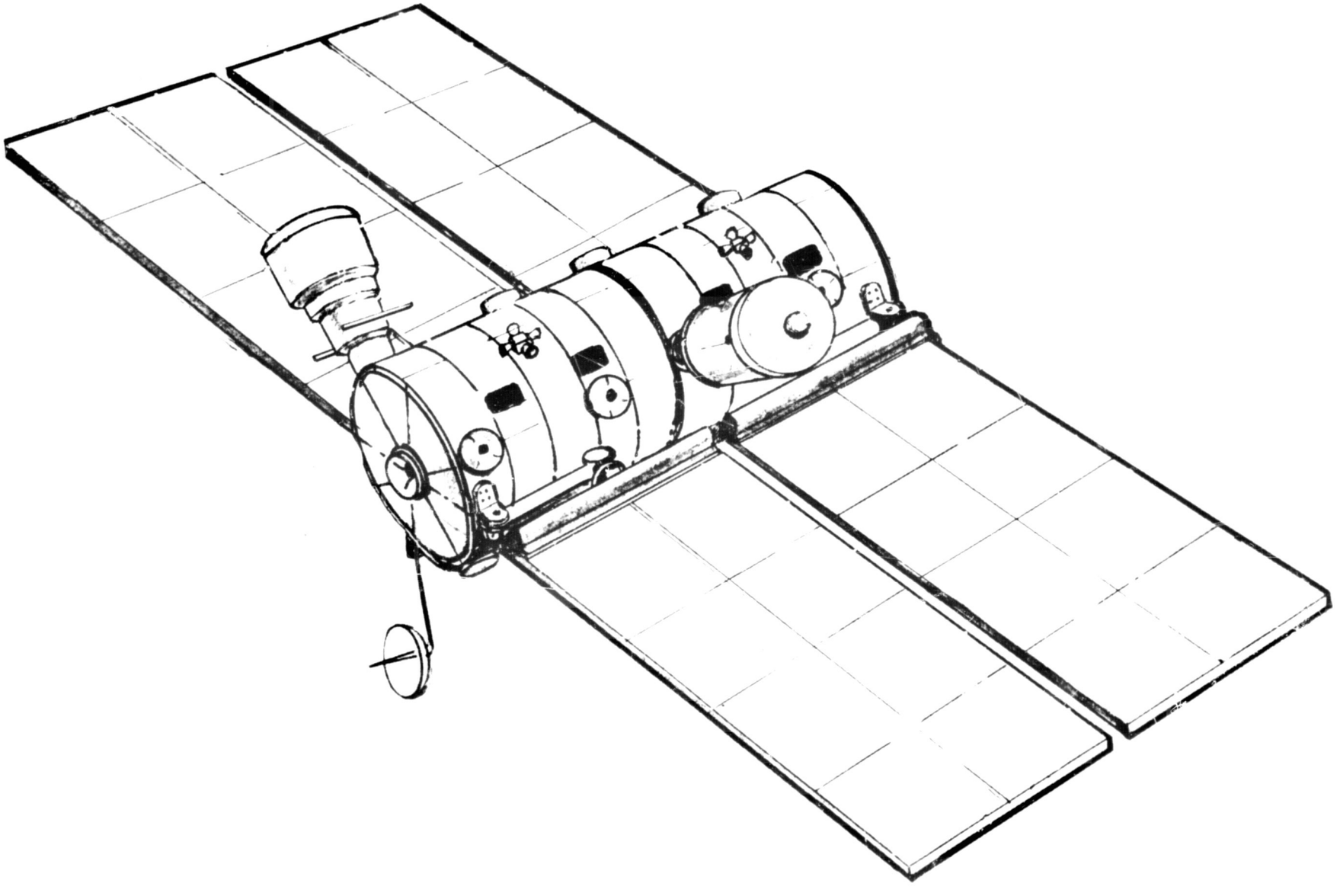


FIGURE 4

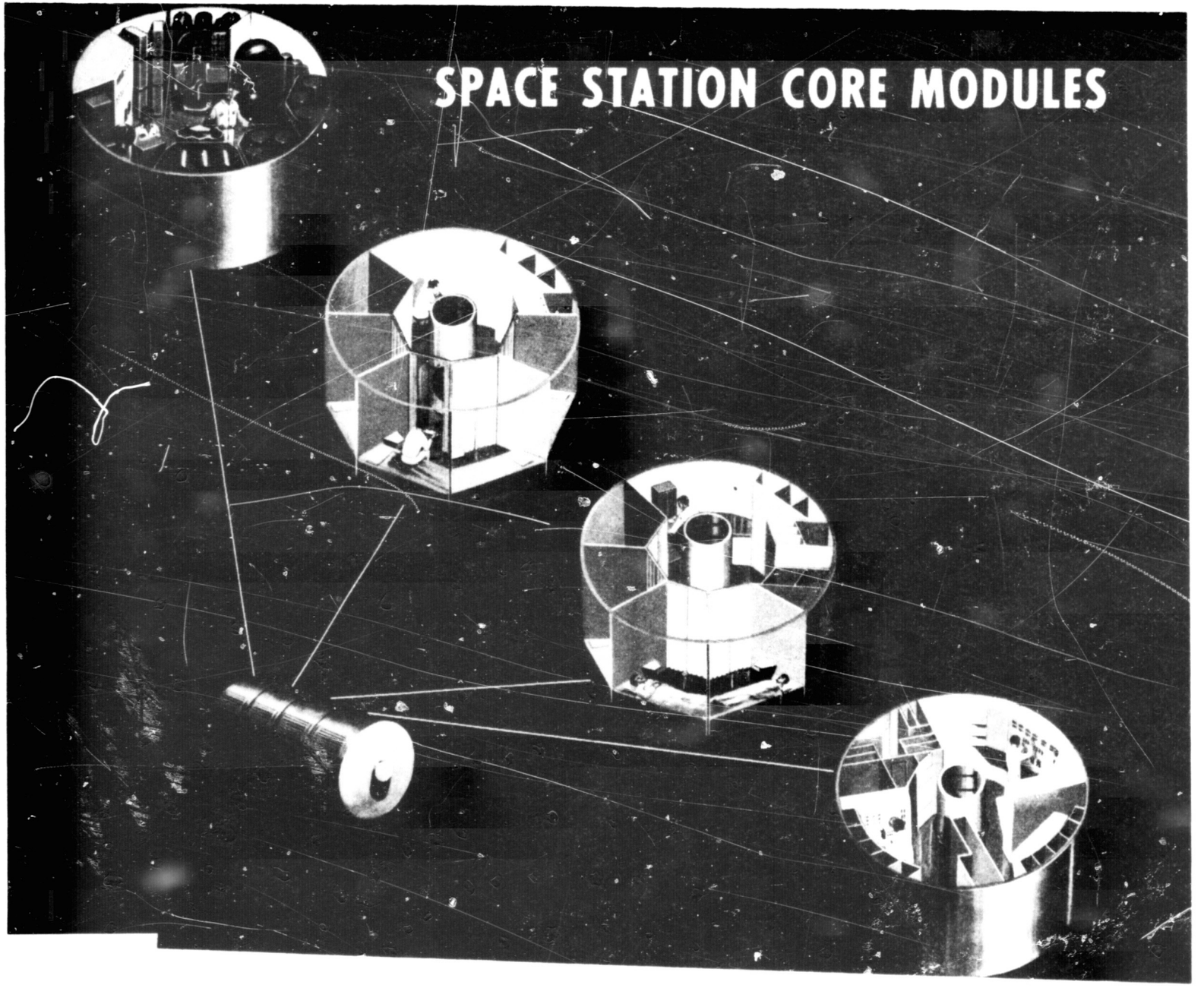


FIGURE 5

R & D ADVANCED TECHNOLOGY LABORATORY

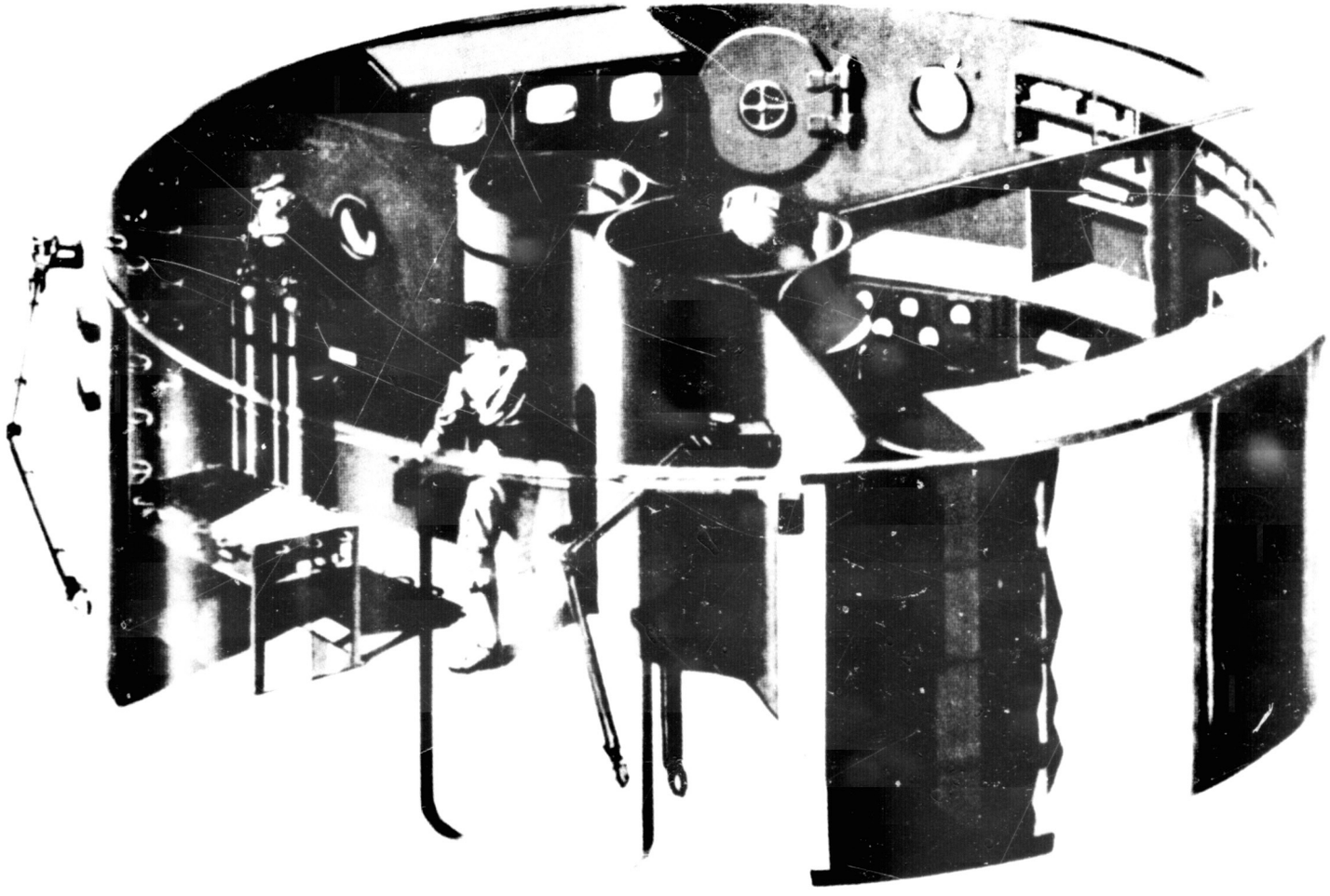


FIGURE 6

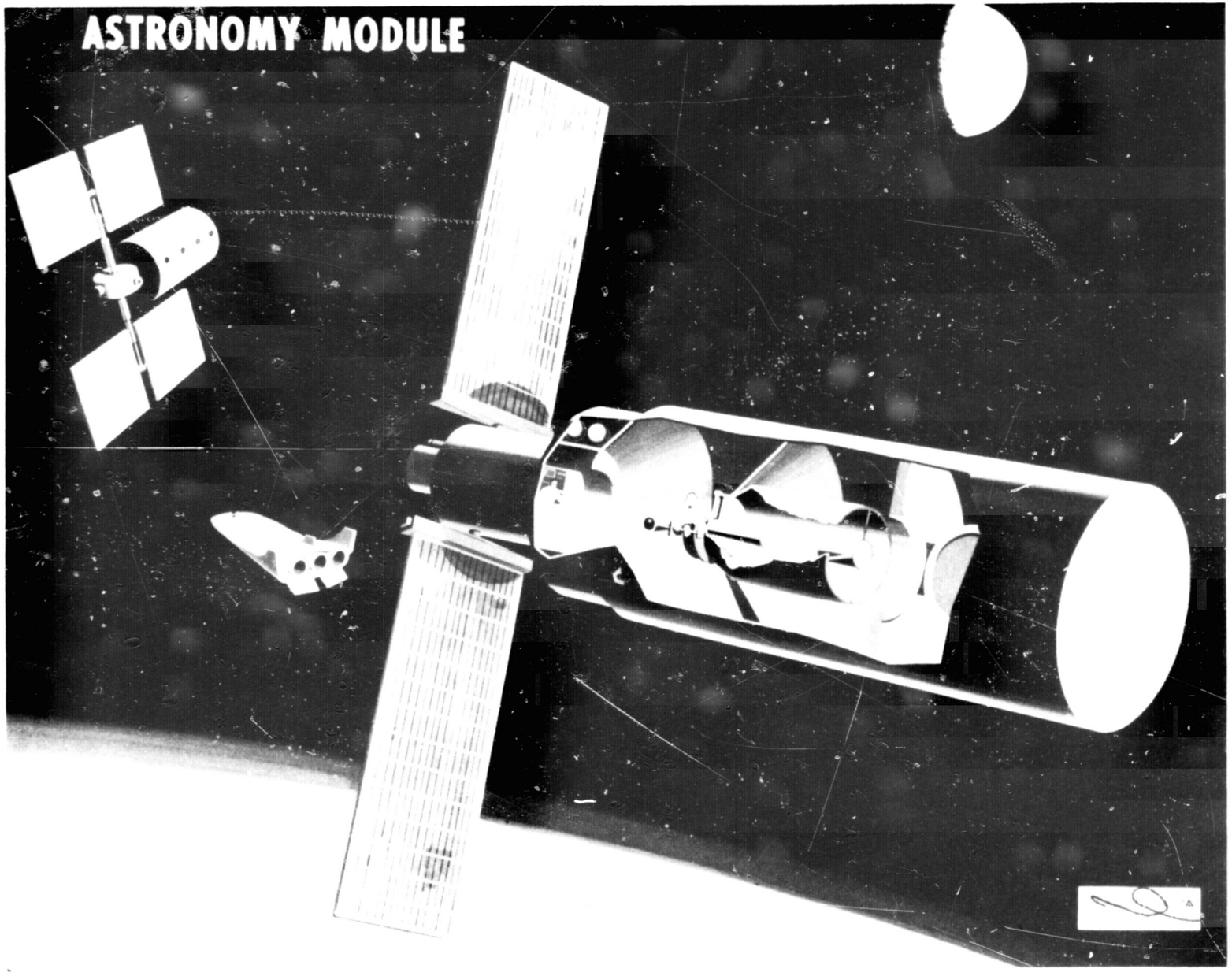


FIGURE 7

INTEGRAL LAUNCH AND REENTRY VEHICLE

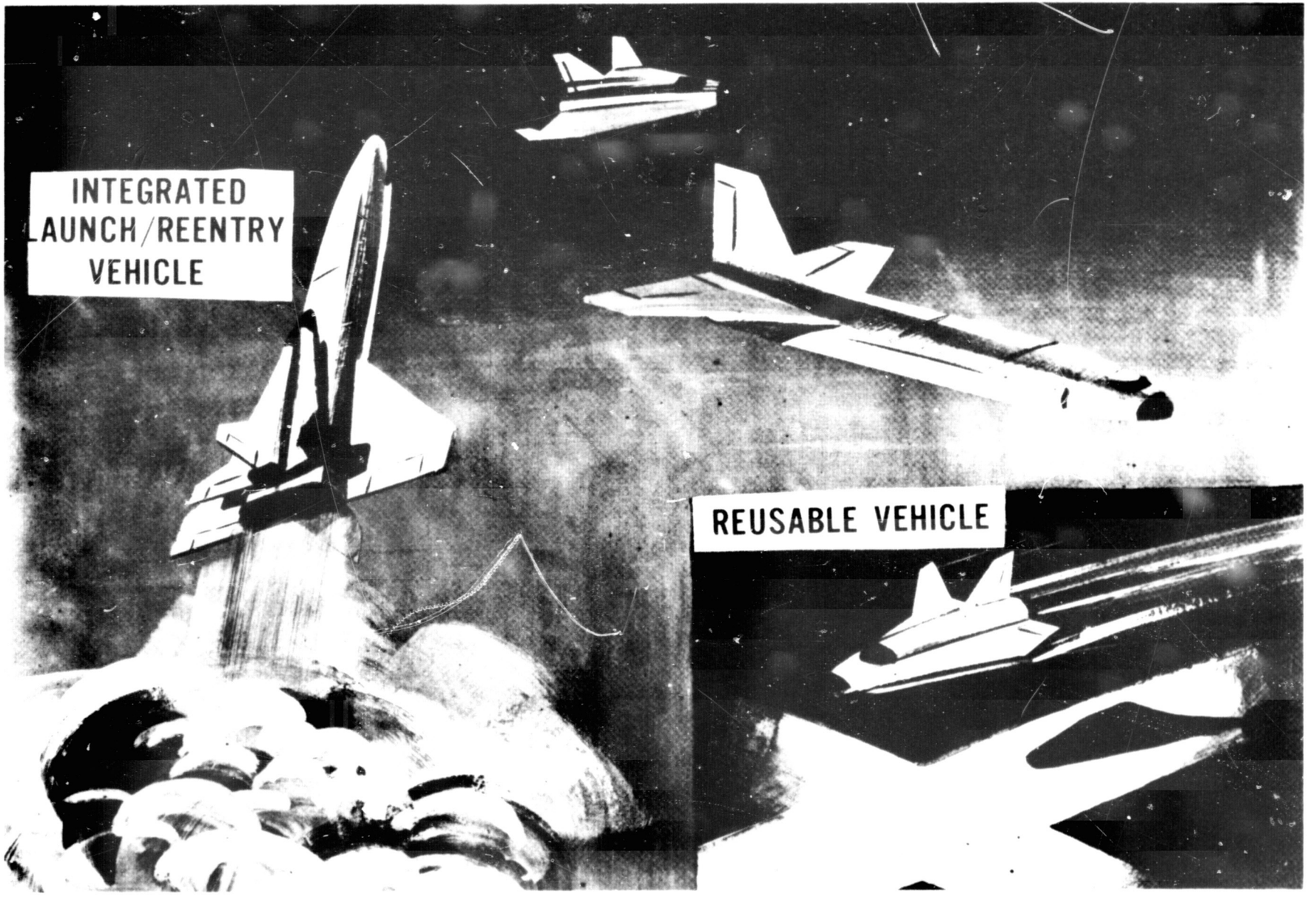


FIGURE 8

SPACE SHUTTLE

OPERATIONAL CONCEPT

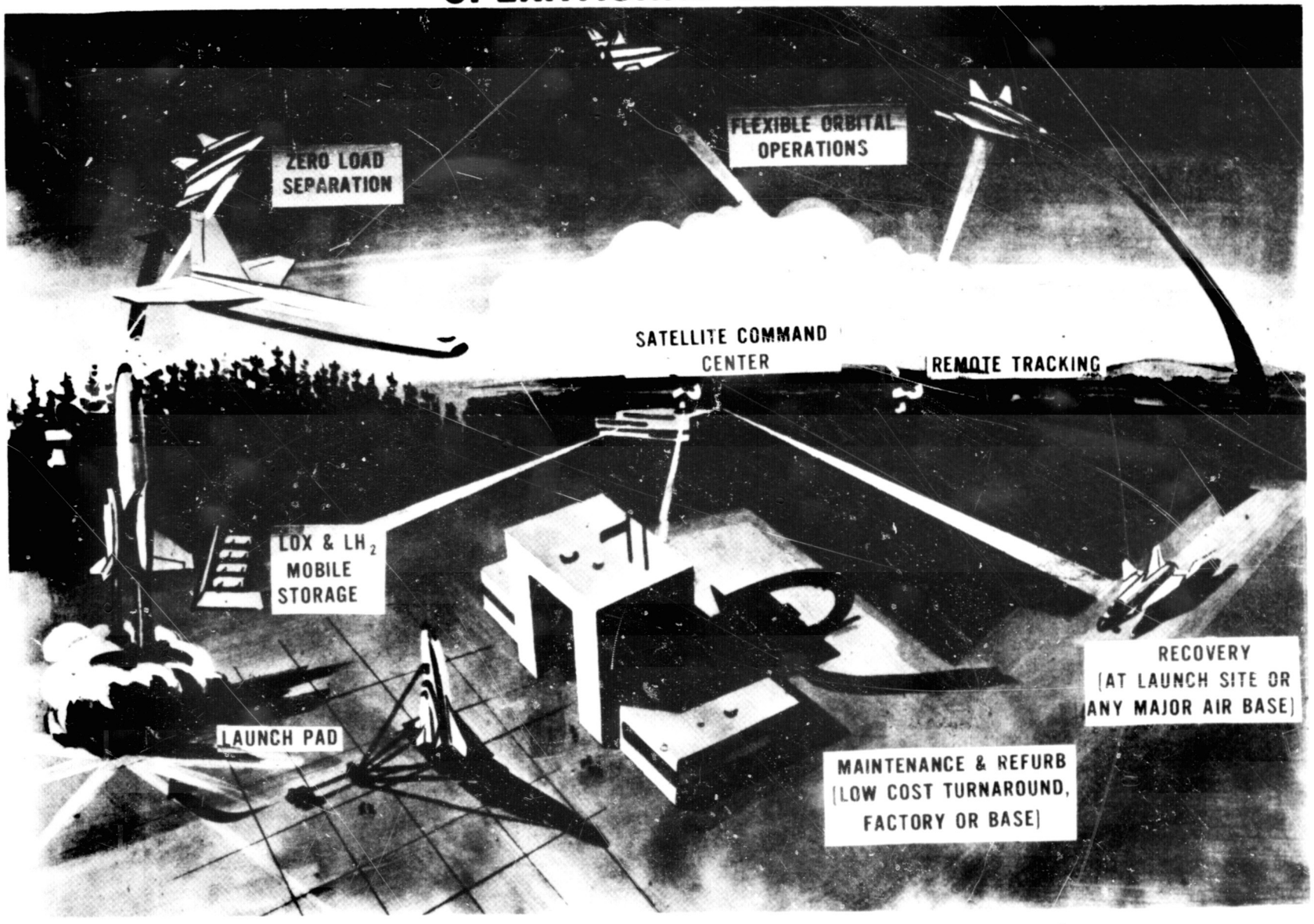


FIGURE 9

PROGRAM APPROACH TO MATERIALS PROCESSING IN SPACE

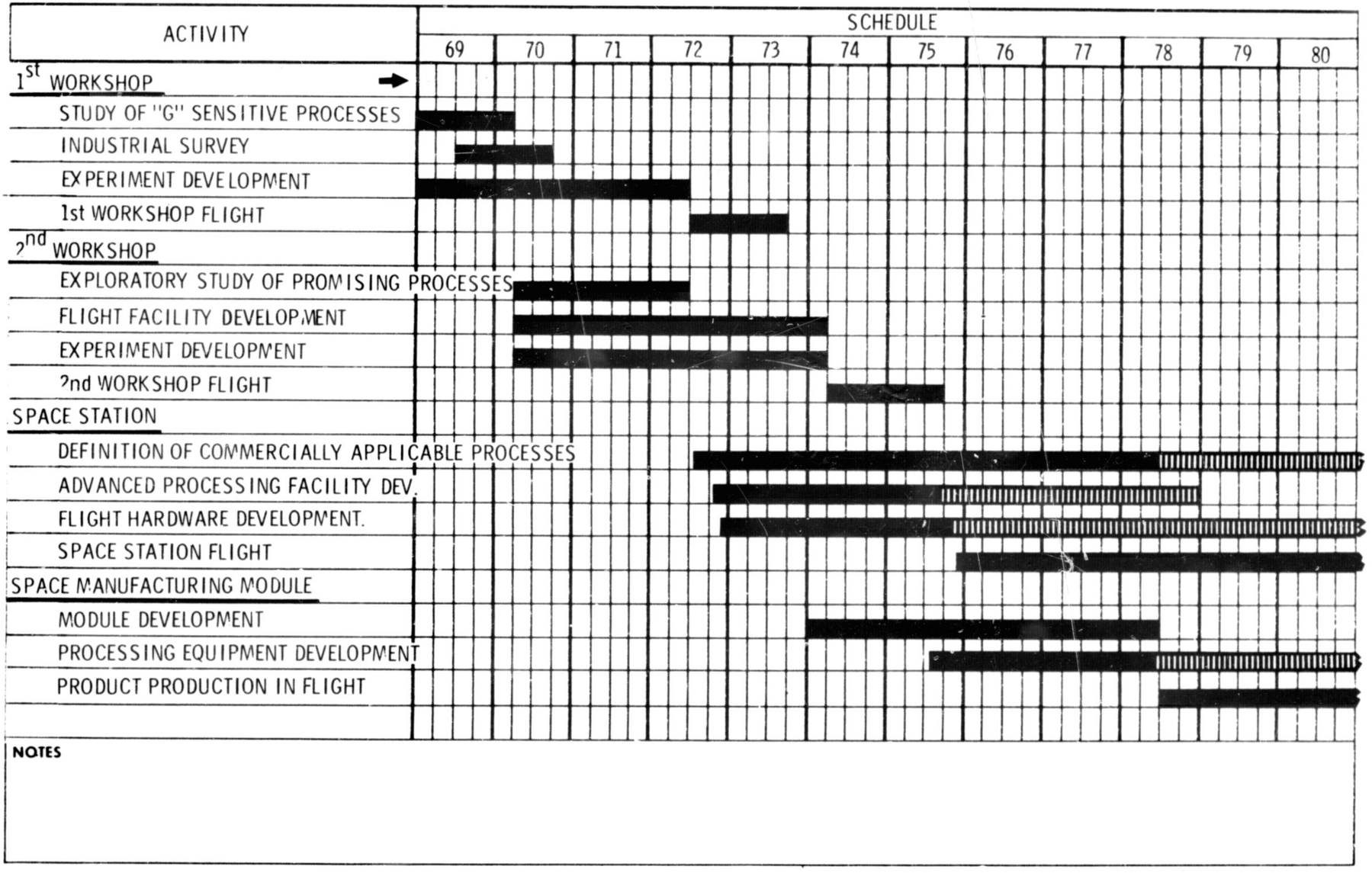
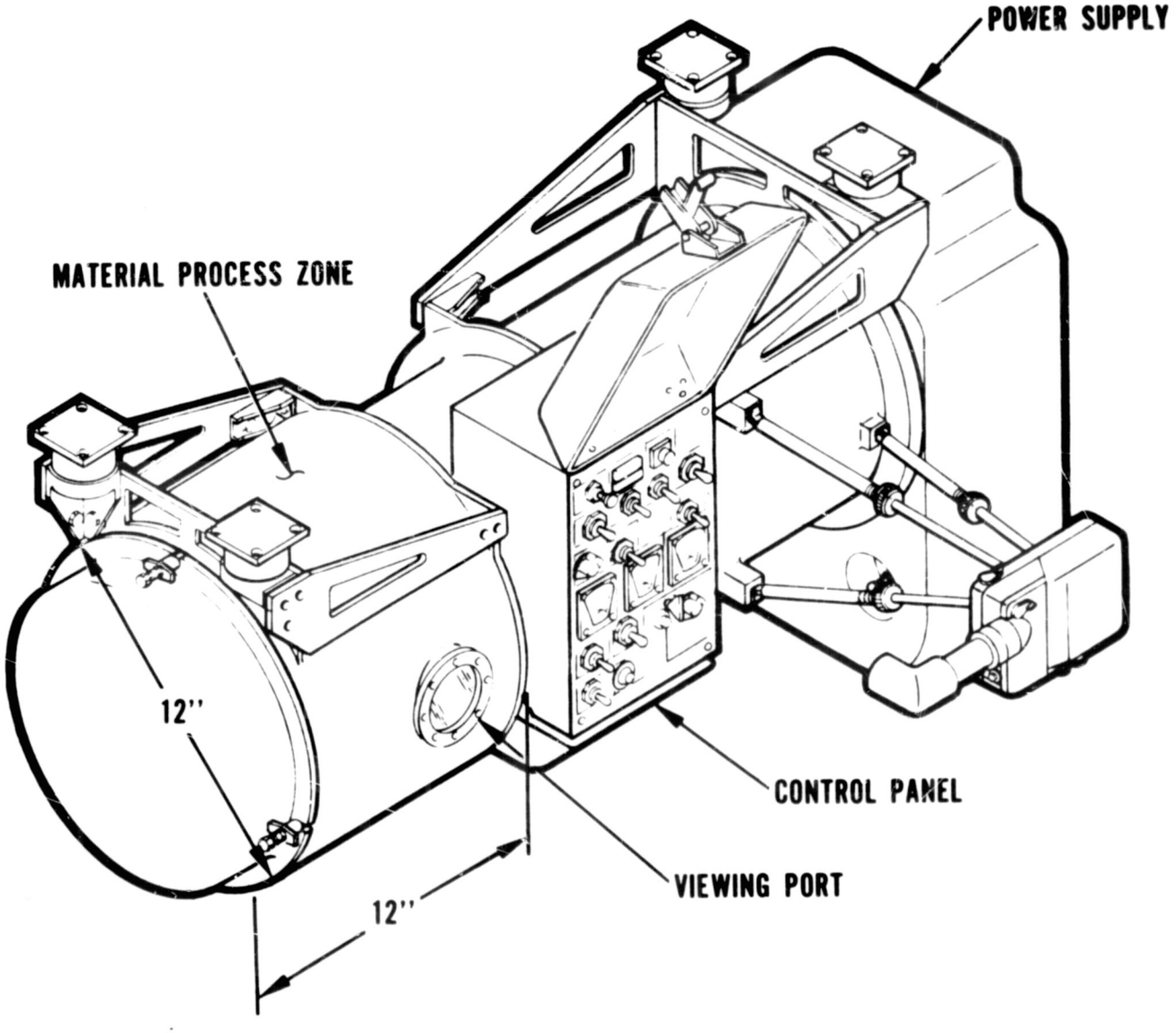


FIGURE 10

MSFC STUDIES ON SPACE PROCESSING OF MATERIALS

STUDY	INVESTIGATOR	ORGANIZATION	PURPOSE
THEORETICAL STUDIES			
• CRYSTAL WHISKER GROWTH	DR. DAVIS	UNIV. OF ALA.	• STUDY EFFECT OF GRAVITY ON CRYSTAL WHISKER GROWTH
• ZERO "G" EFFECT ON CRYSTAL GROWTH	DR. ROY	UNIV OF ALA.	• THEO INVEST. OF SOLIDIFICATION MECHANISMS IN ZERO "G"
• INVESTIGATION OF GAS MANAGEMENT	DR. BAUER	GEORGIA TECH	• EXAMINE GAS - LIQUID INTERACTION IN ZERO GRAVITY
• SPACE ENVIRONMENT EFFECTS ON SOLIDIFICATION	DR. GRODZKA	LOCKHEED	• EFFECTS OF SURFACE TENSION & CONVECTION ON CRYSTAL GROWTH
• SPACE ENVIRONMENT EFFECTS ON DISPERSION IN METALS	DRs FABINIAK	CORNELL AERO	• GROWTH CHARACTERISTICS OF MATERIALS IN ZERO "G"
STUDIES OF SPECIFIC PROCESSES			
• CRYSTAL GROWTH	DR. FROST	G. E.	• DEFINITION OF CRYSTAL GROWTH EXP. FOR FLIGHT
• ZERO "G" CRYSTAL GROWTH	BANNISTER	S. S. L. (MSFC)	• PHOTOGRAPHING CRYSTAL GROWTH IN ZERO "G"
• DROP TOWER EXPERMINTATION	BANNISTER HOPPES	S. S. L. (MSFC) M. E.	• STUDY SOLIDIFICATION OF MOLTEN METALS IN FREE-FALL
• GROWTH OF CRYSTALLINE MATERIALS	BANNISTER	S. S. L. (MSFC)	• LAB. STUDIES OF CRYSTALLINE MATERIALS FORMATION
SURVEY STUDIES			
• PROCESSES FOR SPACE MANUFACTURING	DR. STEURER	G D/CONVAIR	• IDENTIFY PROMISING "G" SENSITIVE PROCESSES FOR FLIGHT
• USE OF OUTER SPACE - DESIGN COURSE	DR. SHAW	CARNEGIE-MELLON	• SENIOR CLASS PROJECT TO IDENTIFY POTENIAL USES OF SPACE FOR IND. APP.
INDUSTRIAL CANVASS	LAKE	MSFC	• SURVEY OF SCIENCE & INDUSTRY INTERESTS IN SPACE PROCESSING & MANUFACTURING
FACILITY DEVELPOPMENT			
• DESIGN STUDIES OF EXPERIMENTAL SUPPORT HARDWARE	DR. FROST MC CREIGHT	G. E.	• DESIGN OF POSITIONING, HEATING, COOLING & SEPARATION EXP. EQUIP.
• DESIGN STUDIES OF PROCESS CHAMBER	RASQUIN	M. E. (MSFC)	• DESIGN & FAB. OF PROCESSING CHAMBER FOR 2ND WORKSHOP
SUPPORT OF AAP EXPERIMENTS			
• CRYSTAL GROWTH IN ZERO "G"	DR. MAZELSKY	WESTINGHOUSE	• DEVELOP TECHNIQUES & EQUIP. FOR AAP CRYSTAL GROWTH EXP.
• SPHERICAL CASTING & COMPOSITE MELTING	DR. WECHSLER	A. D. LITTLE	• DEVELOP TECHNIQUES & EQ. FOR BLENDING & CASTING OF MATERIALS IN SPACE
• METALS MELTING	PARKS	M. E. (MSFC)	• EXP. DEF. TO EVALUATE MELTING & FREEZING OF METALS IN ZERO "G"

FIGURE 11



MANUFACTURING PROCESS CHAMBER

FIGURE 12

SATURN WORKSHOP I INVESTIGATIONS

- METALS MELTING
- EXOTHERMIC BRAZING
- SINGLE CRYSTAL GROWTH
- COMPOSITE CASTING
- ZERO GRAVITY FLAMMABILITY
- SPHERICAL CASTING

FIGURE 13



FIGURE 14

ANNOUNCEMENT OF FLIGHT OPPORTUNITY

- MISSION CAPABILITY AND CHARACTERISTICS
- CATEGORY OF INVESTIGATIONS SOLICITED
- INSTRUCTIONS FOR PREPARING PROPOSALS
- SCHEDULE OF MILESTONES FOR FLIGHT

FIGURE 15

SELECTION OF PROPOSED FLIGHT EXPERIMENTS

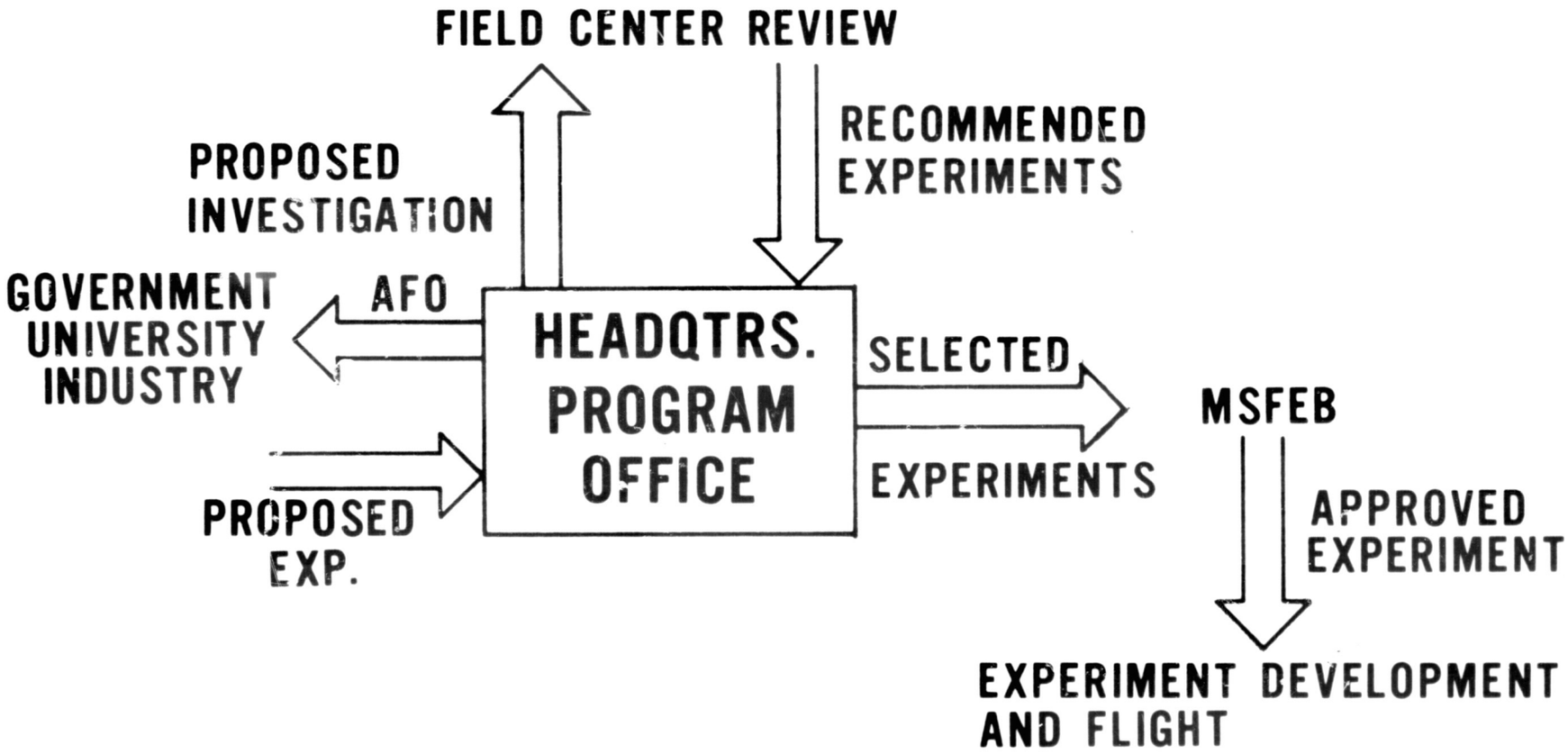


FIGURE 16

INDUSTRY-GOVERNMENT RELATIONS IN SPACE MANUFACTURING

CATEGORY	CHARACTERISTIC OF PROJECT	SUGGESTED POLICY GUIDLINES
GOVERNMENT PROCURED R&D	• GOVERNMENT SOLICITED RESEARCH • COMPETIVE SELECTION OF CONTRACT SUPPORT • GOVERNMENT FUNDED INVESTIGATION	• UNDISTURBED PERIOD OF ACCESS TO DATA • RESULTS PUBLISHED FOR GENERAL USE • DATA & INVENTIONS RETAINED BY GOVERNMENT
SPONSORED FLIGHT RESEARCH IN PRIVATELY DEVELOPED AREA	• OUTGROWTH OF PRIVATE RESEARCH • GOVERNMENT SUPPORT SOLICITED BY COMPANY • DEVELOPMENT THRU SOLE SOURCE PROCUREMENT • GOVERNMENT SPONSORED FLIGHT IMPLEMENTATION	• PRIOR WORK PROTECTED • DATA AND INVENTIONS RETAINED BY GOVERNMENT • WAIVER OF PATENT RIGHTS & DISCLOSURE OF DATA NEGOTIABLE
FLIGHT OF PRIVATLEY OWNED DEVELOPED INVESTIGATION OF PROCESSES	• FLIGHT PROGRAM PRIVATELY CONCEIVED AND DEVELOPED • INTEGRATED & FLOWN AT GOVERNMENT EXPENSE • RESULTS INTENDED FOR PROPRIETARY DEVELOPMENT	• PROPRIETARY INTERESTS PROTECTED • ROYALTY FREE RIGHTS RESERVED BY GOVERNMENT
PRODUCTION FOR COMMERCIAL MARKETING	• PROCESS & PRODUCTION PRIVATELY DEVELOPED • PRIVATE RENTAL OF SPACE FACILITIES • PRODUCT MARKETED COMMERCIALLY	• PRECEDENTS PROVIDEED BY WIND TUNNEL ACT COMSAT AGREEMENT • PRIVATE INTERESTS PRESERVED

FIGURE 17

N70-20519

GLASS PREPARATION IN SPACE

Emil W. Deeg

AMERICAN OPTICAL CORPORATION
SOUTHBRIDGE, MASSACHUSETTS

ABSTRACT

Low gravity, ease of access to high energy radiation and to high vacuum are conditions making an earth orbiting laboratory unique for developing new glass making processes. Among them are crucible free melting, preparation of glasses sensitive to thermal convection, formation of lenses and mirror blanks with fire polished surface directly from the melt, formation of dispersion filters, ruby glasses and glass-ceramics requiring nucleation control through solid powder dispersion. Advantages of these methods and difficulties to be expected in performing the first experiments will be discussed.

INTRODUCTION

Three experimental conditions existing in an earth orbiting space laboratory call for utilization in glass melting experiments:

(a) Low gravity
(b) Ease of access to high energy radiation
(c) Ease of access to high vacuum

Condition (a) alone or in combination with (b) and/or (c) give an orbiting laboratory its unique features.

Glass melts in high vacuum have been and still are made on a commercial scale in conventional factories chiefly to obtain infrared transmitting glasses. Although it is known that already ultraviolet radiation can change the electronic structure of a glass, e.g., by generating color centers, no experiments have been made up to now to expose glass melts during cooling or rigid glass samples during temperature cycling to such radiation. It should be expected that optical and semiconductive properties of a glass prepared under such conditions or treated in such a manner are different from those of the same glass prepared under normal conditions. However, such experiments can be performed in conventional laboratories, too.

Among the manufacturing processes unique to low gravity environment, as described in general by H. F. Wuenscher [1], the following offer special advantages for glass manufacturing:

(aa) Crucible free melting or remelting

(ab) Melting or remelting of thermal convection sensitive glasses

(ac) Conversion of compacted powders into castings

(ad) Surface tension casting

(ae) Controlled density casting

(af) Nucleation control of crucible free melts through solid powder dispersion

To better understand the significance of these processes as applied to glass melting, a brief review of glass preparation techniques may be given.

GLASS FORMATION FROM MELTS

A glass batch, e.g., of the composition given in table 1, is thoroughly mixed and exposed to a temperature-time relation as shown in Figure 1. Different batches and, in many cases, similar batches melted in different furnaces require different temperature-time curves (see e.g. [2]). To obtain a glass article, the viscous melt is shaped by drawing, blowing, pressing or casting and then quenched. That quenching operation in combination with certain properties of the melt determine the existence of a glass body:

> The cooling rate must be high enough to avoid the formation of crystals in the glass body ("devitrification").
>
> The cooling rate must be low enough to avoid intrinsic fracture of the glass body due to thermal shock.

The numerical values of both limits depend on the composition of the glass, the size and the shape of the body to be produced [4]. For a cylinder of radius b with thermally insulated end faces, the difference Δu between initial temperature of the cylinder and the ambient temperature must fall in the interval

$$(1)\quad \frac{b}{k\cdot h}\cdot\frac{v_m^2}{s_c\cdot|v_m'|}\cdot\frac{1}{g(\tau,\beta)} < \Delta u < \sigma_0\cdot\frac{(1-\mu)}{\alpha\cdot E}\cdot\frac{1}{f(\tau_m,\beta)}\quad ,$$

where

u = temperature
b = cylinder radius
h = heat transfer number
β = $(b\cdot h)^{-1}$ = Biot number or modified Nusselt number

} manufacturing parameters

t = time interval during which the center of the cylinder is at a temperature within the devitrification range

t_m = time at which maximum stress occurs in the cylinder surface

$\tau = (k \cdot t)/b^2$ = Fourier modulus

$\tau_m = (k \cdot t_m)/b^2$ = Fourier modulus

} parameters determined by manufacturing conditions and glass properties

k = effective thermal diffusivity

E = Young's modulus

α = coefficient of linear thermal expansion

μ = Poisson's ratio

σ_o = tensile strength

$(v)_m$ = maximum rate of linear crystal growth

v'_m = mean value of (dv/du)

s_c = maximum crystal size allowed for a certain application of the glass — quality parameter

The functions $g(\tau,\beta)$ and $f(\tau_m,\beta)$ are

$$(2) \qquad g(\tau,\beta) = \sum_{\nu=1}^{\infty} \frac{2 \cdot (\beta^2 \cdot \chi_\nu^2)}{\beta \cdot J_o(\chi_\nu) \cdot (1+\beta^2 \chi_\nu^2)} \cdot e^{-\chi_\nu^2 \cdot \tau}$$

$$(3) \qquad f(\tau_m,\beta) = \sum_{\nu=1}^{\infty} \frac{2 \cdot (2\beta^2 - \beta \cdot \chi_\nu)}{\chi_\nu^2 \cdot (1+\beta^2 \chi_\nu^2)} \cdot e^{-\chi_\nu^2 \cdot \tau_m}$$

χ_ν are the positive roots of the equation

$$(4) \qquad \beta \cdot \chi = J_o(\chi)/J_1(\chi)$$

J_i = Bessel function of order i.

The left hand side of relation (1) is valid in the devitrification range, the right hand side for temperatures below the upper annealing point. A rod of approximately 100 cm length and 8 cm diameter, made of a glass with two different devitrification products (see Figure 2) was slowly cooled violating condition (1). The result is shown in Figure 3.

GLASS MELTING IN ZERO GRAVITY

Crystallization of a piece of glass takes place only if nuclei are present. Many glasses form such nuclei during cooling just because of their chemical composition (homogeneous nucleation). In these cases, zero gravity would not affect devitrification. However, there are glasses in which nuclei are introduced from external sources (heterogeneous nucleation). The most important of these sources is crucible attack by the glass melt. R. P. Olsen mentioned this already in [5]. It can be concluded from his discussion and from the above remarks that glasses may be formed from compounds with even a high rate of crystal growth if they do not exhibit homogeneous (or "intrinsic") nucleation and if they are prepared under conditions which eliminate heterogeneous nucleation. Containerless melting in zero gravity environment and in vacuum is such a process. Since under zero gravity no buoyancy exists for gas bubbles developing during the melting process, the standard glass melting techniques as described (see Figure 1) cannot be applied. Compacted powder of the composition wanted would be one choice for such melting experiments. Batch constituents giving rise to gas evolution during melting must be eliminated. Another problem will be to properly homogenize the melt. Normally, this is done by stirring the viscous glass melt. If heterogeneous nucleation is to be avoided, no mechanical stirring using stirrers made of refractory material is possible. It would have to be investigated if homogenization through rapidly varying force fields is possible. Another possibility would be to raise the temperature of the melt to such a degree that diffusion within the melt compensates concentration gradients. However, increase in temperature would also increase the rate of selective volatilization of glass constituents from

the surface of the melt. Usually this process results in surface devitrification or scum formation. In addition, it must be expected that during the preparation of the powder and the additional pressing, unwanted nuclei are introduced. The most promising starting material would be pure single crystals of sufficient size.

Besides studying the possibilities of developing new glasses in low gravity environment, already existing glasses may have to be melted under such conditions. As an example, the problem of producing laser glasses with extremely high damage threshold may be mentioned. Presently available laser glasses damage due to inclusions at energy density levels of approximately 20 joules/cm^2 (pulse duration 30 nsec). As far as we know today, the damage occurs at inclusions which are either present in the raw glass or developed gradually in a laser glass rod after it has been fired several times. Apparently, ceramic inclusions can be as hazardous as metallic inclusions in this respect. Melting laser glasses of stable composition in volumes of about 10 liters under vacuum and entirely eliminating crucibles may be the only solution to the very serious problem of producing Nd-doped laser glasses with high damage threshold. In this case, surface devitrification would not present a problem since the final laser rod can be prepared from the raw glass billet by optical surfacing and possibly redrawing under conventional conditions.

A number of optical glasses, particularly in the low index/high Abbe number range, are difficult to obtain in large pieces. One reason is their tendency to form striae and even devitrified layers and cords inside the melt. The reason for these defects is not completely understood. There is some indication that thermal gradients in the melt give rise to extreme local variations in the structural equilibrium and, therefore, the physical properties of the melt. Thermal convection in combination with mechanical stirring distributes these structurally different zones over the volume of the melt yielding the above mentioned striation. Elimination of thermal convection and crucible free melting offer the possibility to study the effect of thermal gradients on the optical homogeneity of these glasses. Based on the results of such experiments, the question can

be answered if a process can be developed to produce large pieces of these critical but, for optical designers and laser device engineers, important glasses.

All these experiments would utilize processes of the general nature listed above under (aa), (ab) and (ac).

GLASS FORMING IN ZERO GRAVITY

Surface tension casting, modified by inertia and electric field casting methods, offers the possibility to produce optical elements with fire polished surfaces directly from the melt. Lenses and mirror blanks, usually of rotational symmetry, but in many cases with aspheric surfaces, are presently made by grinding and polishing. Although it is possible to prepare rather smooth surfaces by these methods, there are still irregularities left in the order of 1-10 nm. Firepolished surfaces are smoother by about one order of magnitude. In most optical instruments, the degree of smoothness reached by mechanical polishing is satisfactory. However, there are some special instruments which could be improved in performance if the traces of surface roughness caused by mechanical polishing could be eliminated. Besides selecting small areas out of float glass, there is at present no way to achieve such high quality surfaces under conventional conditions. So-called "precision molding" is applied to produce, e.g., condenser lenses with fire-polished surfaces. In that case, metal or ceramic molds are used to shape the viscous glass at high temperature under various pressures. The reproducibility of the lens' curvature and the elimination of chill wrinkles present real problems. The solution would be to shape the lens without having the hot glass in contact with the mold. Mold-free forming would be limited only by the availability of force fields (inertia and electric) and heat sources in an orbiting laboratory.

Experiments and manufacturing processes related to the preparation of optical elements with fire-polished surfaces directly from glass melts would utilize processes of the general nature listed in the introduction under (ac) and (ad).

PREPARATION OF OPTICAL FILTERS

Glasses containing metallic, semiconductive or dielectric particles are commercially widely used as light filters. Some of them change their effective spectral transmission reversibly while exposed to radiation. Phototropic glasses and a rather unique Cd-S-Se-Te striking glass used as passive Q-switch in ruby laser systems are examples.

"Striking glass", also called "ruby glasses" or "temperature colored glasses", contain colloidally dispersed metallic or semiconductive particles, e.g., such as Au, Ag, Ag-halides, Cd-S compounds, Cd-S-Se compounds, CuO. The spectral transmission of these glasses is determined by the complex refractive index, the shape and the size distribution of these particles if dispersed in a homogeneous glass of the same refractive index. Ruby glasses are presently made on an empirical basis, although it has been shown recently that the spectral transmission of these glasses can be described quantitatively by Mie's scattering theory [6, 7, 8]. Therefore, it should be possible to synthesize ruby glasses with wanted and precalculated spectral transmission by dispersing particles with known optical and electronic properties directly in a glass. At present, these glasses are made utilizing batch reactions which, in most cases, are not fully understood. The glass body formed originally from the melt is almost colorless. A subsequent heat treatment of the colorless sample, involving reactions which are not understood either, yields the final ruby glass. If it would be possible to disperse particles of specific properties in a matrix glass without going through these unknown reactions, completely new types of ruby glasses, e.g., passive Q-switches for Nd or Er lasers or with new phototropic characteristics, could be made. Conversion of compacted powders into castings in zero gravity environment offers such a possibility.

Another example of light filters which could be made in such an environment are the Christiansen filters. They consist of a large number of rather coarse, colorless particles dispersed in a homogeneous, colorless matrix [9]. The optical dispersion curve of the particles and the matrix cross each other at a certain wavelength. At that wavelength,

the mixture is optically homogeneous and light of that wavelength will pass through the mixture undeviated by reflection or refraction at the interface between particles and matrix. The most successful approach to utilize this effect was achieved by McAlister [10]. He packed a cuvette with the particles and filled the remaining space with an appropriate liquid. In a zero gravity environment, Christiansen filters could be prepared in the form of solids by dispersing powder of a high melting glass in a low melting glass matrix. Dispersion curves of some, presently available optical glasses, are shown in Figure 4. Table 2 gives the wavelength of filters which could be obtained by combining pairs of these glasses.

The processes to be utilized in the experiments described in this paragraph would fall under the general categories (ab), (ac), (ae) and (af).

RECOMMENDATIONS FOR EXPERIMENTS

Based on these considerations, a set of experiments should be conducted as shown in Table 3. Preliminary experiments are already carried out in our laboratory with the goal to study the effect of vacuum and different atmospheres on the remelting behavior of several glass types.

After completion of the experiments listed in Table 3, studies should be undertaken to prepare for the manufacturing processes according to Table 4. The same table contains a process which yields a flameproof, thermally insulating lightweight material, namely, foam glass. It might be usable as structural material in or around the space laboratory. Its advantage is mainly that the batch itself weighs only comparatively little. The process is so flexible that the main portion of the batch can utilize material found on the surface of the moon.

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[9] Christiansen, C.: Ann. Phys. Chem. 23 (1884), p. 298 and 24 (1885), p. 439.

[10] McAlister, E. D.: Smithsonian Misc. Coll. 93 (1935), No. 7.

Table 1: Batch composition and analysis expressed in terms of oxides of a glass prepared according to the process described in Fig. 1.

Batch Composition		Oxide Composition	
Constituent	Grams	Constituent	Wt. %
SiO_2	32,889.60	SiO_2	68.52
Na_2CO_3	6,033.60	Na_2O	7.35
K_2CO_3	5,016.00	K_2O	11.13
KNO_3	4,147.20		
$Ba(NO_3)_2$	3,998.40	BaO	4.90
Sb_2O_3	489.60	Sb_2O_3	1.02
$Al(OH)_3$	1,123.20	Al_2O_3	1.53
ZnO	734.40	ZnO	1.53
Li_2CO_3	1,209.60	Li_2O	1.02
Nd_2O_3	1,440.00	Nd_2O_3	3.00
	57,081.60		100.00

Table 2: Approximate values for transmission wavelengths of Christiansen filters (a) and properties of glasses recommended for preparing these filters (b).

(a)

Transmission Wavelength in nm	Matrix Glass	Particles Made of Glass	Thermal Expansion Match
405	SF 15	LaF N3	Good
480	SF 8	LaK 24	Poor
535	SF 8	LaK 3	Good
600	SF 1	LaF N3	Fair
710	SF 15	LaK 24	Poor
780	SF 15	LaK 3	Fair

(b)

Glass Type	Density in cm^3	Transformation Temperature °C	Linear Thermal Expansion Coefficient in $(°C)^{-1} \cdot 10^{-7}$
SF 1	4.46	417	81
SF 8	4.22	423	82
SF 15	4.06	455	79
LaF N3	4.34	620	78
LaK 3	4.35	610	82
LaK 24	3.78	654	59

Table 3: Recommendations for small scale experiments to explore the possibilities of glass manufacturing and glass processing in low gravity environment.

	Experiment - Sample Size: Approximately 5 cm^3	Information to be Obtained
1	Melt tablets of carbonate and nitrate containing batches of optical glasses. 5 different samples; no crucibles; air and vacuum. Total of 10 experiments.	To what an extent can the melts be refined and homogenized in low gravity environment and without stirring?
2	Melt tablets of batches consisting only of oxides. 5 different samples; no crucibles; air and vacuum. Total of 10 experiments.	To what an extent can the melt reactions be completed, the melts be refined and homogenized in low gravity environment and without stirring?
3	Remelt glass spheres with roughly ground surface. 5 different samples; no crucibles; air, forming gas, vacuum. Total of 15 experiments.	What is the quality of firepolished surfaces prepared in vacuum and in low gravity environment?

Table 4: Recommendations for glass manufacturing and glass processing in low gravity environment.

	Process	Product
1	Melt column of batch consisting of high purity raw materials into glass rods.	Laser glass billets (Nd - and Er - doped) of 10-20 liters volume. Dimensions of rods: approximately 8-15 cm diameter; 100-200 cm long.
2	Melt tablets of glass powder mixed with semi-conductive, particularly photoconductive particles in vacuum, nitrogen and air.	Light filters with integral transmission depending on intensity and/or spectral distribution of incident light. Volume of individual samples approximately 100 cm^3.
3	Melt tablets of a low melting glass containing coarse particles of high melting glass.	Christiansen filter. Volume of individual samples approximately 100 cm^3.
4	Remelt optical glass blanks in electric field and/or under rotation.	Lenses and mirror blanks with firepolished surface and non-spherical curves.
5	Remelt blanks of glasses sensitive to thermal convection.	Homogeneous low index-low dispersion glasses in large pieces. Volume of individual blanks approximately 20 liters.
6	Melt foam glass batches.	Structural material to be used in and around the space laboratory.

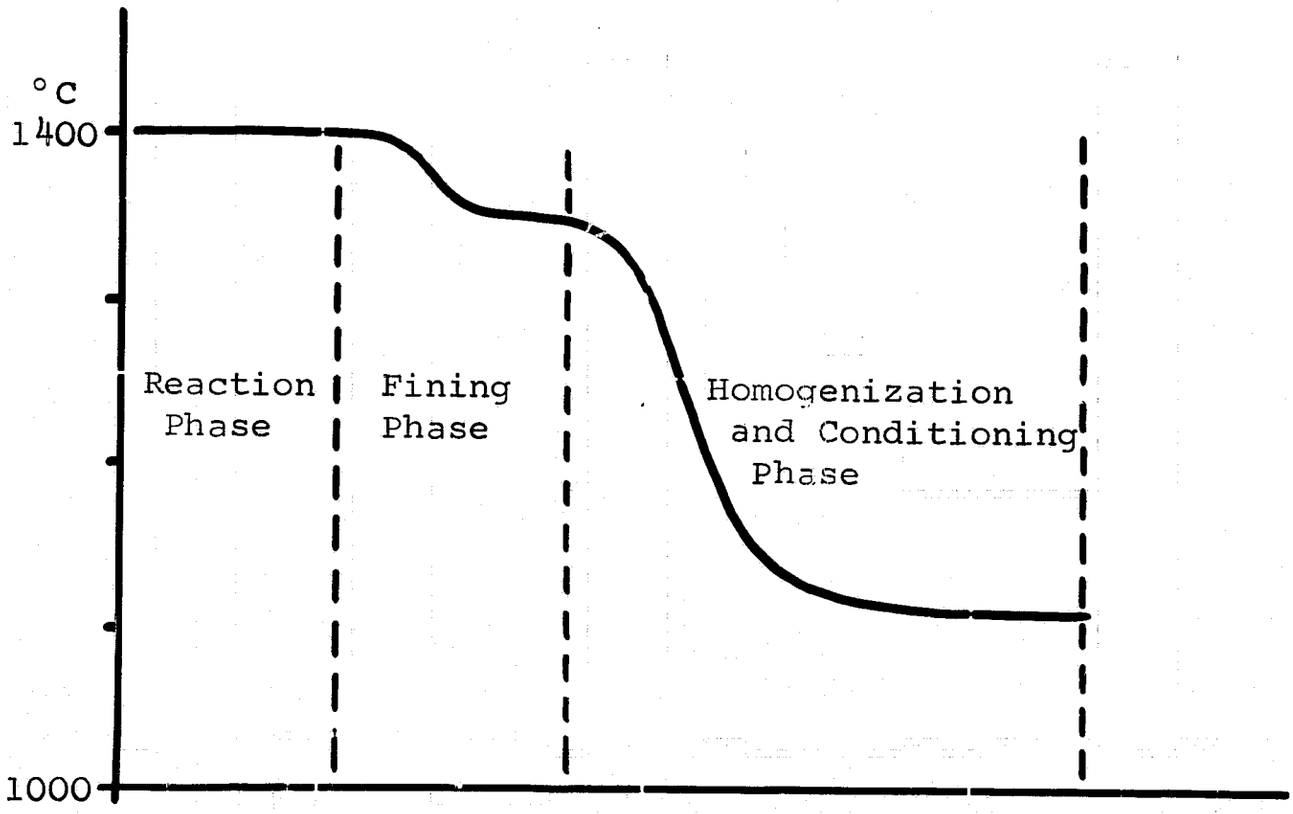


Fig. 1: Temperature-time relation and melting phases of a glass according to Table 1 if prepared in a furnace as described in [3].

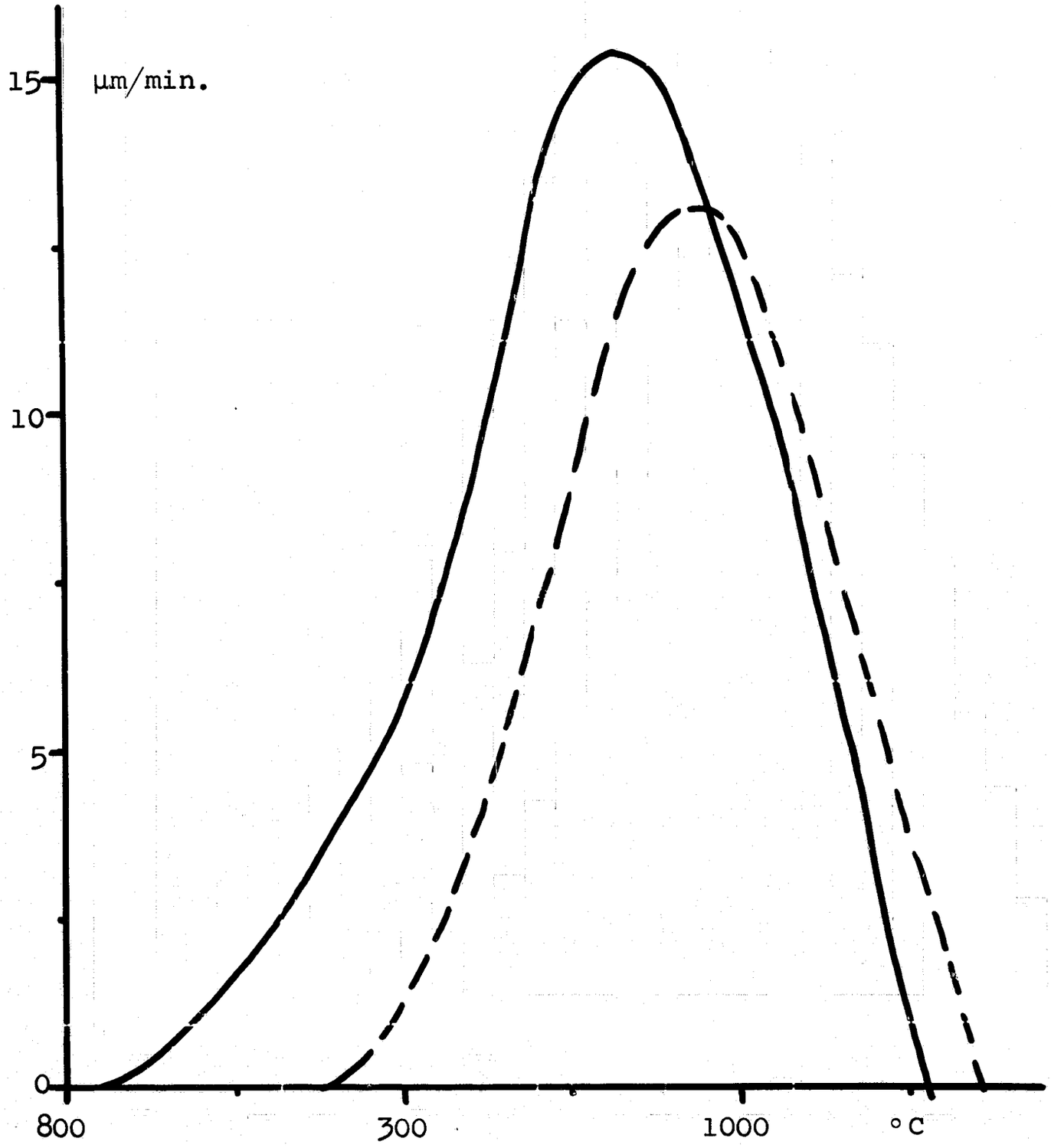


Fig. 2: Rate of linear crystal growth for the two types of devitrification products occurring in a glass of the approximate composition (in weight %):

62 SiO_2, 12 Na_2O, 3 K_2O, 12 CaO, 7 TiO_2, 4 La_2O_3

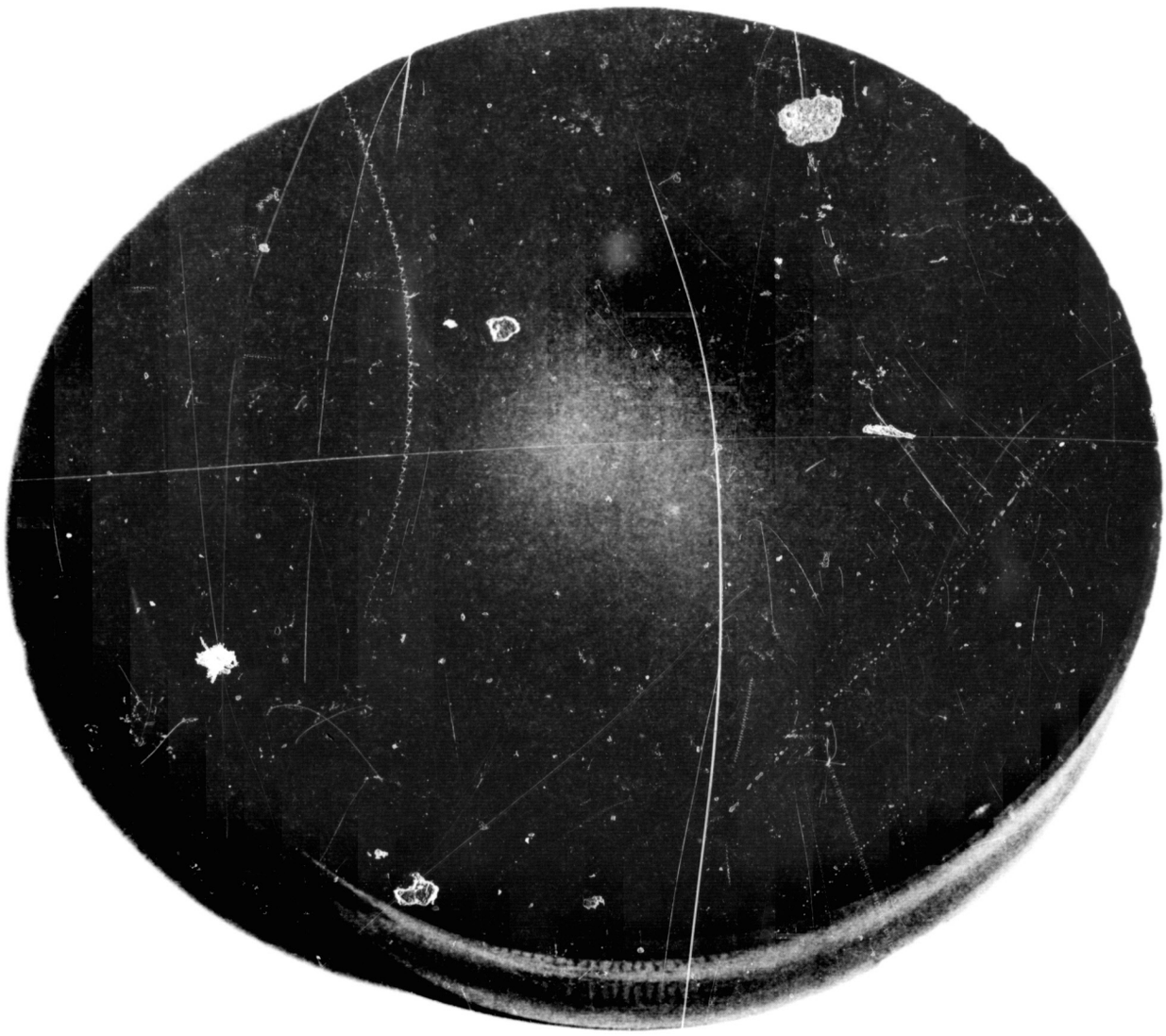


Fig. 3: Cross section through glass cylinder of 7.5 cm diameter quenched under conditions violating relation (1). The bright area in the center of the disc is caused by crystals larger than those in the outer zones.

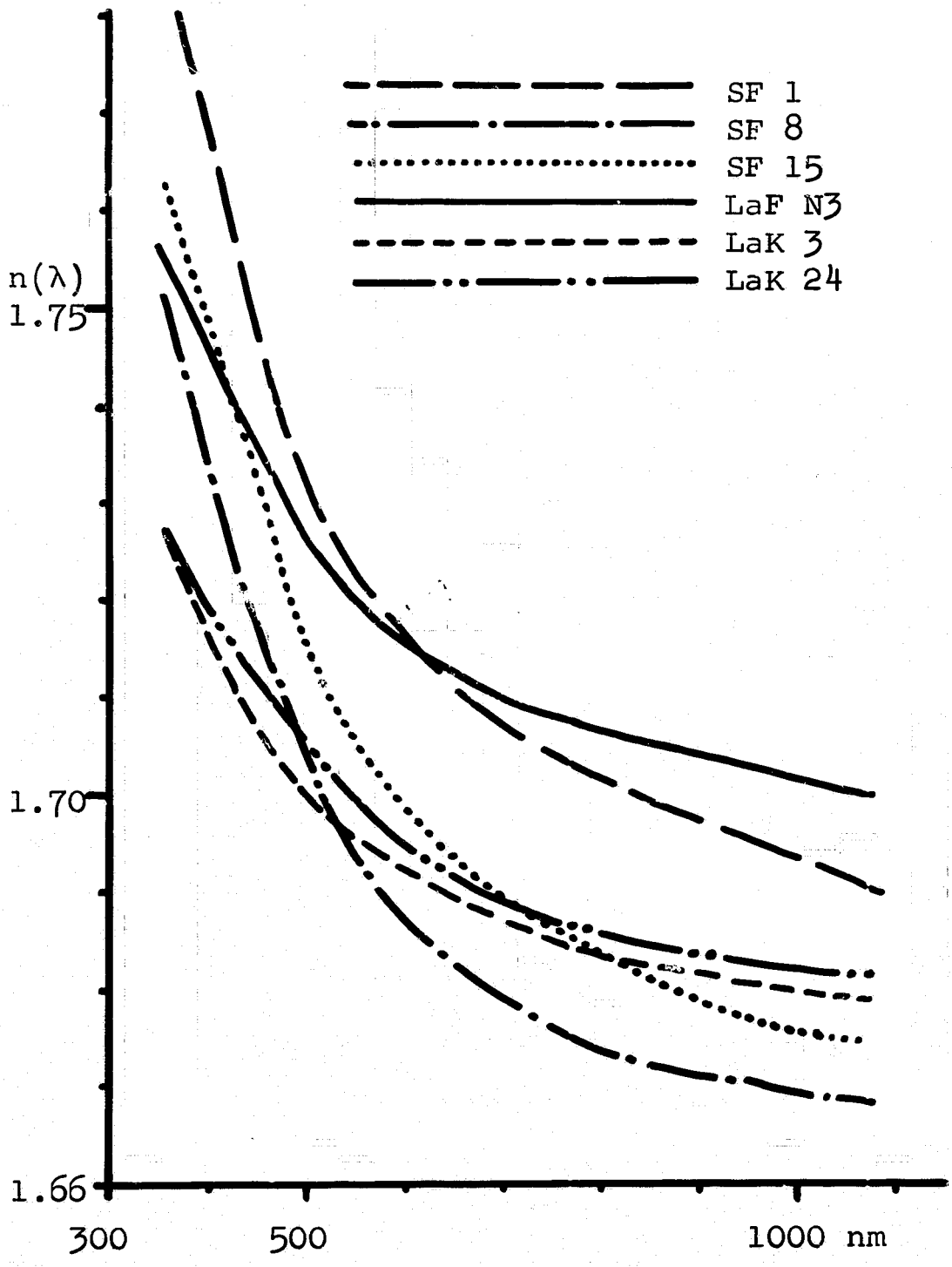


Fig. 4: Dispersion of some optical glasses. Points of intersection of two curves represent the transmission wavelength of a Christiansen filter made by combining the two corresponding glasses.

SPACE PROCESSING OF ELECTRONIC CRYSTALS

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ABSTRACT

A method for growing various high temperature oxidic crystals is described. The crystals are precipitated and grown from a glass solvent in which the desired crystal constituents have been previously dissolved. Typically, the desired crystals have a density of 5-8 grams/cc, and they settle out rapidly, due to gravity, in the much less dense molten glass matrix.

It is proposed to conduct a space experiment on this process of growing crystals as a means of overcoming the gravitational effects, and equally importantly, at the same time conducting the experiment in a manner to obtain crystals with fewer vacancies and dislocations as a consequence of the near absence of convection that zero-g should provide. This latter factor is expected to provide a means for achieving crystals with much higher perfection and improved electronic properties.

Although several compositions of crystals have been grown, the recommended choice for a space experiment is potassium sodium niobate because it has not been previously available as adequate single crystals and has high technological value.

A. INTRODUCTION

The possibilities of growing crystals in space, in an environment essentially free of the influence of gravity and having other peripheral advantages, are quite challenging. One is excited particularly by the potentialities of growing larger, more defect-free crystals of high value materials, with concomitant improvements in properties, while at the same time gaining important new insight into the mechanisms of crystal growth.

In planning an experiment to demonstrate effectively the advantages to be gained on processing crystals in space, it is necessary to select both an appropriate method of crystal growth and an appropriate composition to be grown. At the outset, one is impressed by the fact that, for operations in space, growth from a solution is one of the most appropriate general methods of crystal preparation. It can also be stated emphatically that electronic ceramic (oxidic) compositions are prime candidates for such crystal growth.

Crystals of electronic ceramic compositions are recommended for preparation in space, for the following reasons:

1. They have high dollar value per unit of volume or weight.

2. They have high density (up to 8 gm/cc) which makes it difficult to grow them under the influence of gravity. (They tend to settle and pack in the bottom of the crucible in which they are grown.)

3. Electronic ceramics are at the heart of the technology of many areas in the field of electronics: communication equipment, computers, radar and sonar equipment, infrared sensors, lasers, and the miniaturization of electronic circuits. They perform unique functions essential to the operation of many very complex measuring, counting, sensing or controlling devices, instruments, and systems.

4. Many electronic ceramics are used in polycrystalline form because they are not produced at all as single crytals or cannot be supplied in adequate size or perfection. The availability of satisfactory single crystals of these compositions could result in significant improvements in properties -- increased efficiency or sharper response, for example. Only slight improvements in performance over the best that is presently available would be technologically important in many instances. Improved materials are needed today to permit further advances in the state-of-the-art.

5. Oxidic compositions are disproportionately important among electronic single crystal materials. The results of discussions with growers and users in the field indicate that silicon, preferably but not exclusively made by float zone refining, dominates the high value single crystal field and accounts for an estimated 90% of the single crystal materials used in electronics. Other single-crystal materials such as germanium and gallium arsenide then account for much of the remaining usage. Nevertheless, a large number of compositions and crystals are being grown for specialized functions that cannot be performed by the semiconductors. Because these titanates, niobates, etc. commonly are used as relatively small pieces, comprising the whole or parts of electronic devices or systems, it seems reasonable to expect that there could be a ready market for superior space-produced crystals of this type of material.

6. As a bonus, the electronic properties of these oxidic materials are very sensitive to purity, crystal structure, and crystal perfection. As a consequence, measurements of electronic performance can serve as a powerful aid in evaluating the quality of the crystals produced. Specifically, such measurements provide a most effective means of directly comparing the quality of crystals prepared in space with those prepared under normal gravity.

B. SELECTION OF COMPOSITIONS OF CRYSTALS TO BE GROWN

Numerous compositions of oxidic electronic materials are candidates for space crystal growth. These compositions include (1) those predominantly showing ferroelectric and piezoelectric properties such as barium titanate, potassium sodium niobate, lead metaniobate, lead metatantalate, and the lead zirconate titanates, (2) those having strong magnetic characteristics, including the magnetic spinels such as lithium, nickel, cobalt, etc. ferrites and the magnetic garnets YIG (yttrium iron garnet) and YAG (yttrium aluminum garnet); (3) electro-optical materials such as lithium niobate and barium sodium niobate; (4) the dielectrics, characterized by high electrical resistivity and high energy-storage capabilities, and (5) single-crystal low-attenuation acoustic materials.

1. Potassium-Sodium Niobate, PSN, $K_{0.5}Na_{0.5}NbO_3$, Recommended for Preparation in Space

Among the electronic compositions listed, potassium sodium niobate (PSN) is one of the leading candidates for crystal-growth. This material is a solid solution of potassium niobate and sodium niobate, but it has more desirable electronic properties than either ingredient alone. It is difficult to obtain dense ceramic pieces of this material by conventional sintering, and special procedures of hot-pressing and pressure-sintering must be employed. Single crystals of this composition are not readily pulled from the melt, but growth from a molten solution appears quite promising.

Potassium sodium niobate has high electromechanical coupling efficiency, low dielectric constant, and high acoustic velocity. These properties combine to make the material unusually desirable for use as a transducer for high frequency operations: for filters, resonators, frequency control units, and the like. Small wafers of such material can be prepared very thin, capable of resonating at high frequency, without having to develop unwanted high capacitance locally in the circuit. The high acoustic velocity further permits operation at a higher frequency for a given thickness of material. Polarized transducers of potassium sodium niobate, 0.015 x 0.015 x 0.75 inch in size, for example, sliced from a larger crystal, should give superior performance in various ultrasonic and dispersive delay lines, some of which cost up to $5000

each. Highly sophisticated delay lines are employed in the electronics of the Sentinal system, while others are widely used in European color television circuits.

Potassium sodium niobate has other technical advantages. The material can be used effectively over a wide temperature range. There is very little change in dielectric constant, for example, from -10°C to +225°C, at which temperature the material changes from one ferroelectric crystal structure to another. PSN does not lose its ferroelectricity until above 400°C, whereas barium titanate ceases to be ferroelectric when heated only to 120°C.

The properties of $K_{0.5}Na_{0.5}NbO_3$ reported by Jaeger and Egerton [1] are of interest because of the improvements found on hot pressing this material as compared with air firing (conventional sintering), as shown in Table I. Enhanced piezoelectric coefficients were noted, and the radial electromechanical coupling coefficient was increased from 32 to approximately 48%. The authors felt that the new material was desirable for electromechanical transducers, particularly in the 10 to 20 MHz range. Still further improvements should be found when single crystals are measured.

The properties of selected transducer materials are compared with those of PSN in Table II. Note that PSN is about equally efficient (has good coupling coefficients) in both shear mode and longitudinal mode operations. Its coupling coefficients are higher than that of barium sodium niobate in shear and greater than lithium niobate longitudinally. Although PZT has high coupling coefficients, its velocity of sound is too low and its dielectric constant is too high for it to be used as a high-frequency transducer. It should be noted, also, that the values for PSN and PZT are for polycrystalline (ceramic) materials whereas the other materials are in single crystal form.

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(1) R. E. Jaeger and L. Egerton, "Hot Pressing of Potassium-Sodium Niobates", J.Am.Ceram.Soc. 45 (5), 209-13 (1962).

TABLE I

Characteristics of $K_{0.5}Na_{0.5}NbO_3$ Ceramics at Room Temperature

	Air Fired	Hot Pressed
Dielectric constant (100 KHz)	290	420
Electrical Q (100 KHz)	~50	~70
Specific resistivity (ohm-cm)	$\sim 10^{12}$	$\sim 10^{12}$
Density	4.25	4.46
Frequency constant (cycles · meters)	1650	1700
Mechanical Q, radial	130	240
Young's modulus (newtons/m^2)	1.04×10^{11}	1.5×10^{11}
Piezoelectric constants		
d_{31} (coulombs/newton)	32×10^{-12}	49×10^{-12}
g_{31} (meter-volts/newton)	12.6×10^{-3}	13.1×10^{-3}
d_{33} (coulombs/newton)	80×10^{-12}*	160×10^{-12}
g_{33} (meter-volts/newton)	31.5×10^{-3}*	43×10^{-3}*
Electromechanical coupling coefficients		
k_r (radial)	0.36	0.45
k_{31}	0.22	0.27
k_{33}	0.[illegible]*	0.53

* Estimated values

Delay lines such as might use PSN transducers are shown schematically in Figure I. An electrical signal passes along a wire at about the speed of light. A sound signal travels at different rates in different materials, but commonly of the order of 1/100,000 the speed of light. The electrical signal to be delayed is fed into a transducer, where it is converted to an acoustic wave. The acoustic energy passes through the sonic transmission medium to the second transducer in which it is converted again into an electrical signal. The acoustic energy may be transmitted through the bulk of the medium or along the surface, depending on the performance characteristics required. A sonic delay line in which two transducers are separated by four inches of glass, for example, can delay an electrical signal by forty microseconds, as long as it would take the electrical signal itself to pass along nearly forty thousand feet of wire. This is only one of the applications of PSN in electronics.

C. CRYSTAL GROWTH FROM MOLTEN SOLUTION

When growing crystals of electronic ceramic compositions from a molten solution, as opposed to growing from a straight melt, most investigators to-date have used molten salts and simple oxides as the solvents, as shown in Table III. Potassium fluoride, bismuth oxide, lead oxide, boron oxide and barium chloride are among the materials so used. For space processing, however, various more complex solvents, chiefly silicate glasses, might be more effective. There are a number of reasons why this should be so. Molten silicate glasses should have much higher viscosity than molten salts, and have less tendency to wet and creep along the walls of the platinum crucible. For both of these reasons, the melt should tend to remain in the container better than otherwise. The glasses would be more stable, chemically, having lower volatility and less tendency to change in composition during the relatively long time allotted to the crystallization procedures. Silicate glass melts show a slow change of viscosity with change in temperature, in comparison with the abrupt changes experienced with molten salts. The groundmass, being glassy and viscous, will inhibit the formation of spontaneous nuclei during cooling and will not, itself, crystallize around the already-grown crystals. One must not overlook the obvious advantage of all the molten solvent systems, that one can prepare a crystal from solution at a convenient temperature well below the melting point of that composition of crystal.

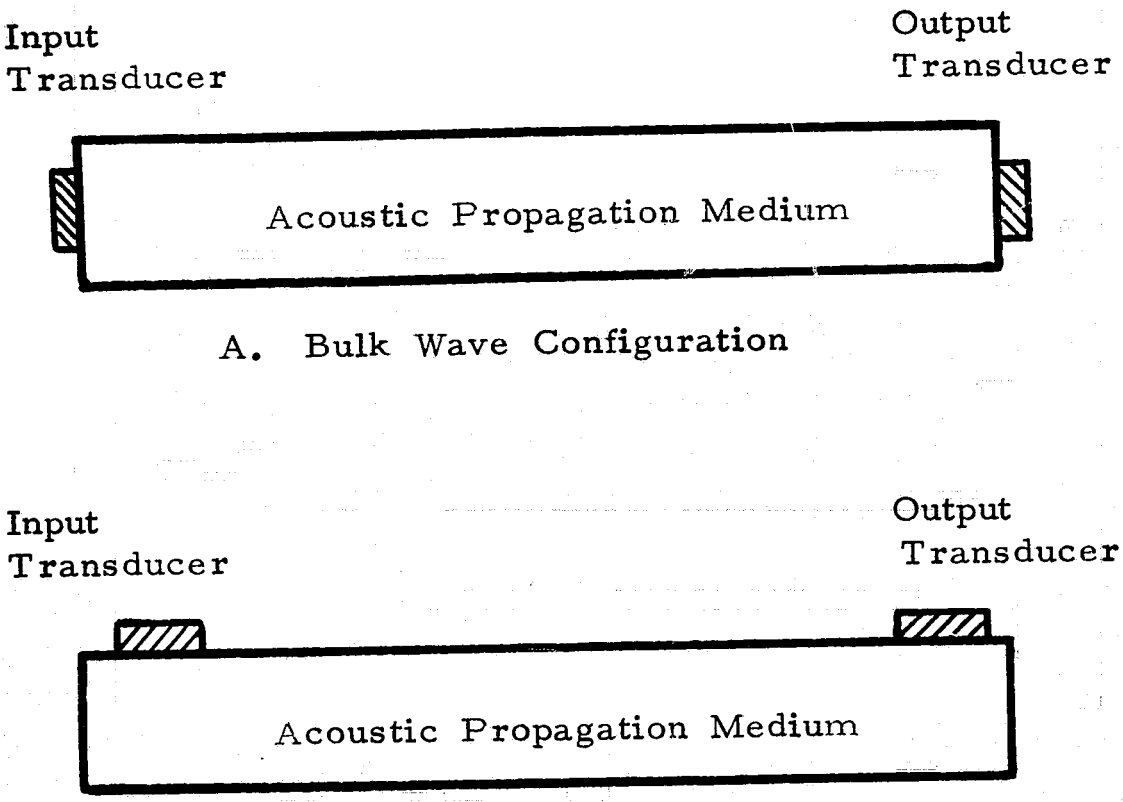


Figure 1. Arrangements of Transducers and Acoustic Transmission Material in a Sonic Delay Line.

TABLE II

PHYSICAL CONSTANTS FOR SELECTED TRANSDUCER MATERIALS

	(Shear Mode Operation)			(Longitudinal Mode Operation)			
Material	$V_S \times 10^5$ cm/sec	Impedance ρc	Coupling k_s	$V_L \times 10^5$ cm/sec	Impedence ρc	Coupling k_t	Dielectric Constant
X cut Quartz	3.8	10	0.137	5.7	15.2	0.10	4.58
Y cut Quartz	5.5	13	0.11				4.58
AC cut Quartz	3.2	10	0.13				4.58
Lithium Niobate	3.7	!7.8	0.68	7.2	34	0.19	30-80
Z Barium Sodium Niobate	3.58			6.53	32.6	0.57	30
X-Y Barium Sodium Niobate	3.58 3.37		0.2 0.2	7.27 6.98			30
PZT PSN	2.3 3.0	16 13.5	0.7 0.64	4.4 6.2	31 28	0.7 0.6	1200 375

TABLE III

CRYSTALS GROWN FROM MOLTEN SALTS[2]

Composition	Flux	Temp. Range (°C)	Rate of Cooling (°/hr)	Crystals Leached from Matrix with
$BaTiO_3$	KF	1200 - 850	1 - 5	Hot water
$Bi_4Ti_3O_{12}$	Bi_2O_3	1200 - 800	2 - 5	Strong mineral acids
$KNbO_3$	KF/KCl	1100 - 800	1 - 10	Hot water
YIG ($Y_3Fe_5O_{12}$)	PbO	1350 - 930	1 - 5	Hot 25% NHO_3
YIG	$PbO-PbF_2$	1260 - 950	0.5 - 5	Hot 25% HNO_3 50% HAc
YIG	$BaO-B_2O_3$	1260 - 900	1	Hot 25% HNO_3
YAG	$PbO-B_2O_3$	1250 - 950	1	Hot 25% HNO_3
RFe_2O_4	PbO	1300 - 800	10	Hot 25% HNO_3
$NiF3_2O_4$	$Na_2B_4O_7 \cdot 10H_2O$	1330 - 1250	2	Hot HNO_3

(2) J. J. Gilman, The Art and Science of Growing Crystals, (1963) John Wiley and Sons, Inc., New York, pp. 268-269.

Table IV lists some of the crystal-glass systems that have been investigated at the Space Sciences Laboratory. PSN can be grown readily from potassium sodium silicate glasses. Other electronic oxidic compositions can be grown from similar glasses.

1. Advance Preparation of Space Experiment Materials

There is an outstanding advantage of using a molten glass rather than a molten salt as the solvent. Because of the unique properties of glass, described above, it is possible to prepare the space experiment in advance. Carrying out this operation prior to the space flight saves time, conserves spacecraft power, and helps assure process reproducibility. One is able to dissolve the electronic ceramic constituents in the glass in the earth environment. The molten solution can be held for any desired length of time, 24 hours for instance if necessary, to homogenize the materials. Extraneous nuclei are dissolved and bubbles are removed as the glass is "fined". The melt can be examined, to assure that all of the charge has been taken into solution. The melt is then cooled rapidly to form a glass of almost optical quality, which again is inspected. During space operations it is necessary only to remelt the glass, reach a satisfactory temperature uniformity in the crucible, and begin the crystal-growing operation.

2. Slow Cooling of Melt Essential

When growing crystals of oxidic materials from a flux, it is necessary to cool the solution slowly in order to produce crystals of good quality. Experts have recommended cooling rates as low as $1/2^{\circ}C$ per hour, which might be impractical in short space flights. Rates of 1° and 2° per hour are commonly reported to yield good results, while 10° per hour appears to be a maximum. We have chosen to investigate 4° per hour, as a practical compromise. It is planned to investigate the feasibility of adjusting the concentrations of the ingredients, that is, the degree of saturation, so that crystallization will take place over a range of approximately $200^{\circ}C$ (50 hours at $4^{\circ}C$ per hour).

TABLE IV INVESTIGATION OF GROWTH OF CRYSTALS OF ELECTRONIC COMPOSITIONS AT GE/SPACE SCIENCES LABORATORY

Electronic Material Incorporated	Composition Of Host Glass	Weight Ratio Electronic Mat'l to Host Glass	Estimated Densities	
			Crystal Phase	Glass Phase
A. Compositions Proved Capable of Being Quenched to Homogeneous Glasses				
$BaTiO_3$	$BaAl_2Si_2O_8$	70-30	6.0	3.3
$BaTiO_3$	$BaO \cdot 2B_2O_3$	70-30	6.0	2.8
$K_{.5}Na_{.5}NbO_3$	$KNaO \cdot 3SiO_2$	80-20	4.6	2.4
Ni, Fe, Co Ferrite	$MnO-Al_2O_3-SiO_2$	---	4.3	---
Ni, Fe, Co Ferrite	$MnO-Al_2O_3-SiO_2$ (33%) $PbO \cdot 0.67SiO_2$ (67%)		4.3	---
$Pb(Zr_{0.53}Ti_{0.47})O_3$	$PbO \cdot 0.67SiO_2$	33-67	7.6	6.9
B. Additional Compositions Under Investigation				
$(BaSr)TiO_3$	$(BaSr)O \cdot 2B_2O_3$	70-30	5.4	2.7
$PbNb_2O_6$	$PbO \cdot 0.03Al_2O_3 \cdot 1.94SiO_2$	50-50	5.8	4.7

D. INVESTIGATION OF CRYSTAL-GROWTH PARAMETERS

Once one has chosen a method of crystal growth and has selected the composition of crystal to be grown, it is necessary to determine the conditions under which good crystals can be grown and recovered. Under some combinations of conditions no crystals will be formed at all; under other conditions a multitude of crystals may be formed, although of poor quality. In any event, it is important to be able to recover the crystals after they have been produced. If the crystals are formed at an elevated temperature in a molten solution and left in place as the liquid cools and is solidified, recovery is best accomplished by leaching away the groundmass, thus exposing the crystals. The leaching agent should be capable of dissolving the groundmass selectively without attacking the primary crystals.

Following are key variables which we have examined with a view to determining their influence in the selected growth system:

1. Composition of solvent (silicate) phase
2. Solubility of solvent and crystal phases
3. Concentration of constituents of the crystal phase incorporated in the solution
4. Temperature at which spontaneous crystallization begins
5. Temperature at which seed is introduced
6. Characteristics of grown crystals

By investigating these variables, one at a time, we are zeroing in on the growth procedure to be recommended for a space experiment.

1. Composition of Solvent Phase

Studies were made of the growth of PSN crystals from solutions of K_2O, Na_2O and Nb_2O_5 in melts of the following silicates. Note, the ratio of K_2O to Na_2O in the solvent is the same as that in PSN. This serves to provide a large common-ion effect.

$KNaO \cdot 3SiO_2$
$KNaO \cdot 2SiO_2$
$KNaO \cdot 1.5SiO_2$
$KNaO \cdot SiO_2$

X-ray diffraction measurements indicate that PSN appears spontaneously as the first crystalline phase from each of these silicates. Within the range studied, the ratio of KNaO to SiO_2 does not seem to influence the nature of the primary phase. The melting points of equivalent solutions were found to decrease with decreasing SiO_2 contact, as did also the lowest temperatures at which the melts could be poured from the platinum crucible.

2. Solubility of Glassy and Crystal Phases

The solubility of the above silicates increased with decreasing SiO_2, that is, the $KNaO \cdot 3SiO_2$ was largely insoluble in hot water while the $KNaO \cdot SiO_2$ glass dissolved almost completely. Crystals of PSN prepared separately were held in warm water for three days; no decrease in weight was observed. It appears, therefore, that water should be a satisfactory leaching agent for these compositions.

3. Effects of Concentration of the Solution

Batches of K_2CO_3, Na_2CO_3, Nb_2O_5 and SiO_2 have been weighed out and melted, representing not only variations in the ratio of KNaO to SiO_2 as reported above, but also variations in the weight percent PSN in the silicate glass. The largest amount of PSN successfully incorporated in the $KNaO \cdot 3SiO_2$ glass was 85 per cent, that is, 85 parts of PSN were dissolved in 15 parts silicate. For the recent crystal-growth studies, the most common concentration has been 60 weight per cent PSN and 40 weight per cent silicate solvent. Qualitative evidence has indicated, however, that the solutions containing 60 per cent PSN tend to become saturated too soon, and lower concentrations (40 and 20 per cent) are being investigated.

4. Temperature of Spontaneous Crystallization

Various melts were made up, stabilized, and allowed to cool at 20° to 50°C per hour. Drops of glass of each melt were poured at about 50° intervals, annealed at 300°C, and then examined with a binocular microscope. The temperatures at which the first crystals (small cubes) were seen was noted, as well as the number and size of crystals appearing in later (cooler) drops. A regular relationship was seen between the composition of the solvent phase and the concentration of PSN constituents, as shown in Table V.

TABLE V

CRYSTALLIZATION CHARACTERISTICS OF VARIOUS MELTS OF PSN IN $KNaO \cdot x\ SiO_2$

Comp. No.	Crystal to Glass Ratio	KNaO to SiO_2 Ratio	Clear Glass Temp. °C	First Few Crystals	More Crystals	Minimum Pouring Temp.
FF-30	60-40	1 : 3	1200 1100	1040	1010	Below 980
FF-31	60-40	1 : 2	1200 1030	1000	1000	
FF-37	60-40	1 : 1.5	1030	950	900	Below 880
FF-36	60-40	1 : 1	Above 900	900	850 800 750	Below 750
FF-40	40-60	1 : 1	850 800	760	720	Below 700

5. Temperature for Introducing Seeds

In producing crystals it is planned to introduce a seed of PSN into the cooling silicate melt, and to allow further PSN to deposit on the seed. If the temperature at which the seed is introduced is too high, the solution will be insufficiently saturated and the seed will dissolve in the melt. If the temperature is too low, spontaneous crystallization will have started, and the introduced seed will have to compete with the other crystals already present. The seed will then not grow as rapidly as otherwise, and the many crystals present may interfere with each other.

Three preliminary crystals have been grown from seeds, to date. Crystal No. 1 was prepared by placing a seed of PSN in melt FF-30 (see Table IV) at 1100°C, cooling slowly, and removing it at 1040°. Crystal No. 2 was grown by inserting a seed in the same composition at 1040° and quickly dropping the temperature to 980° to 1000°, where it was held for two hours, and then removed. Crystal No. 3 was grown in melt FF-36. The seed was introduced at 990° and withdrawn at 800°. The seeds used, in each instance, were small cubes of pure PSN, about 1 mm on a side, placed in a small basket-like container made of 10-mil platinum wire.

6. Characteristics of Grown Crystals

The crystals grown on the three seeds were annealed on being removed from the molten solution. They were then encapsulated in a clear epoxy (Stycast 1269, cured 16 hours at 200°F). The epoxy mounting served to hold and protect the crystal as it was lapped down far enough to expose a cross section including the original seed. The crystals were then examined with the electron microprobe, with a view to determining the growth mechanisms. The evidence presented indicates that the crystals grew too rapidly. At one stage silicon was not adequately eliminated, and later the growth was so rapid as to surround and trap globules of the solvent glass.

Two factors seem equally responsible for the rapid growth of the crystals: (1) the rate of cooling used in these preliminary experiments is considerably greater than that which

is commonly employed in such crystal growth. It will be advisable now to cool the melts at a slower rate. (2) It is believed that the degree of saturation of PSN is too high in the solutions prepared thus far. There is commonly a significant amount of PSN in the bottom of the platinum crucible during cooling, at all except the highest temperatures and regardless of the rate of cooling (within limits), when the concentration of PSN is of the order of 60 per cent. It is planned to reduce the concentration of PSN to 40 per cent or lower, to lessen the tendency for this precipitation to take place.

Early in the investigation, the composition of the solvent glass was standardized at $KNaO \cdot 3SiO_2$. This is the composition in which crystal No. 1 was grown. Later, other compositions were employed. Glass $KNaO \cdot SiO_2$ currently recommends itself because of its easy solubility in hot water, facilitating the recovery of crystals from the groundmass. However, this glass is readily attacked by water vapor in the air. It may be better, therefore, if possible, to use glass of a compromise composition. It is desired to maintain adequate solubility, but provide somewhat greater chemical durability. The solubility of the $KNaO \cdot 2SiO_2$ glass does not seem to be sufficient for this purpose. It is planned to investigate composition $KNaO \cdot 1.5SiO_2$ to see if it will meet the requirements.

Thus, the work now will be directed at defining more precisely three variables: (1) the rate of cooling the melts, (2) the concentration of PSN to be incorporated into the solutions and (3) the ratio of KNaO to SiO_2 for the molten solvent. Using the newly-defined conditions, seeds will then be introduced at appropriate temperatures and attempts will be made to grow larger, faceted crystals. The information obtained from these crystals will be used in determining the requirements for further refinements and optimization of the growth conditions.

E. RECOMMENDATIONS FOR SPACE EXPERIMENT ON CRYSTAL GROWTH

At this stage of the investigation, the recommendation of the use of a molten glass solvent appears to be well justified. PSN is the favored composition of crystal to be grown, but the basic approach for the development of a space experiment would be

continued if another, similar oxidic composition were selected. Many of the details of a recommended experimental procedure are unresolved, but certain conclusions are beginning to emerge.

The growth of large crystals would be favored by using a large volume of melt, two liters, for instance. However, limitations of space and power call for a small volume of melt and a correspondingly small furnace, particularly for demonstrating feasibility. It is likely, therefore, that 100 ml. of melt, in a furnace occupying 1 to 2 cubic feet, would be a reasonable compromise. The minimum practical volume of melt is assumed to be about 35 ml. (100 grams of material). The 2-liter melt might be appropriate for a scale-up operation.

Power requirements will demand special consideration. Bringing the melt to top temperature prior to starting to grow a crystal should require the largest amount of electrical energy. A simple compact furnace is envisioned, rugged enough to withstand the forces of launch and re-entry. The design maximizes the heat transfer from platinum heater windings to the platinum melting crucible by incorporating the crucible into the system. Heat loss to the surroundings is controlled by a combination of super and fibrous insulation. It is anticipated that the ambient atmosphere for the experiment will be that of the space vehicle. Electrical controls will be consistent with the kind of power available. Depending on the power sources, one will need to plan in terms of using a limited amount of power for a considerable time (slow heating) or of using stored energy at a faster rate for a shorter time (rapid heating). Because slow cooling is so important, an exceptionally well-insulated furnace will be required, and a smaller amount of auxiliary power may still be needed to control the time-temperature schedule during crystal growth.

The need to recover the grown crystals undamaged must be kept in mind. It is hoped that it will continue to look feasible to use hot water as the leaching agent. Fortunately, it appears that adequate standard test procedures have been developed for the physical and electronic evaluation of the crystals. It is at this point, in fact, that the merits of the space preparation of these crystals will ultimately be established.

1. Proposed Program

The proposed program stems directly from the foregoing technical discussions. Problems to be investigated, in essence, include the following:

(a) Final selection of the crystal composition or compositions to be grown
(b) Selection of the composition of solvent glass
(c) Determination of the required concentration of crystal composition in the glass
(d) Determination of the temperature range of crystallization of the selected system
(e) Determination of the configuration and operational characteristics of the furnace
(f) Design and assembly of prototype equipment
(g) Operation of prototype equipment according to proposed schedules and procedures, to assure meeting of program objectives.

The procedures for a typical space experiment in crystal growth are presented in Table VI.

TABLE VI FLOW DIAGRAM OF CRYSTAL GROWTH EXPERIMENT

Initial Preparation (Pre-Launch): (a) Fill crucible with melt, "fine" and solidify (b) Affix seed to sting (c) Lock movable parts (d) Connect and check all wired circuits
Experimental Procedures (In Orbit): (a) Turn on power (settings to be determined) (b) Stabilize melt temperature at _____ °C (to be determined) (c) Unlock furnace hood and rotate to uncover melt (d) Unlock sting dial and insert seed to proper depth (indicator on sting) (e) Release seed and remove sting (instructions will be supplied) (f) Rotate furnace hood to cover position and lock (g) Lower temperature 4°C/hr. for 50 hours (control to be determined) (h) Cut power at °C, cool to RT.
Post-Experimental Procedures: (a) Unlock and remove hood-sting component (b) Disconnect power and thermocouple (c) Unbolt and remove furnace assembly (d) Leach the solidified melt with hot water (e) Recover crystals formed.

BORON FILAMENT MANUFACTURE IN SPACE — A LITERATURE FEASIBILITY STUDY

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ABSTRACT

This paper presents a comprehensive review of technical literature pertaining to the manufacture of boron filament on Earth. A possible space manufacturing process for boron filament is described. Several central substrate deposition techniques, using different core materials, electric decomposition, and other boron-containing raw materials, are discussed. Nonsubstrate deposition techniques, such as glow discharge on a rotating disc or between two pointed tungsten electrodes, are described. Several techniques to manufacture boron filament from the melt are discussed. These include point destruction of surface tension, electrical discharge forming, melt drawing, Czochralski crystal growth, the Taylor process, drawing a substrate through a melt, and melt extrusion. This survey points out a way to manufacture boron filament in space that involves heating high-purity boron to 2800°F in boron nitride crucibles, and then transferring it into an RF-positioning field for further heating by induction coils or hot gas.

I. INTRODUCTION

NASA is presently attempting to simulate interest in private industry for their idea of manufacturing goods in space for eventual use on Earth, utilizing the unique environment available in Earth orbit of near-zero gravity, huge vacuum, and nearly infinite black body.[1-5] Although the concept is now a few years old at NASA, its first extensive presentation to industry was at a 1968 conference[2] attended by invited heads of various American companies, including President Lew Evans of Grumman. At the end of this conference, at which NASA

summarized the possible uses of the space environment for manufacturing, a call went out for private companies to identify and develop areas of potential cost saving to themselves by manufacturing in space. This report summarizes one of the two areas considered by Grumman to hold some promise for our own development.

The use of zero-gravity must be the central focus of any manufacturing process designed for the space factory. In general, this limits uniqueness considerations to the liquid state, although certain gaseous state processes might be significantly improved in space. One specific category of liquid processes that might be considered is the processing of highly corrosive or high melting point materials, such as boron, which could be held by RF fields without crucible contact in the liquid state. Boron melts at 3755 ±30°F and is extremely corrosive above this temperature. There is no known crucible material that will not erode or corrode in contact with this liquid metal.

Filaments of boron are in great demand at this time primarily for composite filler material. By far the cheapest method of manufacturing filaments (Figure 1) of any substance is to draw from the melt. Highly viscous materials, such as glasses and plastics are presently manufactured in this way. Unfortunately, the rheology of molten metals and many other materials has so far disallowed this process. As a result, filaments of these materials must be manufactured by more expensive means. Materials with a reasonable amount of ductility can be solid extruded through ever smaller dies. Others, including boron, must be formed electrochemically or by chemical vapor deposition (CVD) on a substrate.[6]

It would be highly desirable for boron filaments to be fabricable from the melt. Not only could cost be reduced to a level competitive with graphite in the future, at about $30 to $50 per pound, but the filament itself might be improved in strength from the 400,000 psi of present material to well over a million psi.[7] In addition, rates of production could be increased a hundred to a thousandfold, smaller diameter filaments would be economically possible, and boron composites would be used in various nuclear applications for which they are presently restricted by the tungsten core of boron filaments. In order to do this, however, a method of holding and shaping the boron into filaments without touching a crucible must be developed. Several possibilities can be considered for this, but the best appears to involve holding the boron mass in a high-frequency coil arrangement under zero-gravity conditions in space. Filaments might then be formed from the mass by: Czochralski crystal growing, filament drawing, breaking the surface tension with a point heat source, electroforming, or melt extrusion through a field die.

II. PRESENT METHOD OF MANUFACTURE OF BORON FILAMENTS

A. Structure

Commercial quantities of continuous boron filaments are today made by chemical vapor deposition on a 0.0005-inch diameter hot tungsten filament from BCl_3 gas.[8-19] This process has been described by many writers, and its exact details are unimportant here (Figure 2). The filaments so produced range in diameter from 0.003 to 0.005 inch and in lengths up to 10,000 feet or more.

During the course of deposition, the tungsten core generally disappears entirely, being replaced by reacted tungsten borides, mostly W_2B_5 and WB_4 (Figure 3). The cylindrical boride core thus formed in the filament center is only 0.00065 inch in diameter, and shows a very distinct interface with the bulk boron due to the much higher diffusivity of boron in tungsten than vice versa. Very little tungsten manages to cross this boundary into the bulk boron. The interface area is full of small voids produced by a Kirkendall vacancy condensation effect after rapid boron diffusion into the core.

The surface of CVD-produced boron filaments has a characteristic noduled or grainy appearance. These nodules grow larger as the filament diameter increases up to 0.0035 inch, but become smaller beyond this diameter. Their absolute size varies from run to run. The cause of this nodule effect has been found to be die marks on the surface of the original tungsten filament. The die marks provide sites of preferred nucleation and growth for the boron, which grows in cones outward. It is highly important, therefore, for the substrate material to be as smooth as possible.

In addition to nodules, the filament surface occasionally contains inclusions, most probably picked up at the mercury contact seal at the exit of the reaction chamber. Electron microprobe analysis has shown that these inclusions contain Mg, Cl, Cr, and Ca.

The bulk boron has a crystal structure, called "amorphous" which has been identified in X-ray, electron diffraction, and grain grown growth studies[20] as a microcrystalline β-rhombohedral structure. There is some controversey over the size of these crystallites. X-ray studies place them at approximately 20 Å. Some electron-diffraction investigations confirm the 20 Å value. However, other electron-diffraction studies indicate a highly strained, oriented, layered platelet structure with crystallites of 2000 Å size.

High residual stresses are known to occur in CVD-produced boron filaments. The core is in a compression of 150,000 to 200,000 psi, the surface in compression at 70,000 psi, and the first deposited layers in tension at 120,000 psi. The primary cause of these stresses appears to be the increase in core size as the filament forms, although other factors, such as temperature fluctuations during growth, thermal expansion mismatch between boron and core materials, and quenching at the mercury exit contact seal, also play a part. The stress

pattern apparently varies, greatly from filament to filament. These high stresses cause radial cracks (extending from the compressed interface across the tensed first layers of bulk boron to the outer, compressed layers) to occur in all CVD-produced boron filaments.

B. Properties

CVD-produced boron filaments have mechanical properties highly desirable for composite materials (Figure 4). Tensile strength values average 400,000 psi with a standard deviation of about 125,000 psi, measured for a standard 1-inch gage length; torsion shear strength values are about 500,000 psi. The Young's modulus ranges consistently from 55 to 60 x 10^6 psi, while the modulus of rigidity is measured at 26 x 10^6 psi. The Poisson's ratio is 0.21.

The density of boron is very low. Bulk material has a density of 2.34 g/cm^3 (compared to 2.70 for aluminum and 1.8 for beryllium), and the tungsten boride core of a 0.004-inch diameter filament only increases this value to 2.6 g/cm^3. Its specific tensile strength value is therefore 4.0 x 10^6 inches. Comparisons show these to be the best combination of filament properties available for composites. However, despite these high values, tests have shown they are actually quite low compared to what is possible for boron.

There are basically four major sites for fracture initiation in CVD-produced filaments (Figure 5). The temperature range necessary to obtain the "amorphous" boron is somewhat narrow. As a result large crystals of β-rhombohedral boron are formed occasionally and these markedly decrease strength values to below 200,000 psi.

At somewhat higher strength values - between 200,000 and 400,000 psi - large inclusions, due to impure deposition conditions, initiate fracture. These inclusions range in size from 2.5 to 20μ; the strength effect of particles smaller than these is masked by other factors.

The third strength-limiting site, again applicable in the range 200,000 to 400,000 psi, is the noduled surface of the CVD filaments. Under the right deposition conditions this is eliminated in as-produced filaments; alternatively, chemical polishing, removing approximately 0.005 inch from the surface, will eliminate the nodule effect. In general, chemical polishing is necessary to eliminate this strength-limiter.

Bend-test and other evidence has shown the existence of a fourth strength limitation site to be the core at the 400,000 to 500,000 psi level. Weibull has shown theoretically and experimentally that the bend-to-tensile strength ratio for a rectangular homogeneous material is 1.41. Despite a difference in test geometry, the same ratio for as-produced boron filaments is about 1.6. However, chemically polished filaments without surface flaws show a ratio of 3.8, much too high for accord with the theory. The explanation for this

discrepancy lies with the filament core. In the tensile case, the stress is applied uniformly over the cross-section so that any flaw present in the specimen will concentrate stresses and cause failure. However, in the bend case, the central plane of the filament (the core area) experiences no stress, while the surface is stressed to a maximum. Thus, the core area limits strength in the tensile tests, but not in the bend tests, causing the high 3.8 ratio.

The bend test indicates the true stress levels possible to bulk boron, if the core could be eliminated. That strength has been conservatively calculated as 26×10^5 psi in tension and 39×10^5 psi in bending. These calculated values, obtained from the measured modulus of elasticity of CVD-produced filaments, are probably too low, since higher moduli up to 70×10^6 psi have been measured on micro-crystalline boron[21] In fact values of flexural strength exceeding 2×10^6, and as high as 2.7×10^6 psi, have been obtained on chemically polished specimens. According to the Weibull ratio, therefore, pure boron filaments should easily give tensile strengths of 5/8 of 2×10^6 psi, or at least 1.25×10^6 psi. (Actually these values should be higher since the core has a finite size in small filaments and will reduce bend test values to some extent.)

There is further direct evidence that the core area limits strength. In tests on split boron filaments, with an average tensile strength of 250,000 psi, the core was etched out. These filaments then presented average strengths of 650,000 psi, with high values of 890,000 psi. And finally fractography studies confirm its role as a stress limiter.

There are several reasons for the tungsten/tungsten-boride interface to act as a stress concentration.[20] First, the two materials have markedly different mechanical and physical properties. Second, the high compression/tension stress difference across the interface already discussed adds to any applied stresses. Third, the Kirkendall voids along the core interface act as stress concentrators.

In addition to limiting strength, all four of these fracture sites (i.e., structural irregularities, surface defects, bulk inclusions, and the core interface) produce the great variation in strength values presently obtained on boron filaments.

To what extent can these stress-limiting and stress varying factors be eliminated? With careful processing, all but the core interface problem can be eliminated.[11] It remains as a strength-limiter in all filaments produced by chemical vapor deposition on tungsten.

C. Further problems (Figure 6.)

Strength values are only one of the problems encountered in chemical-vapor-deposited boron filaments. In addition to this, however, are (1) the nature of the tungsten core, which eliminates boron composite as a nuclear material, due to the nuclear properties of tungsten, (2) the cost of boron filaments, (3) the speed of the manufacturing, and (4) the ultimate size of the filaments, limited by the size of the tungsten core.

Boron can be used in nuclear applications as a neutron absorber and shield, having a thermal neutron cross-section of 750 barns. However, the small amount of tungsten in CVD-produced filaments disallows this use. As a result, boron composite material will not be usable in nuclear applications unless the tungsten core can be eliminated. The future potential usage in this application, if the core can be eliminated, has been estimated at 25% of the future aerospace market, which is indeed large.[22]

The present cost of boron filaments produced by chemical vapor deposition on tungsten is at least $251 per pound (in lots of 3000 lbs.)[23] For the time being this figure provides a competitive edge over graphite (at over $300 per pound) and other potential reinforcement materials.[7] Of course, boron does have certain properties which may continue to make it competitive, e.g. higher strength and slightly higher modulus than graphite. However, projected cost values for the 1970's show that, with increasing usage and manufacturing skill, graphite will far outshine boron-on-tungsten in cost as a composite material. Of the $251 figure for boron on tungsten, over $100 is tied up in the tungsten. Processing costs for this size tungsten filaments are not expected to decrease significantly without major technological breakthroughs. Boron-on-tungsten filaments, as a result, will level out in cost at a predicted level of about $145 per pound by 1975. Graphite, on the other hand, is expected to reach $30 per pound by that time (about the cost of bulk boron). Clearly, unless some major change takes place in manufacture of boron filaments, the material will soon run into strong competition from graphite.

The speed of manufacturing boron filaments is about 1 to 10 feet per minute per filament depending upon the length of the chambers. This is much faster than a method such as Czochralski single-crystal growing; however, melt extrusion processes promise rates on the order of 100 to 1000 times greater per filament.[32] This is considered a highly significant difference.

Finally, the tungsten core can only be manufactured to a certain minimum diameter. Both handling problems and production economies mark this limit. If any smaller diameter is desired, a different process will be required to produce the filament.

III. POSSIBLE METHODS AND PRESENT STATUS

A. Other Chemical Vapor Deposition Methods

Several investigators have attempted to chemically vapor deposit boron on hot wire substrates other than tungsten[12, 15] (Figure 7). Though induction and radiant heating have been tried, resistance heating has been most satisfactory to heat the wire and is the only method developed to date. The temperature necessary to decompose BCl_3 and form "amorphous" boron greatly restricts the possible candidates for the hot wire (B^{24}, Rh, Ta, Ti, Mo, and graphite have been used), and tantalum is the only one to date which could conceivably compete with tungsten. However, the tantalum filaments are more expensive than tungsten and cannot withstand the high temperatures as long, so that today tungsten is used exclusively for the hot-wire process.

If diborane, B_2H_6, is used instead of BCl_3, lower deposition temperatures can be used, because of the lower decomposition temperature of the diborane (500 to 750°C).[13, 17, 25, 26] In this case, other substrate materials can be considered in the hot wire apparatus. One such substrate, which was considered promising and was thoroughly investigated, is fused silica. The price of this composite filament would be about $30 per pound, if it could be made with the same properties as the boron-tungsten. However, average strength levels attained are only 200,000 to 300,000 psi, with normal maximums about 350,000 psi. The strength limiters appear to be two-fold: (1) lack of bonding between boron and core evidenced by fracture origin in the interface and by pullout of the core; and (2) low density apparently caused by polymer and gaseous void formation at the temperatures necessary for deposition. Although it was originally though that diborane would provide faster deposition rates than BCl_3, the deposition has been found to be diffusion limited and maximum rates without detrimental effects on filament strength are no more than are possible with BCl_3.

Chemical vapor deposition on a substrate can also be accomplished by electrical rather than thermal decomposition of a boron-compound gas (Figure 8). This process has the distinct advantage of allowing plating on conductive or nonconductive filaments, since the filament can be a passive receiver surface (although in some configurations it is used as an electrode). These electrical discharge methods are presently in development, but there are many design problems to be overcome including electrode fouling and discharge plasma and field instability. No examples of quality boron filaments produced by these methods are known and they are relatively slow - about 0.8 feet per minute.

All of the processes mentioned so far require a central substrate filament for deposition. This remains as a weak link and/or high cost item in the system. Several systems have been proposed which would eliminate this in CVD-produced filaments.

One of these uses a glow discharge to deposit a thin line of boron on the outside of a rotating disc. This is peeled off to form a continuous filament without a central substrate. Generally, this process suffers from the same problems as normal glow discharge deposition on a substrate, namely electrode and chamber surface foul-ups and instability in the discharge plasma. The filaments obtained are unsymmetrical in cross-section, and initial start-up is very difficult.

Fortunately there is a better means of obtaining substrateless filaments.[27] If a DC glow discharge is ignited between two pointed tungsten electrodes in an atmosphere of BCl_3 and H_2, a boron deposit of filament characteristic forms on the anode and a boron stub of non-filament characteristic forms on the cathode. By withdrawing the anode from the cathode slowly, maintaining a constant discharge gap, short length filaments can be drawn which are limited by the electrical resistance of the filament and by the friable nature of the stub. The process can be made continuous by supplying electricity to the filament at a point near the glow discharge by means of a secondary discharge or a

mercury contact and by continual removal of the cathodic boron deposit. No success has been achieved in attempts to produce more than one filament from the same cathode because of electrical interference between glow discharges.

The gaseous conversion in this process is primarily thermal rather than electrical; temperatures range from 1700°C in the discharge to 1400°C at the cathode to 900°C at the anode. The rate-controlling step was found to be the diffusion rate through the glow discharge surface. One of the major problems with this process results from this — the maximum filament formation rate is only 0.1 feet per minute, which cannot begin to compete with even the CVD on tungsten process. Other major problems or disadvantages of this process are highly critical parameters, such as: difficulty of maintaining clear chambers (as in all glow discharge deposition processes); high fixed-capital and production costs; limitation in diameter of filaments to less than 0.0026 inch; low average strength of filaments of 300,000 to 400,000 psi and large variations in strength values (from well under 300,000 up to 800,000 psi), with little chance for improvement; and, finally, warping of the filaments.

In summary, then, it can be stated that none of the alternative CVD processes, with or without substrate, can compete in the foreseeable future with the deposition on tungsten route. Three of the major disadvantages of the latter — namely, high cost, low strength, and slow production rate — are unlikely to be improved upon, and in fact, would probably be worse, in the alternate processes, even if they were perfected.

B. Melt Processes

As indicated before, there are alternate methods to manufacture filaments other than CVD. Mechanical extrusion cannot be considered for boron because of its high hardness[28] and lack of ductility.[13] In fact, under strain of 400 μ in/in and stress of 30,000 psi in continuous load-unload cycles, polycrystalline boron displays no mechanical hysteresis (perfect elasticity) at a strain sensitivity of 2 μ in/in.[29] And in hardness boron is next to diamond among the known elements with a Mohs scale reading greater than 9. Of the other two possibilities, very little work has been performed on electrochemical boron filament manufacture, which leaves the melt processes for consideration.

There are at least seven distinct possibilities for boron filament manufacture from the melt in various stages of development:

- Point destruction of surface tension
- Electrical discharge forming
- Melt drawing
- Czochralski crystal growth

- Taylor process
- Drawing of substrate through the melt
- Melt extrusion.

The first two processes in this list have not been attempted as far as we know (Figure 9). Point destruction of surface tension was suggested by Dr. C. Lee of Grumman's Research Department.[30] If the surface tension on a liquid is broken at a point, material from the liquid mass will shoot out perpendicular to the surface. One way of breaking the surface tension is to superheat locally, e.g., with an electron beam or continuous laser. Under proper conditions, the material ejected from underneath the interrupted surface might shoot out as a continuous filament. Because no known work has been performed on this subject and even the workability of the basic principles of the process are in some doubt, no further consideration was given to it.

If current is passed through a wire, a cylindrical magnetic force field will form around the wire with the field vector tangential to the wire circumference, and the force vector radially inward. If two parallel wires with currents running in the same directions are placed in close proximity, the interaction of their force fields will tend to attract them to each other. A current-carrying rod may be considered as a bundle of wires with parallel currents. Because of the attraction of parallel currents, the field of this rod will tend to collapse it. While in the solid state, the rigidity of the rod will maintain its shape under high current levels, conducting liquids or gases (plasma) will constrict with a high enough current. Although no known work has been performed on liquids, a great deal of effort has been expended on plasma constriction.[31] Many instability problems are encountered with the plasmas, and there could likewise be expected to present problems in the liquid.

Metals and many other materials cannot in general be drawn from a melt, as is done with glass, because of low viscosity, and boron is probably no exception. Certainly at temperatures at or above the listed melting temperature, the viscosity of 99% pure boron, at only 41 to 50 centipoise, is much too low for either upward or downward drawing. The latter requires a viscosity of around 3000 to 4000 poise (estimated for glass) and a small variation of viscosity with temperature.[33] Boron evidently does have a much higher viscosity just below the melting temperature, sufficient, according to Aerojet-General, to blow bubbles.[32] This requires about 1000 poise[33]; however, the reproducibility of this result is in great doubt. First the existence of a melting range designates an impurity content in the material. Duplication of this impurity content ($\ll 1\%$) and maintenance of the very narrow temperature range at which this viscosity occurred would be improbable at best. In conclusion there is little or no prospect of being able to draw boron from a melt.

In the Czochralski crystal growth process[24, 34-37] (Figure 10), a seed crystal attached to a rod is used to nucleate crystalline material from a melt. The seed is gradually pulled out of the liquid as the crystal forms producing a rod. This process has been used to manufacture pure crystalline rods of boron. However, the rods grown are of large diameter, must be zone refined for proper shape and structure, and seem to be limited in length to about 3 inches. The process is very slow (about 0.5 inches per hour) and holds little promise for continuous filament production.

In the Taylor process[38] molten metal is poured into a hollow tube, usually glass. The tube is then softened, pulled, and cooled, leaving a filament inside. Although the process has been used to manufacture long, extremely smooth, very high-strength filaments of various metals, its applicability to boron composite filaments is doubtful. First, it is difficult to imagine continuous filament production; second, the process is extremely costly; and third, no material is known that can withstand corrosion from liquid boron and could be used as a tube. Therefore, the Taylor process can be eliminated from consideration for boron filament production.

As an intermediate process, utilizing the advantages of speed of the melt process and ease of the tungsten substrate process, an attempt has been made to draw tungsten and silica filaments through molten boron to form a boron filament.[39]

The coatings obtained were highly nonuniform, very thin, and irregularly grained. The tungsten tended to dissolve in the boron, making a tungsten/tungsten-boride filament, instead of one primarily of boron, and contaminating the liquid boron source. Strength was very low, with a maximum of 76,000 psi and average of 58,100 psi; the reasons for this were not examined in detail. Even if rapidly manufactured filaments were obtained, they would retain at least two of the four disadvantages of the CVD boron-on-tungsten process.

IV. MELT EXTRUSION PROCESS

A. Work by Aerojet-General

One of the melt processes, melt extrusion or melt spinning, has shown considerable promise in work performed under Air Force sponsorship by Aerojet-General and Monsanto.[33] Filaments are formed in this process by forcing liquid boron held in a crucible through a tiny orifice using inert gas pressure and solidifying it in a catch chamber below (Figure 11).

Aerojet investigated three basic areas: (1) molten-boron properties pertinent to fiberization, (2) materials for the heating and containment of boron, and (3) techniques and operational parameters related to fiberization. Since the design of melt-extrusion apparatus depends upon knowing certain fundamental physical properties of molten boron, Aerojet first investigated these. The melting point of their technical-grade boron (98.9% purity) was found to be

3736 ±30°F. Higher purity material (99.5%) melted slightly higher at 3755 ±40°F. A thermal arrest, accompanied by softening of the boron, was noted between 3625 and 3675 °F. Boron could be supercooled by more than 100 °F without freezing, even with alloying additions of up to 13.7 wt% titanium or 30.7 wt% zirconium.

It was thought that a low-melting-point eutectic might occur at about 2 wt% carbon in the boron-carbon phase diagram. Carbon was indeed found to decrease the melting point, but only by 25 to 50 °F (with additions of 0.3 to 0.5 wt%C). Neither titanium nor zirconium additions were found to have any effect on the boron melting temperature up to 13.7 wt% titanium or 21 wt% zirconium, although the volume contraction upon freezing was greater with these two additions than with pure or carbon-doped boron.

The viscosity of liquid boron at or near its melting point was found to be 45 ±5 centipoise for the grade investigated. Just below the melting point, over a very narrow temperature range, a viscosity high enough to allow blowing bubbles of boron existed. The normal viscosity of glass under these conditions is about 1000 poise. Carbon contents of 0.4 to 0.7 wt% increased the viscosity to 85 to 100 centipose; however, additions up to 20.7 wt% zirconium or 13.7 wt% titanium had no effect.

The surface tension of molten boron just above the melting point was found to be 1000 dynes/cm.

Aerojet tested many materials for the crucibles and orifices. Boron attacked MfB_2, TaB_2, ZrB_2, NbB_2, in order from least to greatest attack. None could be used in contact with molten boron because of excessive erosion. The same was true of both tantalum and tungsten. The most satisfactory results were obtained with boron nitride, especially when pretreated. For crucibles, satisfactory curing of BN was obtained with a cycle of 5 hours at 3150 °F plus 15 minutes at 3400 °F in argon at 1 atmosphere, while a satisfactory curing cycle for orifice inserts was 1 hour at 2800°F in vacuum followed by 5 minutes at 3400°F in argon at 1 atmosphere. Born will wet BN when: (1) the temperature is raised above 4000 °F. (2) the BN is not properly pretreated, (3) the BN has a low density structure, or (4) more than 0.75% carbon is added to the melt. Wetting is very undesirable in melt extrusion, since it restricts the smooth flow of liquid through the orifice. Even BN was rather unsatisfactory for both crucibles and orifices. Crucibles lasted a maximum of seven extrusion operations (about 12 seconds and 4 grams average for each extrusion – 84 seconds total), while orifice openings gained in area an average of 20% for each such extrusion. Worse, orifice enlargement varied from 2 to 120% unpredictably. While Aerojet claims that "repeated remelting of boron in BN crucibles does not cause significant pickup of impurities by the melt", the erosion indicated above hardly supports this conclusion. In fact, it is evident that BN is not a satisfactory container material for melt extrusion.

Aerojet's attempts to make fibers from the melt were highly unsatisfactory. The maximum length they attained was 0.150 inch, and most of their tests resulted in either no product or spherical shot. The apparatus is standard for this type of work, consisting basically of a crucible with changeable orifice insert; an RF heating coil with tantalum susceptor; a chamber above the crucible which is pressurized with argon gas; and a 6-foot long helium-filled chamber for solidification of the melt below the orifice. All of the fibers manufactured were of the β-rhombohedral variety. The Weber number, defined by $N_{We} = V^2 \rho d / \sigma$, where V = velocity, ρ = density, d = orifice diameter, and σ = surface tension, was found to be a good indication of fiberizability. Best results were obtained in the N_{We} range from 30 to 60. Added carbon up to 0.75 wt%, zirconium up to 20.7 wt%, and titanium up to 13.7% had no effect on the product. The solidification rate was not increased markedly with helium flow added to the area just below the orifice. No tensile tests were reported.

The poor Aerojet results can be attributed to many factors, but chief among them are the following:

- Short solidification chamber; fibers either could not solidify before hitting the bottom of the chamber or, if solidified, broke against the bottom.
- Inability to maintain a constant jet diameter due to orifice enlargement.
- Poor equipment design, resulting in nonrepeatibility of flowing.
- Crucible erosion.

B. Work by Monsanto Research

Monsanto Research has had much greater success with the melt extrusion process. Their investigation covered six basic areas:

- Define the basic parameters of the process and raw material and process control equipment, requirements.
- Investigate and evaluate the fundamental concepts for improving the behavioral characteristics of the charge material.
- Develop the melt spinning apparatus to the level of a filament forming unit capable of precise control over the appropriate operating parameters.
- Determine the broad range of conditions applicable to the formation of continuous boron filament.

- Determine the physical, mechanical, and chemical characteristics of filaments formed and correlate when applicable to process conditions.

- Design and construct a process unit tailored to investigate initial engineering scale-up factors and to reflect proper automatic control techniques.

A discussion of these areas will provide a state-of-the-art look at the melt-extrusion process.

Monsanto's equipment was basically the same as Aerojet's, consisting of a crucible and removable orifice insert; an upper chamber capable of argon gas pressurization; RF heating coils; a graphite ring susceptor to heat the boron charge to a temperature where direct RF coupling becomes efficient (approximately 2730 ^{o}F.); and a catch chamber below the crucible.

Monsanto's first effort was with a research scale unit, the crucible containing only 3.4 cubic centimeters of charge. A large capacity unit was built near the end of the program, but not extensively tested. Successful fiberization was accomplished with their technical-grade boron (99.5% pure); a series of boron minor alloys containing 1 to 2 wt% Ta, W, Zr, Ti, Nb, and V; and two boron compounds, aluminum boride, AlB_{12}, and yttrium hectoboride, YB_{70}.

The factors affecting filament formation were melt temperature and temperature uniformity (extreme sensitivity), extrusion pressure, and charge and fiber purity. For best results the temperature must be held below 4000^{o}F; the higher the melt temperature the worse the final results were.

Orifice wetting by the liquid boron was found to be highly undesirable for fiberizing. Wettability in turn was found to depend upon crucible material and pretreatment. If boron nitride is to be used, it must first be fired to remove volatile impurities. The best compatibility and contact angle were obtained using hot pressed boron nitride pretreated with ammonia at 2700^{o}F or methanol extracted, followed by prefiring at 4000^{o}F under argon. Preliminary results with isotropic and anisotropic pyrolytic boron nitride showed promise of increased mechanical strength.

Overall, boron nitride, aluminum nitride, and thoria were investigated as crucible materials. Only boron nitride showed any promise. However, even this is not a very satisfactory crucible material, suffering serious erosion. And for orifices it is quite unsatisfactory —a 3-gram charge, forced through an orifice made in the very best material, expanded the opening from 0.008- to 0.009-inch diameter, an area increased of 27%. Results show very much worse results at temperatures above 3900^{o}F and with other materials.

A total of 251 fiberization tests were run on the research scale equipment. Streaming occured in 185 of these and filaments formed 85 times. Once proper settings were established, the process was repeatable. An orifice range from

0.002- to 0.006- inch diameter, extruding pressure from 20 to 80 psi, and melt temperature of 3550 to 4500°F were studied, with filaments 0.0035- to 0.008-inch diameter and 1/4- to 11- inch length resulting, in yields varying from 1 to 90 wt%. Actually, high-speed photographic studies showed lengths of up to 2 or 3 feet being produced, but, upon impact at the collection chamber bottom, these broke into the shorter lengths. A "production-scale" unit was built utilizing 25- to 50- gram charges and a longer collection chamber, but testing was not finished.

Monsanto performed a lengthy investigation of the properties of the filament they obtained from the research-scale extrusion unit. All of the filaments were limited in tensile strength by surface pitting to the 50,000 to 60,000 psi range, with best results up to 89,000 psi. Bending strength was somewhat higher, as expected, ranging from 100,000 to 124,000 psi. Thus, the bending/tensile strength ratio is about 2.0. This is somewhat high, but not unexpected considering the existence of both surface and internal defects, and the wide range of tensile and bend strength values. No Young's modulus data were reported; however, bending moduli in the 70×10^6 psi range were measured in simple bend tests, with comparative tests indicating that melt-extruded filaments are stiffer than vapor-deposited boron filaments (measured at 45×10^6 psi).

An exhaustive examination was made of the possible reasons for surface pitting, including mushy solidification due to alloying elements; entrainment of solid BN, liquid B_2O_3 or various gases; hydrogen from the ambient NH_3 diffusing into the liquid stream and out at the liquid-solid interface; hot tearing; corrosion from catch chamber gas; and plane-front solidification pitting. Monsanto considers that this last explanation is the predominant cause of the surface defects. According to this, the solid-liquid interface of β-rhombohedral boron is likely to be inclined to the fiber cross-section because of its low symmetry crystallographic structure. The mechanism of nucleation and growth in an impurity-laden liquid leads, under this condition, to a pitted surface. There is, however, some ambiguity in Monsanto's conclusions, since in the summary of their work they claim that pitting is not solidification controlled, but rather due to some kind of corrosion. Although Monsanto eliminated BN from consideration as a solid impurity because they said they had not found it either in the body of the filament or in the pits, there is no work reported to this effect, and there is no place for corroded BN from the crucible and orifice to go except to be carried along with the filament. Therefore, it seems likely that BN is to be a prime cause for surface pitting as an impurity, either in solution or as a solid inclusion.

The basic problem with the strength of boron filaments, however, is not pitting, but grain structure. Much of the strength of CVD-produced boron filaments is due to the extreme fineness of the boron microcrystals. In fact, any macrocrystalline material in these filaments greatly weakens them. The grain size of melt-produced boron filaments is generally large in comparison with filament diameter, but varies greatly along the length. Many crystals extend

across the filament completely, while the size of others averages 1/8 to 1/4 of the filament diameter. Because of the low-symmetry crystal structure of boron, it is believed to be highly anisotropic in thermal and mechanical properties. Thus, large non-uniform grains can be expected to act as stress risers under an applied stress. Large grains, also, will tend to cleave catastrophically once a fracture has been initiated, while small grains will resist the propagation of a small crack.

In addition, a smaller grain size will reduce the pitting phenomenon, if this were due to impurity discharge in plane-front solidification. Smaller grain size would indicate more nucleation sites. If enough of these were present, nucleation would be essentially homogeneous and the inclination of the plane front to the filament would disappear. Therefore, no pits would be formed.

The mode of solidification evidenced by the microstructure of Monsanto's filaments shows that nucleation of the large grains takes place at the filament surface. This is due to the lower temperature of the surface and means that potential nucleation sites inside the filament are being overshadowed by nucleation and growth from the surface. It is evident, therefore, that a change in cooling conditions is needed to allow the internal nucleation sites to be active before the surface site in order for smaller grains to form. More heat should be removed longitudinally and less radially from the filament. Of course, high solidification rates must be maintained to form the small grains.

The most effective method for achieving a fine grain structure in a cast material is by adding alloying elements of the proper kind and amount to induce homogeneous nucleation at sites ahead of the advancing solidification front. There are two ways this can be accomplished: stable particles added to the original melt, or precipitation of stable particles at the liquidus from a homogeneous solution. Monsanto did not consider solid particle addition to the melt feasible for the extrusion process, so no work has been performed on this aspect of the problem. They did, however, perform some work on alloying for nucleation.

Theoretically, the most effective alloy nucleant for boron must form a compound that is stable at the liquidus of the melt either with the boron itself or with an impurity, must have a crystal structure similar to the rhombohedral system, and have a unit cell size near that of boron. Monsanto made a literature search for binary and ternary borides, carbides, and nitrides that might be effective nucleating agents. None with theoretically perfect characteristics was found, so trial and error was employed.

From a series of preliminary melts of boron alloys, several were chosen for melt extrusion because of their fine grain size. The best filament results were obtained with B + 2 wt% W alloy. In some areas a very fine grain size was obtained with this alloy, but other areas showed much larger grains. It is thought that incomplete mixing in the charge material is the explanation of the grain size variations. In general, the results of grain refinement show great

promise. Although it was hoped that alloying would reduce surface pitting, no such effect was noted.

Monsanto further characterized the high-temperature thermal arrest, describing it as a "plastic" creep region occurring at 3670°F.

From this discussion, it is clear that a number of Monsanto's problems are due to the contact between molten boron and any crucible or orifice (Figure 12). The process itself looks highly promising if the many problems associated with the crucible/orifice can be overcome. On the other hand, if the mechanical crucible/orifice cannot be eliminated, there is little prospect of this process becoming feasible for manufacture of boron filaments.

V. RF FIELD EXTRUSION PROCESS

A. General Description

In order to eliminate the problems with the crucibles in the melt extrusion process, it is necessary to support, contain, and extrude molten boron without contact from reactive materials. No solid material has been found suitable; no known liquids would be inert at these temperatures, liquid boron control with liquid streams is out of the question, and inert gas control of the boron would also be virtually impossible.

This leaves electric or magnetic field control. However, neither liquid nor solid boron is magnetic. Electrically, boron is a semiconductor[40-47], which means its conductivity increases with rising temperature (unlike metals). At room temperature, boron has a resistivity of 4×10^{6} ohm-cm; at 3495°F the resistivity has dropped to 5×10^{-2} ohm-cm, a change of 8 orders of magnitude. Addition of alloying elements greatly changes the room temperature values toward greater conductivity, but at high temperatures the values for alloys merge with those for pure boron. Because of the high conductivity at high temperatures of boron, electrostatic field positioning is out of the question. However, RF alternating electric fields can be used. For positioning this involves an arrangement sililar to levitation melting.

In levitation melting[48-55], a charge is placed in a high-frequency alternating electric field, in which it is levitated and melted without contact (Figure 13). From this state it can be "poured" out of the field by reducing the field strength and allowing gravity to pull on it. The field constricts the melt as it pours, forming it into a rod which can be solidified. The idea is to further constrict the poured rod down to filament diameter, thus using non-contracting fields to position and form the boron filaments.

There are severe problems with RF levitation melting and pouring semiconductors on Earth. Levitation must be performed against the gravity force, which limits the size of molten material that can be supported on Earth. In addition, gravity provides a fixed force field pulling on the boron. Finally, heating and levitation force cannot, in general, be independently controlled. It becomes desirable, therefore, for these and other reasons, to consider manufacturing boron under zero-gravity conditions, using RF fields to position and hold the boron, while heating, and extruding through a nozzle-shaped field.

B. Levitation Melting

Levitation of a solid or liquid conductor results from placement in a high-frequency alternating electromagnetic field generated between two coaxial coils with currents circulating in opposite directions. Eddy currents induced in the conductor interact with the field to produce supporting and laterally stabilizing forces. A levitated metal floats in space and usually melts.

Levitation melting on Earth was first proposed in 1923, but was not used until 1952, when its feasibility for crucibleless production of ultra-high purity refractory metals was investigated [51]. Though the process thrived for a short while, the inability to stably levitate more than about 20 grams of the denser metals and the development of other methods to accomplish the original levitation melting objectives has slowed the enthusiasm of many researchers.

Two basic parameters determine the levitation force on a sample – the coil current and the frequency. For materials of moderate electrical conductivity like boron, no significant increase in levitation force results as the frequency is increased at very high frequencies. However, the energy absorbed by the conductor becomes so large that melting results, and the temperature rises beyond the desired level. Maximum levitation force with minimum heating is attained at low frequencies and high field strengths and gradients. The value of the frequency to be used depends on the radius and nature of the metal and the temperature desired. Frequency tuning is not normally available over a very wide band, and temperature control thus becomes difficult at best. For a controlled drop out of a coil, in which the charge size is constantly changing, the difficulty is magnified.

The severity of this problem is great. In vacuum melting, separate controls for current and frequency are required for long duration experiments. It has even been proposed that separate means of heating, such as arc, electron beam, or a high-frequency indiction coil, be used in conjunction with the low-frequency levitation coil. However, boron is a low-conductivity material even up to the melting point, and there is no certainty that low frequencies will provide sufficient levitation force. And the lower the conductivity of a material, the more difficult it becomes to control temperature. As we have seen, however, in the melt extrusion of boron temperature must be controlled very closely. It is known, in addition, that RF melting of boron is not possible from the solid state, because of the low conductivity of the material. Thus, a

susceptor was used in Monsanto's equipment to raise the temperature sufficiently for the conductivity to allow direct RF heating of the boron to take place.

Some consideration has been given to the stability of the molten charge and of the pouring liquid in levitation melting. Evidently the surface tension and density determine whether liquid metals will drip during levitation. The levitation force acts solely off the central axis of the coil center, so that surface tension is the sole force holding up the charge on the vertical axis. If the field is sufficiently weak, the surface tension will be insufficient to hold it up, and it will drip or pour at the axis from the bottom of the charge. Though calculations have been made of the steady state conditions (charge surface tension, density, and radii of curvature) necessary to prevent dripping, no calculations of dynamics conditions have yet been performed to take into account a moving charge or oscillations in the system. However, surface tension forces can be expected to inhibit growth of short-wavelength instabilities in the system.

Coil design is still largely empirical. Small tubing diameter is preferable to provide more turns per unit length of coil. Tubing of oval cross-section can be employed for this reason. In practice, 1/8-inch diameter tubing of 0.020-inch wall thickness is the smallest that can be adequately cooled. Coil shape is critical. The smaller the diameter of the coil, the higher the field strength. Cylindrical coils give maximum levitating force, but require coils of reverse current direction on each end for melt stability. Other configurations tried include pancakes, rings, multilayered turns, and inverted cones. Recently some work has been undertaken to provide a more basic characterization of optimum levitation coil design, but the process is still largely trial and error. Specifically, obtaining a proper coil design to form a nozzle for filament formation will have to be the subject of experimentation. In fact, two researchers in the field of levitation melting have indicated doubt that such a design will be found.

Although at least 38 elements have been successfully levitation melted (Figure 14), no reports have been found indicating boron to be among them. However, semiconductors, such as silicon and germanium, have been levitated, and boron has higher conductivity at high temperatures than either of these two, so there is no reason to believe that any special problem will exist with boron. High vapor pressure in the liquid state has prevented certain elements from being levitatable, but molten boron has a relatively low vapor pressure and no such problem is expected. Extremely high melting temperature has prevented molten levitation of tungsten, but again Monsanto used RF melting in their boron work, so boron should melt in levitation also.

Besides the lack of crucible contact, other advantages exist in levitation melting over other means of processing liquid metals. First, the melt is homogenized very rapidly due to very efficient frictionless stirring. Monsanto believed that major difficulties arose in their alloying experiments due to inhomogeneity of the melt during pouring. Thus the great homogeneity possible

to levitation melts should aid the solidification of alloyed boron filaments. Secondly, very rapid heating and cooling rates are possible in a levitation melt, and homogeneity will therefore be retained in the solidified material. Thirdly, it is possible to remove gases from a metal very rapidly and completely in vacuum melting and therefore to control gas content level.

C. RF Positioning Fields

Dr. R. T. Frost discussed the subject of RF field positioning in space at the November, 1968, Huntsville Conference.[2] The accelerational forces that would be present in a space factory would be from two sources: spacecraft thrust, and astronaut body movement. Since thrusting could be controlled during material processing, only the latter need be considered. Dr. Frost's calculations show that for a 25,000-pound space station the maximum accelerations encountered would be 10^{-3} to 10^{-4} g. Since the translational motion of the spacecraft, due to astronaut movement across a 20-foot compartment, is only about 2 inches, it is probable that the design objective for the factory positioner could be a control acceleration of 10^{-4} g. Though a low frequency would be desirable for maximum control of melt shape, it is probable that high frequencies will be necessary, either for heating or for sufficient levitating force, because of the semiconducting nature of boron. For the same reason, high power will also be necessary. The maximum size of a position-controlled melt in space will be limited by the amplitude of oscillations of the molten mass. These oscillations would be initiated by the position restoring forces and, if large enough, would break the surface tension forces of the molten material. They would damp with time due to the viscosity of the melt. Order-of-magnitude calculations show that the mass limitation due to surface oscillations would allow positioning of 10^3 to 10^4 times as much material in space as can be levitated on Earth. For most materials this would mean positioning control of approximately 10 kilograms. For a 10-cm radius sphere, calculations show that these oscillations would disappear after 1000 seconds; for a sphere of radius 1 to several cm, the damping time would drop to 10 to 100 seconds. These order-of-magnitude figures are believed to be applicable to boron melts.

The best coil design for RF positioning could depend upon many factors. In any case, positioning and extruding coil design will have to be integrated. Possible positioning coil designs would include those used presently in levitation work — basically two-coil positioners — or, for more stability, an arrangement consisting of three pairs of orthogonal coils. The exact coil design necessary would be a major problem to overcome in implementing the proposed program.

D. RF Extrusion Nozzle Field And Heat Sources

Just as an RF field must be used to position molten boron in space, one must likewise be used to act as an extrusion die for filament formation. Any of the coils in the two or six-coil designs might be used for this, since a uniform field strength would exist at the center of each coil, and the liquid boron would

form into a cylinder as it passed through. Alternatively a separate coil arrangement might be used, if the field strength necessary to form filaments is significantly different from that necessary to position the boron in space.

The diameter of the extruded boron filament would depend on several factors, including the viscosity of the boron, the strength of the field, the diameter of the coil, and the speed of the extrusion process.

The force necessary to extrude the boron through the field nozzle could be supplied by increasing the strength of the opposing coil in either the two or six-coil arrangements. If this is not possible, an additional RF coil could be added to supply the extrusion force. Another possibility for this is inert gas pressure, although it would be difficult to control this to provide even heating and proper extrusion rate.

NASA has considered the heat sources that might be used for the AAP experiments[54], and their conclusions are equally applicable to the space factory concept. The sources included induction coil, electron beam, laser, electric arc, hot gas, electrical resistance, solar radiation, and chemical heating methods. Of these the electric arc and electron beam are impractical for the present project; with the former there is danger of contamination of the specimen by the electrode material, with the latter there is direct contamination because of the requirement of grounding the specimen. The other methods are all possible, though the laser is heavy, inefficient, and relatively unreliable for production processes at the present time; solar radiation would require orientation capability to keep the collector aimed at the sun; and chemical heating would be expensive and difficult to control. In conclusion, use of either hot gas or induction coil heating could be recommended for heating the boron mass.

VI. SUMMARY

A. Description of Process

From the preceeding discussion, a fairly complete description of the proposed process to manufacture boron filaments in space can be set forth (Figure 15). In barest outline, high-purity boron, doped as necessary for proper crystallization, is placed in a volume in space, where it is heated, either by hot inert gas or other means, to a temperature of about 2800°F. Up to this temperature the boron may be held in boron nitride crucibles. Then it is placed, still in the solid state, in an RF positioning field for holding, and heated further by either induction coils or hot gas. At the melting point, the boron is forced by the hot gas or by an induction coil to exit through the field forming nozzle. There it is cooled by experimentally determined means and collected on spools.

B. Advantages of Process

The potential advantages of space manufacture of boron filaments (Figure 16) are:

- Lower cost
- Higher quality filaments
- Faster production rates
- More potential uses.

The costs of this process should make boron filaments competitive with graphite, especially if the expected material benefit can be realized. Commercial grade boron (90 to 92% pure) could be obtained at a cost of $14 per pound in 5000-pound lots; this could then be purified fairly simply in space where no crucible contact would be necessary for containment. Alternatively technical grade boron (99.5% pure) could be obtained for $50 per pound in 5000-pound lots and used directly. These costs[55] are likely to decline rather sharply as demand for boron increases. Add to this the transportation costs at $5 to $10 per pound, as predicted by Dr. Von Braun[2], and the equipment, labor, and operating costs of the system. The estimated total should be quite competitive with graphite and well below the cost of present filament.

All of the strength problems associated with the core present in CVD-produced filaments should be eliminated by manufacture from the melt. The noduled surface (caused by the uneven surface of the original tungsten wire), the interface voids and cracks, and the residual stresses and different mechanical properties across the core interface all contribute to lowering the tensile and bending stresses that the present boron fibers can withstand. Assuming that proper grain size and fiber surface can be obtained on the melt-produced filaments in space, average tensile strengths of well over a million psi, and bend strengths of over two million psi should be attainable on a production basis. In addition, preliminary results have shown that melt-produced filaments have higher moduli. And the great scatter in strength values, associated with the core and surface defects, should be eliminated, permitting higher design allowables.

Several other advantages should acrue from use of the proposed process. Filaments of much smaller diameter should be manufacturable, if desired, by elimination of the fixed-size core. Production rates should be attained on the order of 100 to 1000 times greater than presently possible. In addition, boron composites would be usable in nuclear applications.

C. Problem Areas and Suggestions for Future Work

There are several major problem areas associated with the proposed process, and these would have to be investigated on a research level (Figure 17).

- Methods must be developed to crystallize molten boron to obtain a fine, even-grain structure. This involves investigations of cooling rates and methods and nucleation techniques. Much of this could be investigated on Earth, utilizing Earth levitation techniques.

- Levitation characteristics of molten boron must be investigated, including a search for stable coil designs. This knowledge should be used for designing space positioning devices for large masses, after experimenting in space with coil positioners. In conjunction with this, an effort should be expended to attempt to extrude molten boron from a levitation melt in filament-sized streams on Earth. If this proves impossible or when scale-up is necessary, these experiments should be performed in Earth orbit.

- The characteristics of fine-grained, high-quality, boron rods or filaments must be tested when these become available to make certain that the mechanical properties anticipated are actually attained.

- The exact design for a production machine must be drawn up. The proper heat source, extrusion force mechanism, environment, coil designs, etc., must be investigated and chosen.

- Once some of these questions have been answered with more certainty, an analysis of costs will have to be made in order to make certain that continuation of the effort will really be worthwhile.

In conclusion, it is clear that any further effort expended on this project must be of a research nature, and that there are many questions which would have to be answered before a production process could be designed. However, the process itself appears to be promising enough to warrant this further research.

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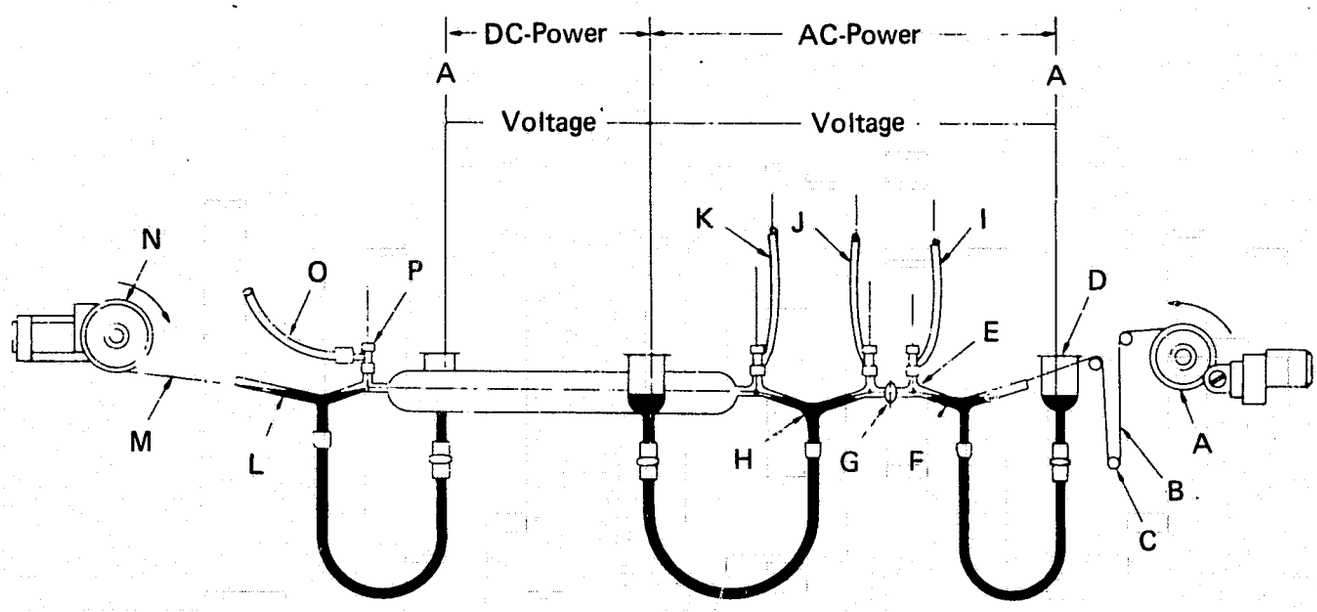
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- Mechanical (Wire Drawing, Stretching, Pin Drawing, Broaching, Foil Slitting etc.)
- Electrochemical
- Vapor - Desposition (With Or Without Substrate)
- Liquid - Metal

Figure 1. Methods of Filament Manufacture



A Power-driven substrate feed
B Substrate
C Tension device
D Mercury reservoir
E Guide loop
F Mercury contact seal
G Outgas chamber
I Hydrogen in
J Hydrogen out
K Exhaust gases
L Mercury contact seal
M Boron filament
N Power-driven take-up spool
O Hydrogen and boron trichloride
P T-connector

Figure 2. Apparatus for Continuous Chemical-Vapor-Deposition of Boron on Tungsten From Boron Halide Process[13]

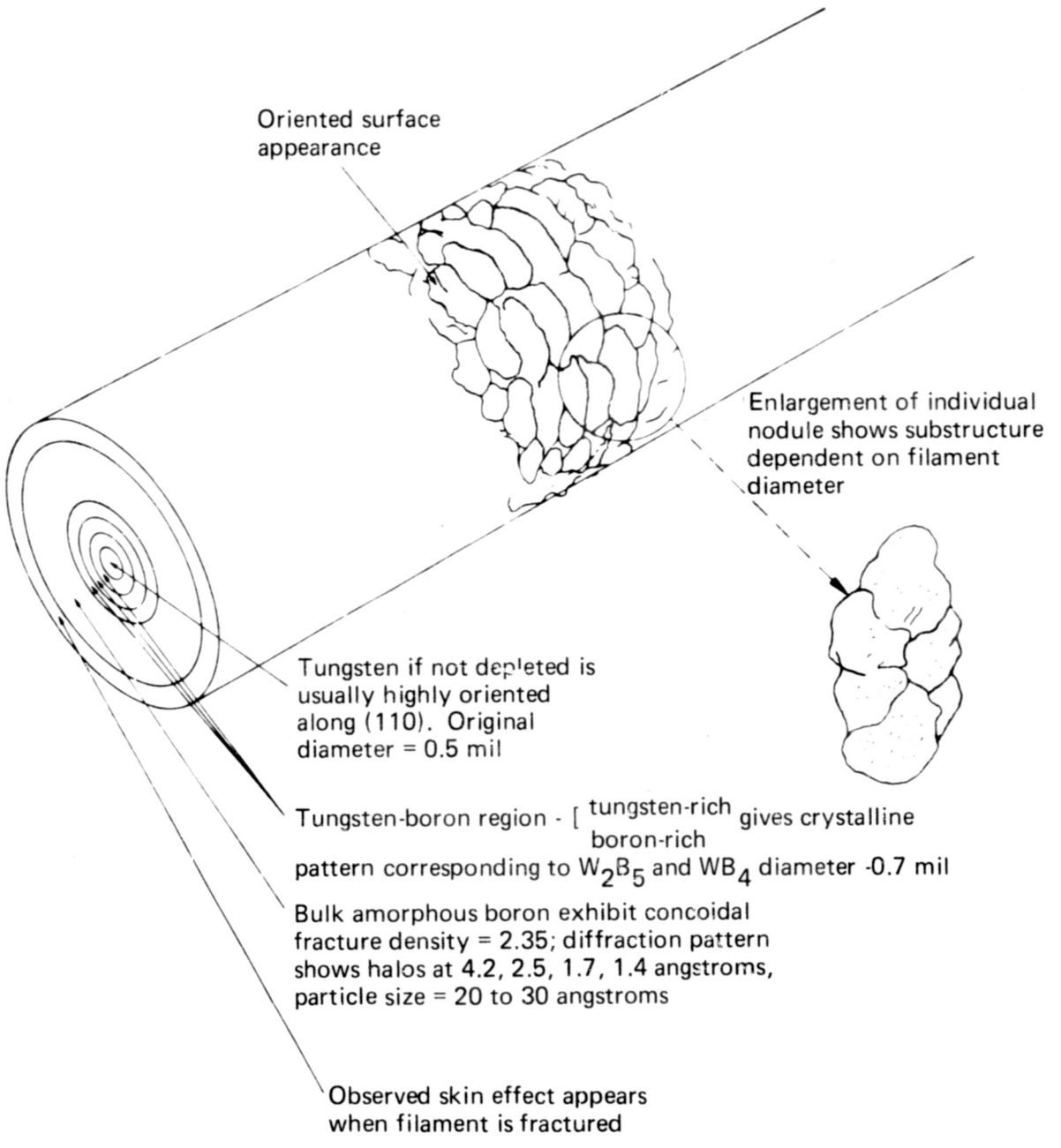


Figure 3. Structure of CVD-Produced Boron-on-Tungsten Filaments[13]

- High Tensile and Shear Strengths
- High Young's and Rigidity Moduli
- Low Density
- High Specific Strengths and Moduli

} Compared to Other Filament Materials

Figure 4. Properties of CVD-Produced Boron-on-Tungsten Filaments

Site	Tensile Strength Limitation (psi)
Crystals of amorphous boron	less than 200,000
Inclusions of 2.5 to 20 μ size	200,000 to 400,000
Noduled surface	200,000 to 400,000
Core - interface	400,000 to 500,000

Figure 5. Fracture - Initiation Sites

- Low tensile and bending strengths compared to theoretical values
- Low moduli compared to melt-produced filaments
- Large variation of strength values
- Limitation on use in nuclear applications
- High cost
- Low production rate
- Limitation on minimum diameter

Figure 6. Summary of Present Process Disadvantages

A. With Substrate Core

1. Thermal Decomposition
   a. Conductive (W, Ta, B, Rh, Ti, Mo, graphite) or nonconductive (silica) substrates
   b. Resistance, induction, or radiant heating methods
   c. Boron halide or diborane source
2. Electrical Decomposition - Conductive or nonconductive Substrates.

B. Without Substrate

1. Deposition on rotating disc
2. Deposition on anode tip

Figure 7. Summary of Chemical-Vapor-Deposition Processes

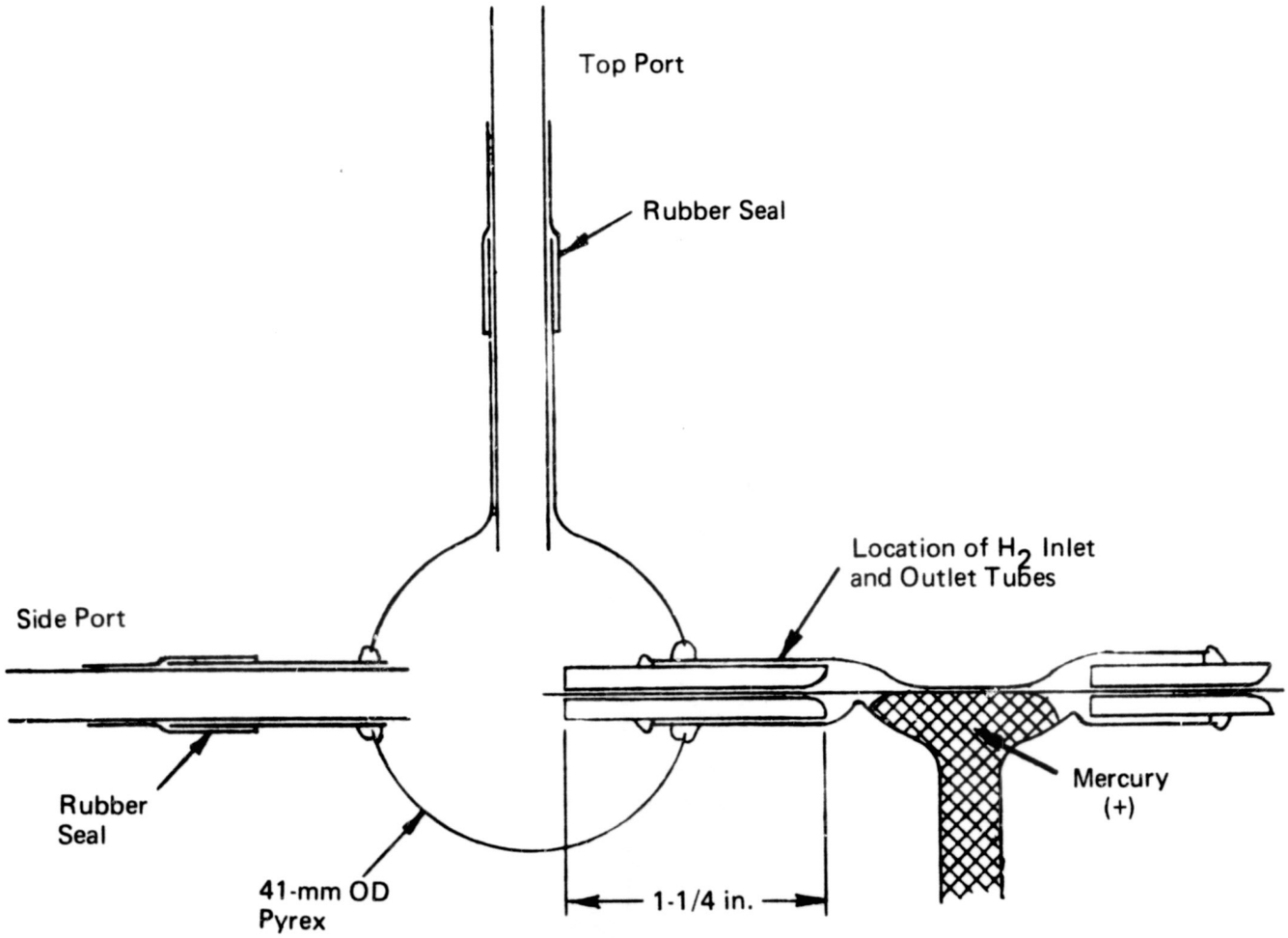
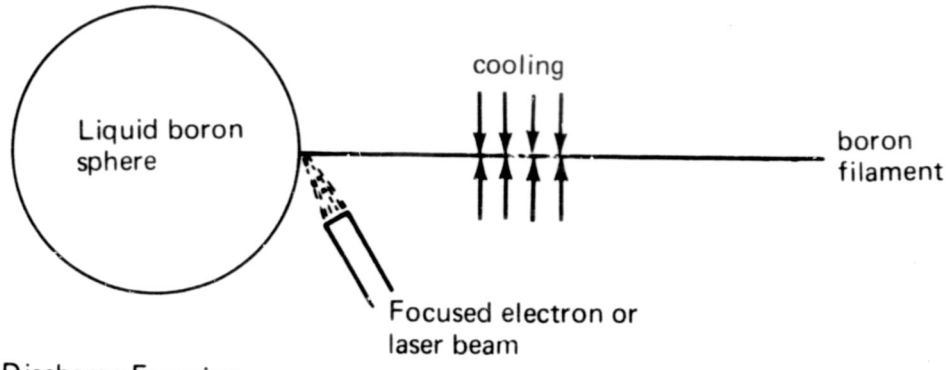
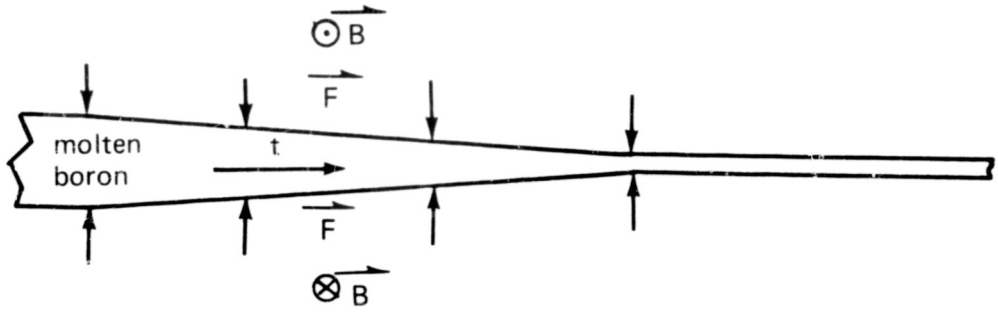


Figure 8. Glow Discharge Apparatus

- Point Destruction of Surface Tension



- Electrical Discharge Forming



- Melt Drawing

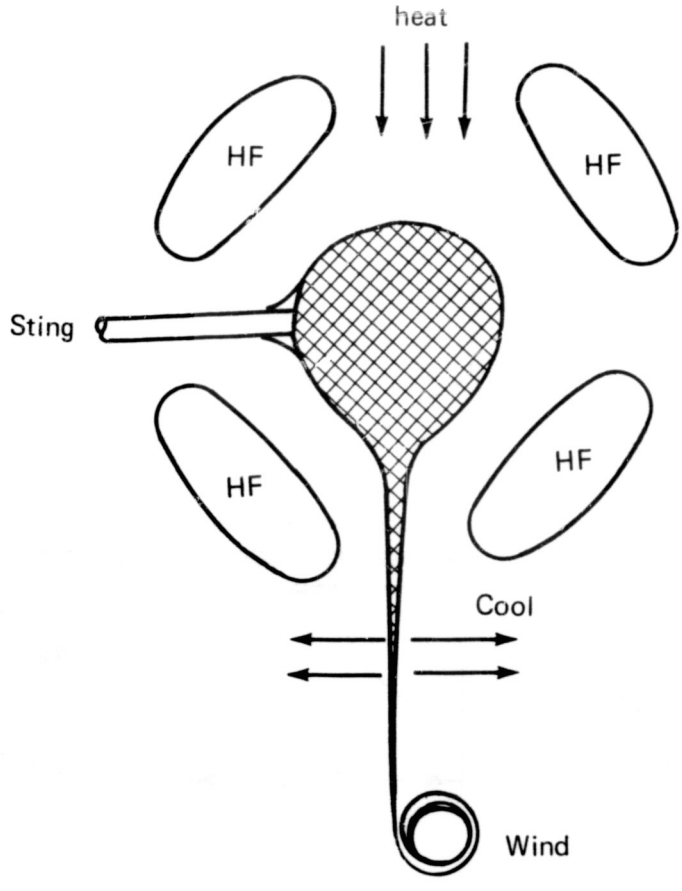
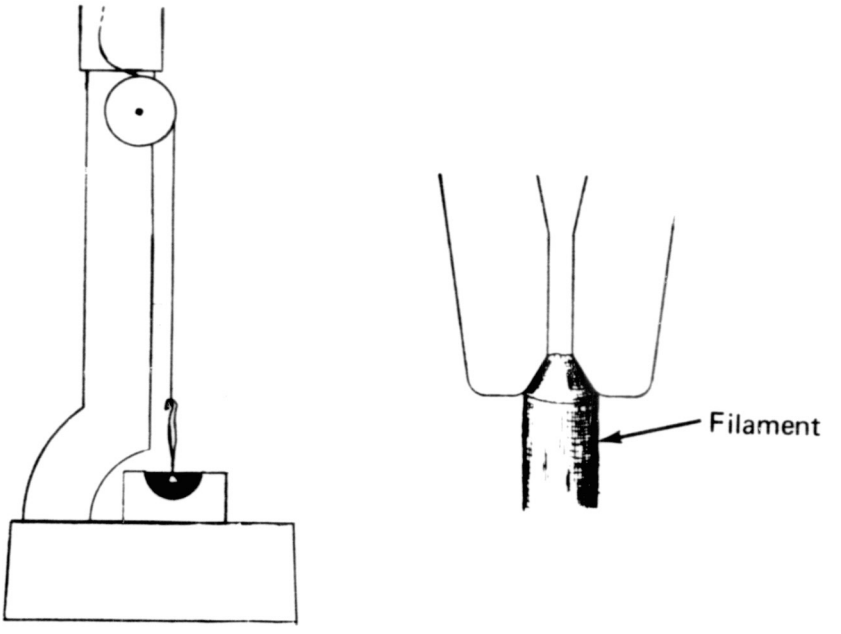
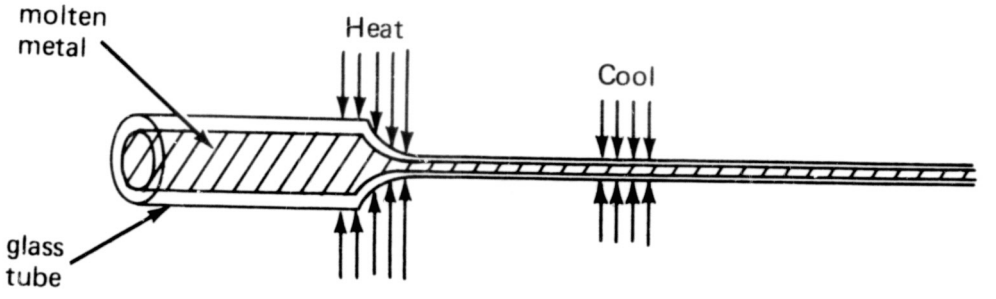


Figure 9. Point Destruction, Forming, and Drawing Processes From the Melt

- Czochralski Crystal Growth[56]



- Taylor Process



- Drawing of Substrate Through Melt[39]

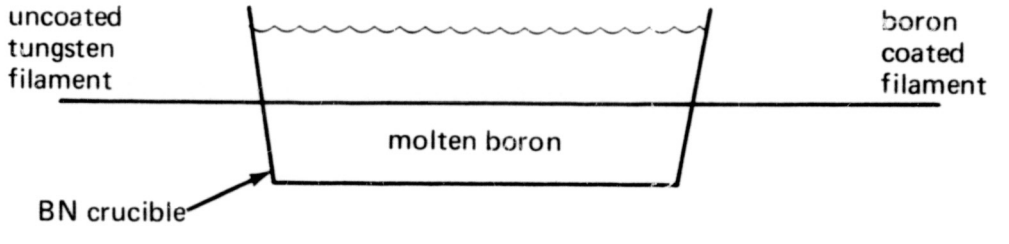


Figure 10. Czochralski, Taylor, and Substrate Drawing Processes From the Melt

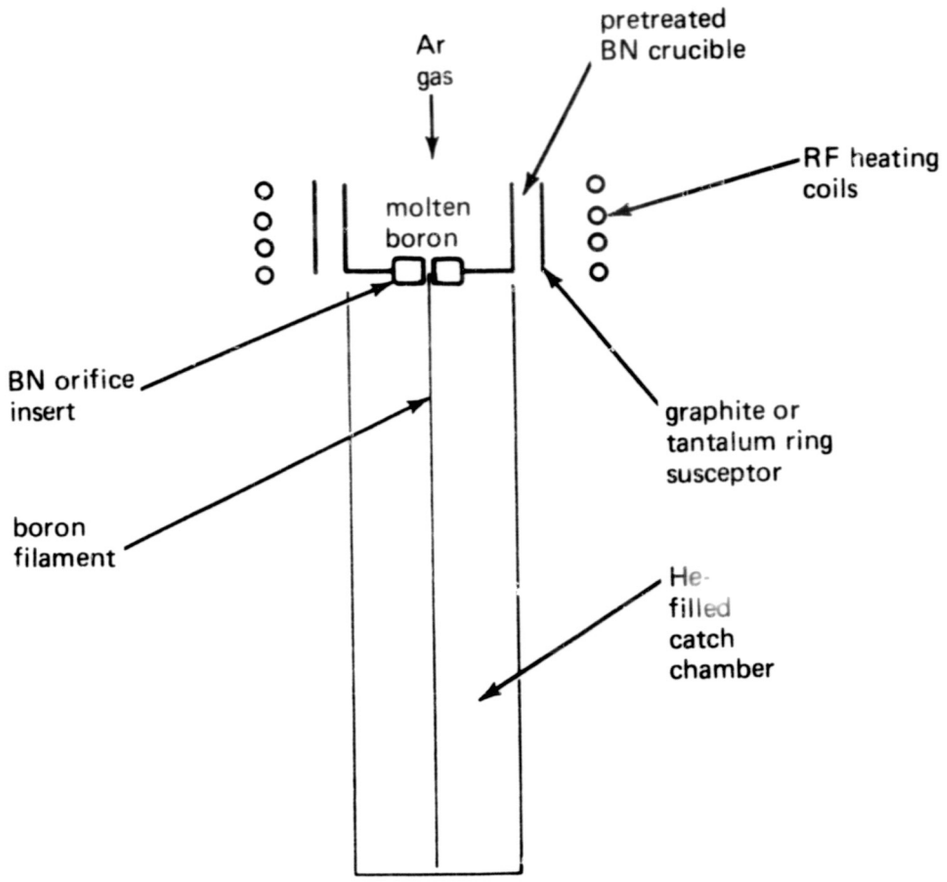


Figure 11. Melt Extrusion Apparatus

- Crucible and Orifice erosion
- Low filament strength due to surface pitting, grain size, and solidification mode
- Incomplete mixing of alloys
- Breakage upon impact in collection chamber

Figure 12. Problems with Melt Extrusion to Date

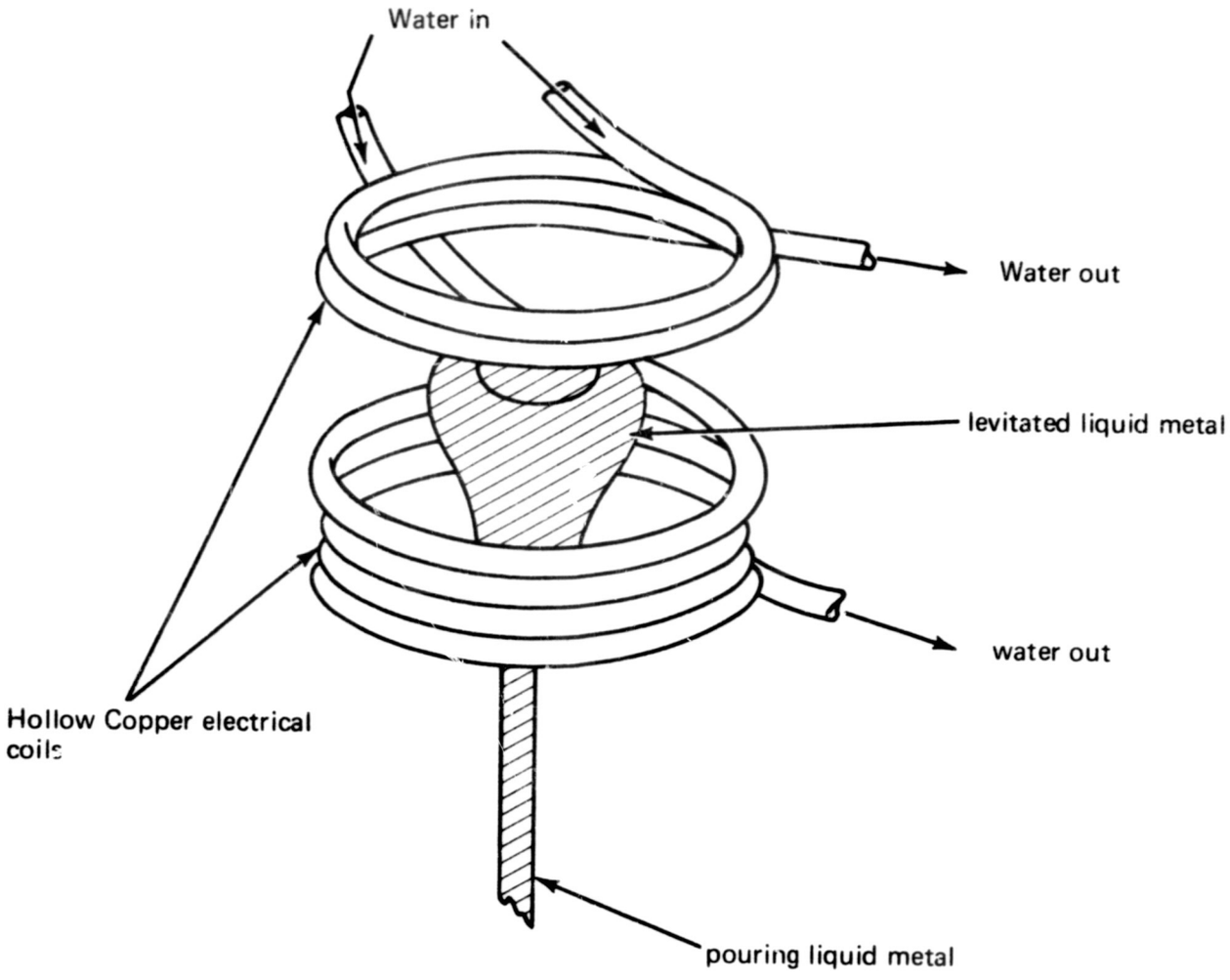


Figure 13. Levitation Melting Apparatus [52]

Ag	Cr	Ga	In	Nd	Pt	Sn	Y
Al	Cu	Gd	Li	Ni	Ru	Ta	Yb
Au	Dy	Ge	Mg	Pb	Sb	Ti	Zr
Be	Er	Hf	Mo	Pd	Si	U	
Co	Fe	Ho	Nb	Pr	Sm	V	

Figure 14. Known Levitation-Melted Elements [48]

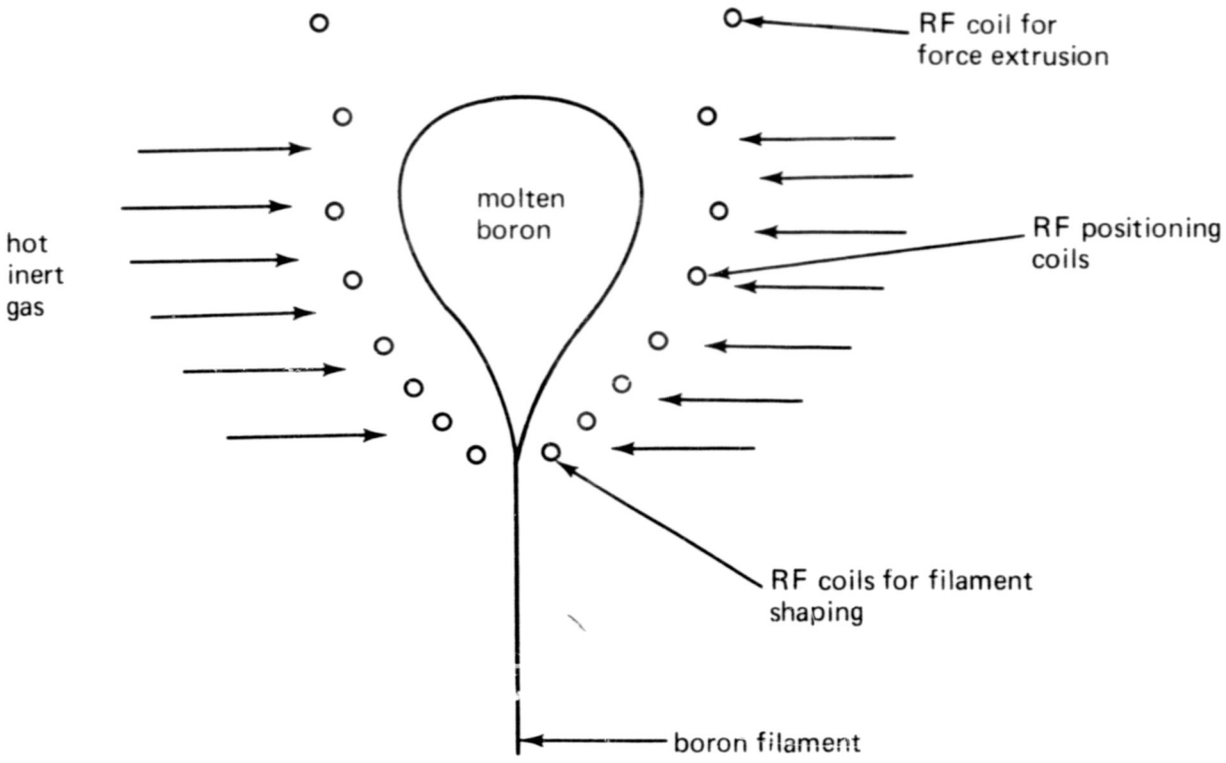


Figure 15. Boron Filament Manufacture in Space

- Lower Cost
- High Quality Filaments
- Faster Production Rate
- More Potential Uses

Figure 16. Summary of Proposed Process Advantages

- Solidification of boron
- Levitation, space positioning, and field extrusion of boron
- Mechanical properties of melt-produced boron
- Design of production machine
- Detailed cost analysis

Figure 17. Summary of Areas For Further Investigation

N70-20522

WEIGHTLESS, CONTAINERLESS MELTING AND SOLIDIFICATION OF POTENTIAL NEW METAL AND CERAMIC PRODUCTS

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ABSTRACT

A number of suggestions have been made for the weightless processing in space of metals and ceramics. The most obvious application of a weightless environment is the removal of buoyancy forces in multi-phase systems and the possibility for containerless melting and solidification processes. Under the first category, processes which can be considered are the casting of superalloy materials containing rare earth oxide inclusions and the casting of metal emulsions where convection currently leads to phase segregation. Under containerless processing we can consider extensions and scale up of processes which have been studied in terrestrial levitation experiments. Possible applications are the preparation of ultrapure materials and solidification under conditions of extreme subcooling. Ultrapure refractory materials which are easily contaminated by molds are logical candidates. Control of grain size by solidification at extreme subcooling is another possibility if a means of inhibiting subsequent grain growth can be devised. Preparation of high density glasses and ceramics by containerless solidification can also be considered.

Initial results in exploring the physical problems associated with weightless, containerless processing in the space environment are described. Analyses and experiments are described which treat the possibilities and limitations for eddy current positioning and handling, surface oscillations and fluid currents affecting the motion of bubbles, scale up and power requirements as a function of material properties such as density, surface tension, viscosity, electrical conductivity, dielectric constant and permeability.

INTRODUCTION

A number of suggestions have been made for the exploitation of the weightless feature of the space environment to develop new or improved processes for preparation of materials. A number of these suggestions involving the melting and solidification of a free floating mass of metal or ceramic involve the handling or transfer of such a mass during some stage of the process. In addition to a more general study of feasible materials preparation processes at General Electric we have begun to study in some depth the initial experiment techniques hardware which will be required to exploit these ideas in space. In order to be able to provide sufficient depth in our study we have at first limited ourselves to the study of the physical phenomena and required experiment hardware associated with the free floating phase of a crucibleless experiment.

Figure 1 lists four general areas of phenomena which can be considered which exploit the weightless state. The most obvious application is the elimination of buoyant segregation in multiphase systems where present forming techniques are limited by separation of phases of different densities. Materials of this type often must be prepared by powder metallurgy techniques which result in low ductility and creep resistance or which prevent molding into precision shapes.

The second example refers to the new possibility of carrying out precision molding of reactive and high melting materials which presently must be prepared by skull melting techniques which do not allow for the provision of superheat. This severely limits the shapes which can be cast. In a free floating state superheat could be provided even for very reactive materials.

A more speculative possibility is the achieving of high degrees of subcooling prior to solidification because of absence of contact between the melt and any solid object. High degrees of subcooling have been observed in limited

terrestrial levitation experiments and new crystal phases have been observed such as Gallium III, to be formed at subcooled temperatures. Another possibility which has been suggested is the preparation of high index of refraction glass where recrystallization due to mold contact is a present limitation. I will show a few specific suggestions in the first two categories by way of introduction to a discussion of the physics and hardware which must be provided for first experiments in these areas.

Figure 2 lists some examples which have been suggested for exploitation of the removal of buoyant segregation of multiphase materials. There is currently some interest in this possibility on the part of our aircraft turbine people and some recent studies have been devoted to this at our Research Laboratory. Accelerated corrosion in a Marine environment can severely limit jet engine life because of blade and vane parts which are of thin walled cast construction and because of the high operating temperatures. Wasielewski has studied the oxidation and hot corrosion of superalloys and has documented the beneficial effects which the rare earth metals have on the hot corrosion process. Additions of Lanthanium and Cerium as metals, however, lead to low melting eutectics at grain boundaries, severely limiting the high temperature capabilities of the alloy. Through these initial efforts, it had been recognized that the rare earth oxides are the effective barrier rather than the metal itself. Work by Seybolt and Allen has further delineated these effects and has shown that the protection mechanism depends wholly on the presence of oxide and that the dispersion or size of the particle need not be critical. Accelerated corrosion occurs as a result of combining sodium with the sulfur in fuels to form sulphates which then rapidly deplete chromium from the matrix as shown in Figure 3. Sulfur from the fuel in the presence of salt diffuses into the matrix and depletes the chromium from the matrix leaving it in the form of chromium sulphate. When the oxide dispersion is added the sulfur is taken up by the cerium and the oxygen is released to oxidize the chromium. The chromium oxide is far less deleterious to the metal matrix than is the chromium sulfide.

Presently, because of the large difference in density between rare earth oxides and superalloy mixtures, only powder metallurgy techniques can be utilized to form oxide-metal dispersions. Figure 4 is a dramatic demonstration of the oxidation/hot corrosion problem and the protective role which the rare earth oxides play. These two specimens of TRW-6A alloys (a modern superalloy developed by Thomson, Ramo, Woolridge) were fabricated from prealloyed powders to one of which 1/2% by weight CeO_2 was added. These samples were initially 1/4" diameter rods which were exposed to 1725^{o} for fifty hours with 100 ppm NaCl added to the intake gases. Present conservative estimates are that rare earth additions to superalloys will more than double their useful life.

Casting of the material including the rare earth oxide leads to segregation due to buoyancy effects. Weightless solidification of such a material can thus be considered as a potential interesting process if means can be found to make castings in a nearly zero gravity environment.

The casting of other materials in a nearly weightless environment in order to improve properties and materials presently limited by powder metallurgy techniques can also be considered. Examples might be nickel thoria and aluminum-alumina materials.

Another general area for consideration of weightless metallurgical processing is the crucibleless melting reaction of high melting point metals. Figure 5 gives some examples. Present skull melting techniques without the possibility of providing superheat generally exclude precision casting. One metal which is currently of great interest to General Electric for switching and conductor applications is pure beryllium. Present high voltage underground distribution systems in cities are severely limited by the ohmic resistance of aluminum and copper and our company has recently carried out a study for the Edison Electric Institute on the possibility for cryogenically cooled transmission lines which would reduce the joule heat by two decades or so. Figure 6 shows qualitatively the variation of electrical resistivity of copper, aluminum and beryllium as a function of temperature. Cooling at liquid hydrogen temperatures would be necessary in order to reduce the resistivity of aluminum or copper by the required amount. For beryllium on the other hand sufficiently low resistivity for desired applications can be achieved at liquid nitrogen temperatures which appear much more practical. The possibility for the crucibleless formation of a billet of this material free from contamination and in a form suitable for later extrusion seems to us worthy of further study.

Many optical devices would benefit from the use of isotropic transparent materials (glasses) with high index of refraction. Thin lenses would be one feature and would lead to smaller optical instruments. Many glassy systems are known to have high index of refraction but they are usually susceptible to devitrification (recrystallization). Most recrystallization in glassy materials is surface nucleated from contact with crucibles in which melts are made. Levitation melting offers the ability to melt out of contact with crucibles and to explore the possibility of glass forming from compositions which normally would be considered unstable. The possibility also exists that molten materials, which do not normally form amorphous, glassy solids, would do so if they were supercooled and solidified out of contact with crucible materials.

Examples of compositions that are worthy of study in this context are $PbO:SiO_2$ systems rich in PbO (max. RI=2.6) and $PbO:TeO_2$ systems. Glasses of RI=2.2 have been obtained from these systems by normal glassforming techniques.

ELECTROMAGNETIC POSITIONING OF A FREELY FLOATING MASS

The basic theory associated with the application of forces to a conducting sphere by eddy currents has been treated by Smythe in his textbook on electromagnetic theory. Figure 7 shows a spherical object, here considered to be a conducting sphere located between circular coils excited with audio or radio frequency currents. I shall later say a few words about position control schemes for dielectrics such as glass or ceramics. Smythe's treatment assumes an oscillating magnetic field in the direction of the coil axis uniform over the sphere volume. The analysis is best done in terms of the magnetic potential A rather than the magnetic field B. The vector potential A has a circular configuration centered about the coil axis and is considerably simpler to compute, given the coil configuration, than is the magnetic field itself. The force per unit volume within the conducting mass is given by the vector product of current density and magnetic induction B. From electromagnetic theory we can write the electric current density as $\vec{J} = \frac{\sigma}{c} \frac{\partial \vec{A}}{\partial t}$ where σ is the conductivity. The magnetic induction B is given by $\vec{B} = \overrightarrow{\text{curl}}\, \vec{A}$. The total force acting on the sphere can be obtained by integrating the force per unit volume over the sphere. There is also a simpler method. However, we are interested in the force per unit volume since its distribution is important in setting up fluid current circulation patterns within the molten mass. The body distributed forces will affect the motion of bubbles which may be included in the melt and bubble motion from this will probably be more important than bubble motion due to rotation of the mass or other effects. The nonuniform distribution of forces can also give rise to shape oscillations of the spherical mass which I shall discuss later.

We have developed a servo control which applies translational forces to the sphere based on sensing of position errors by means of the mutual induction between the eddy currents within the sphere and the driving coils. Since the electric field is simply the time derivative of A it will be in the same direction as A and hence the current will flow in circular loops of the type shown for A on the slide. The summation of these circular currents can be thought of as a single winding transformer secondary which will have a reflected impedance as viewed from the driving coil terminals. The power dissipation per unit volume W is given by the resistivity (reciprocal sigma) times the square of the current density.

We have plotted the average current distribution (Figure 8) for a radial traverse in the equatorial plane. The curve labeled (1) is the cycle average distribution within a .4 inch radius aluminum ball when the frequency is 11 kilocycles. The current waves propagate along the radius and die out rapidly

a short distance within the spherical boundary. The length within which the waves attenuate to 1/e of their surface value is called the skin depth and for this particular curve the ratio of sphere radius to skin depth is 13. At lower frequencies the skin depth increases and the current remains flat as we proceed inward. At lower audio frequencies the magnetic field is nearly uniform throughout the sphere.

We have also plotted the distribution of instantaneous magnetic field within the sphere. At the lower frequencies the field decreases only slightly within the sphere. At the higher frequencies the field reverses as we travel into the sphere. (Figure 9)

We have also computed the vector product of the electric current and magnetic field within the sphere. We find that the resultant force field within the sphere is rather complex at the higher frequencies. I shall discuss this later. At the lower frequencies the force distribution within the sphere becomes simple. The force is radially inward at the surface of the sphere. We are dealing with the phenomenon of magnetostriction which will give rise to fluid currents within the sphere, spheroidal shape oscillations and sound wave generation. It is only for the latter phenomenon that we are interested in the instantaneous forces as they vary at audio or radio rates. For prediction of fluid currents, and excitation of low frequency shape oscillations, we are more interested in the average forces over a full cycle of oscillation of the applied field. We have also computed these cycle averages for some interesting cases.

Because of the necessity of controlling the position of the processed material in relation to a heat source or other apparatus and to compensate for small accelerations due to spacecraft station keeping, attitude motions, astronaut motions, or location other than at the vehicle center of mass, it will be necessary to provide position sensing and control devices. We have developed a position sensing system based on electromagnetic principles so it is possible to position sense and control even without optical windows. This might be highly desirable when processing materials which will outgas and tend to plate optical windows. The force exerted by a control coil on a nonmagnetic conducting sphere depends of course on the coil current, dimensions, frequency, sphere radius and sphere conductivity. The frequency and conductivity enter the problem in determining the skin depth of penetration of electromagnetic waves into the sphere. Figure 10 shows theoretical curves for the total force on an aluminum sphere with the parameter R_2/δ which gives the ratio of sphere radius to skin depth and where the absissa is the ratio of coil to sphere separation divided by coil radius. The ordinate has been expressed in terms of acceleration of an aluminum sphere per unit ampere turn of coil excitation.

For position control in a weightless environment we can scale very low values of control acceleration--for example, in our initial tests which I will describe we use an ampere turn value on the order of several hundred which gives an ampere turn squared value of about 10^5. This means that the maximum ordinates 10^{-3} cm sec^{-2} would be multiplied by 10^5 and this level on the ordinant scale would become 100 cm sec^{-2} or about 1/10g. Values of a few tenths g are easily obtained with a few watts of control power at higher frequencies which give a small skin depth. Since for most applications we can be satisfied with accelerations below 10^{-3} or 10^{-4}g, these curves illustrate that we can consider the use of very low audio frequencies which give skin depths equal to the sphere radius or greater.

Position sensing makes use of the relative phase change between voltage and current in the driving coil due to variation in the reflected impedance from the eddy current loops as the ball position changes. Figure 11 shows the equivalent circuit of the driving coil which is resonated by the use of a tuning capacitor. Of course as the ball position varies exact resonance is not maintained. This curve shows the results of measurement of the sensitivity for position detection by a single driving coil. We see that displacements of a millimeter give a phase change on the order of a degree or so. In our control servo scheme it is this phase change that is detected.

The amplitude of current and voltage in the driving coil depend not only on the ball position but also on the excitation level of the coil. By using phase changes as a position indicator we free ourselves from the dependence on the level of coil excitation and allow for the possibility of using the same coils for RF heating of the sample, if desired.

We have made a number of force measurements for aluminum and copper spheres at various frequencies and coil sphere distances to compare with theory. Figure 12 shows forces measured by a balance technique for an aluminum sphere and frequencies between 10 kHz and 100 Hz. The sphere to coil separations are given in dimensionless form by dividing by coil radius. The force is normalized to 1 ampere turn although in these experiments ampere turn values up to several hundred were used. Shown as the dashed line is a theoretical calculation based on a computation assuming that the currents within the sphere are excited by a uniform oscillating magnetic field. There is some inconsistency in computing the net translational force for the case where the applied field is uniform and this partially explains the discrepancy shown here. Actually if the applied field were uniform there would be no net translational force on the sphere. The procedure which is used in the literature is to compute the currents in the sphere for the uniform field case but then to assume that these currents are acted upon by the nonuniform field near the coil so that a net force is observed.

Figure 13 shows experimental data in a smaller force regime. We have extended the ability to measure forces down to the 10^{-4} to 10^{-5}g regime since for many applications control accelerations of this magnitude will suffice and we wish to size space experiment hardware for these realistic cases. To this end we have begun measurements using a ball suspended as a long pendulum for measurement of weak horizontal forces.

Figure 14 shows the pendulum set up. Here we see some positioning coils, the pendulum enclosed by a plastic case to eliminate the effect of air currents and a telescope for measuring small position displacements. An even more sensitive technique for measuring small horizontal forces is the use of very perfect spheres on the glass tilt table whose tilt is adjusted by 3 micrometer screws serving as legs. Although the measurement of such small forces can be avoided for positioning studies of conducting spheres, for poor conductors and dielectrics such as glass it is easier to measure the small forces rather than scaling up the fields. The coils shown in this set up have been used only for the purpose of observing the operation of the position servo which I will now describe. The actual coils used for metallurgical space processing experiments might be water cooled and fed by transformers to match them to the driving source.

In the zero gravity environment, position sensing and control of a floating mass before and after melting and solidification would be done by three orthogonal sets of coils. If all three sets of coils are excited about equally, the floating mass will find itself in a position of stable equilibrium near the center of the coil configuration. The damping time for positioning oscillations, however, tends to be rather long so that we have designed a servo device which can correct position errors with any desired damping constant.

Figure 15 shows a block diagram for a single axis control with the two coaxial driving coils on either side of the experiment specimen represented schematically. The phase shift detection of position changes is determined by a logic circuit which compares the phases of driving coil current and voltage. To obtain more accurate position sensing a differential circuit is employed which compares the phase differential detected by the two coils. Depending on the size of the position error the power to one or the other driving coils is increased by a modulator under control of the position error signal.

Figure 16 shows the hardware implementation of this circuitry which is rather standard except for the logic circuitry which is unique to this application. I have already shown measurements of the position sensing characteristics for this circuitry and the position control stiffness in terms of force per unit current. The characteristic resonant frequency of this servo loop can be adjusted if desired by furnishing equal excitation to both coils in the absence of an error signal.

BASIC HYDRODYNAMICS

Oscillations

Excitation of the position control coils can be used either to initiate or damp translational motions of the floating mass and shape oscillations as well as any rotations which may occur. The position control and shape oscillation problem is most easily treated by considering individual hydrodynamic modes of a liquid sphere under the action of surface tension forces and the electromagnetic forces due to internal eddy currents.

Figure 17 illustrates the first three hydrodynamic modes. We can describe these modes most easily by expressing the distance from the center of mass to the liquid surface r as a function of a colatitude θ in the way shown at the bottom of the figure. For the zero mode, the radius vector equals a constant a_o multiplied by the 0 order Legendre polynomial which is simply unity. For this mode the mass is a perfect sphere with no distortion motions. For the second hydrodynamic mode which represents a shape oscillation between prolate and oblate spheroid, we must add to the original radius a term $a_2 P_2(\cos \theta) \cos w_2 t$. The center figure illustrates this shape at a given instant of time. The shape oscillates sinosoidally between oblate and prolate. This oscillation mode can be either excited or damped by application of the magnetostriction forces thru excitation of the position control coils. In my paper given to this Symposium last year I discussed the limitations arising from excitation of oscillations and showed that we can consider processing of liquid metal masses at least as large as tens of kilograms without worrying about rupture of the mass due to the necessity of position control in practical cases.

If the position control coils along a given axis are excited asymmetrically, for example if we excite only one, then we will obtain a net translational force which will excite both the first and third mode. The third mode resembles an eggplant and can be treated similarly to the second mode. The first mode illustrated to the left represents pure translation of a spherical shape and must be treated differently from the other modes. The reason for this is that the frequency corresponding to the first mode is zero and for this particular term in the sum we should replace the sinusoidal time term by a term linear in time. We have begun to examine theoretically the excitation or damping of these various modes by excitation of the coils.

Internal Fluid Currents

In addition to generation or damping of surface oscillations and translational motions, we can stimulate circulating currents within the floating mass by the magnetostrictive forces which I discussed earlier. Figure 18 shows a simple current pattern which can be stimulated by exciting a single control axis. These fluid currents can be oriented in various directions by exciting various sets of coils. These currents will be useful for stirring of alloys or dispersions and will also affect bubble motion in an important way.

At the higher frequencies the pressure gradient resulting from the magnetostrictive forces which drive the steady state fluid currents will be concentrated in a thin surface layer centered about the equatorial plane with respect to the excitation axis. After the coils are excited an equilibrium will quickly be reached in which this driving pressure gradient is balanced by viscous forces. At lower frequencies where the skin depth becomes an appreciable fraction of the sphere radius the flow patterns will be altered somewhat. The quasi-quilibrium shape of this spheroid will be influenced not only by the magnetostrictive forces which drive the fluid currents but also by the dynamics of the circulating dense fluid. Since magnetostrictive forces can be applied in an arbitrary manner, and translational acceleration of the mass can be suppressed by simultaneous excitation of opposite members in coil pairs, we see that considerable freedom exists for electromagnetic shaping of the floating mass in various symmetric or asymmetric configurations.

Rotation

In the previous paper the excitation or damping of rotations by the phased excitation of coil pairs was discussed.

If we consider an orthogonal pair of excitation coils to be excited with a phase quadrature so as to produce a rotating magnetic field, we can calculate that the spheroid will be caused to rotate in the manner of the rotor of an induction motor. By proper choice of excitation for various pairs of the positioning coils, angular velocity can be imparted the floating spheroid in any desired direction and with any speed consistent with configurational stability of the mass. This will be limited by the stability furnished by the action of surface tension. Oscillational instability can occur for higher rotational speeds and damping due to viscosity will play a key role in prevention of buildup of catastrophic oscillations. Conversely, properly phased excitation of a given pair of coils can be used to remove an angular velocity orthogonal to both coil axes if such rotation is not desired.

Sound Waves

The high frequency variation of magnetostriction forces can be used to generate sound waves within the floating mass if we desire to go to high level excitation. This might be useful, for example, to prevent aglomeration of oxide dispersion particles within the mass as suggested by our research laboratory people.

POTENTIAL CRUCIBLE-LESS METALLURGICAL/CERAMIC PROCESSES FOR ZERO-GRAVITY APPLICATIONS

ELIMINATION OF BUOYANT SEGREGATION

PRECISION MOLDING OF REACTIVE AND HIGH MELTING METALS

FORMATION OF NEW PHASE OR MICRO-CRYSTAL STRUCTURE THRU SUB-COOLED SOLIDIFICATION

PREVENTION OF CRYSTALLIZATION BY AVOIDANCE OF MOLD CONTACT

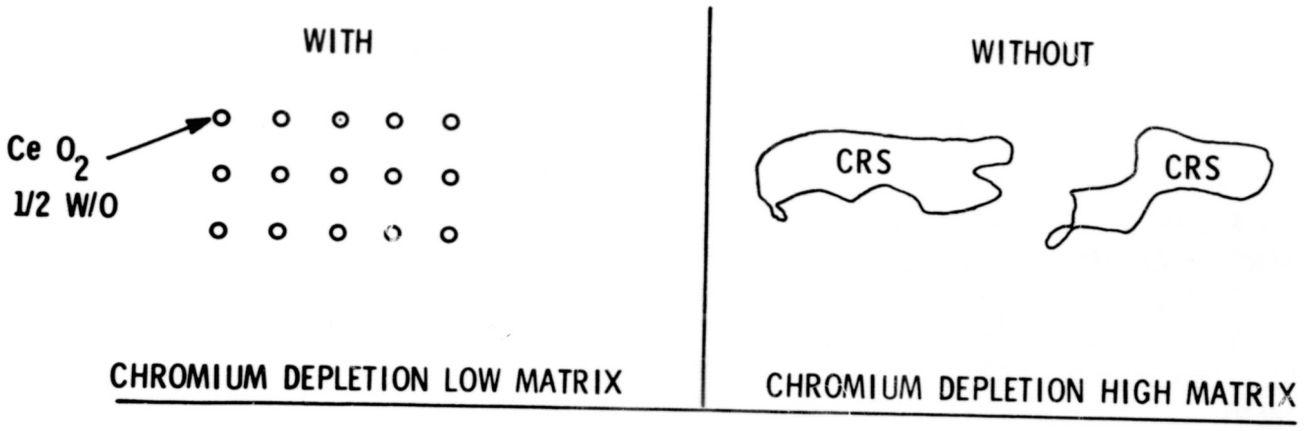
Figure 1

EXAMPLES OF ZERO-BOUYANCY PROCESSING

- OXIDE DISPERSIONS IN SUPER ALLOYS
  Ce O_2 in TRW-6A
- MULTI-PHASE THERMO ELECTRIC ALLOYS
  Pb Sn Te
- METAL EMULSIONS FOR ELECTRICAL CONTACT APPLICATIONS
  Ag + WC, W etc.
- DISPERSION HARDENED ALLOYS
  Ni + Th O_2, Al + Al_2O
- REACTOR COMPONENTS
  Pu O_2 - Mg O

Figure 2

RARE EARTH OXIDE DISPERSIONS IN SUPER ALLOYS



$$Ce\ O_2 + \begin{matrix} Cr \\ Ti \\ Al \\ Ni \end{matrix} + S \rightarrow C_e\ O_2\ S + Cr_2\ O_3$$

Figure 3

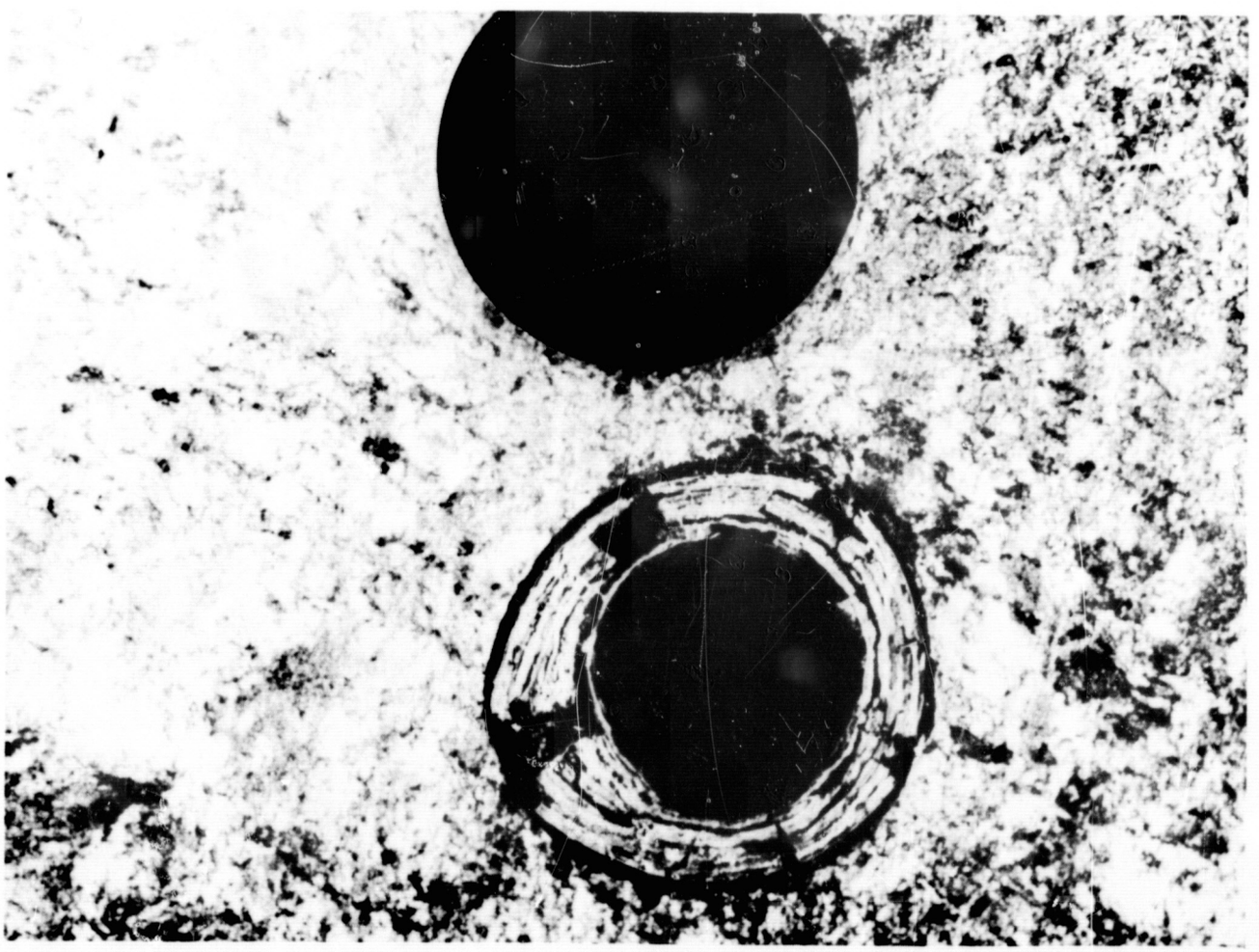


Figure 4

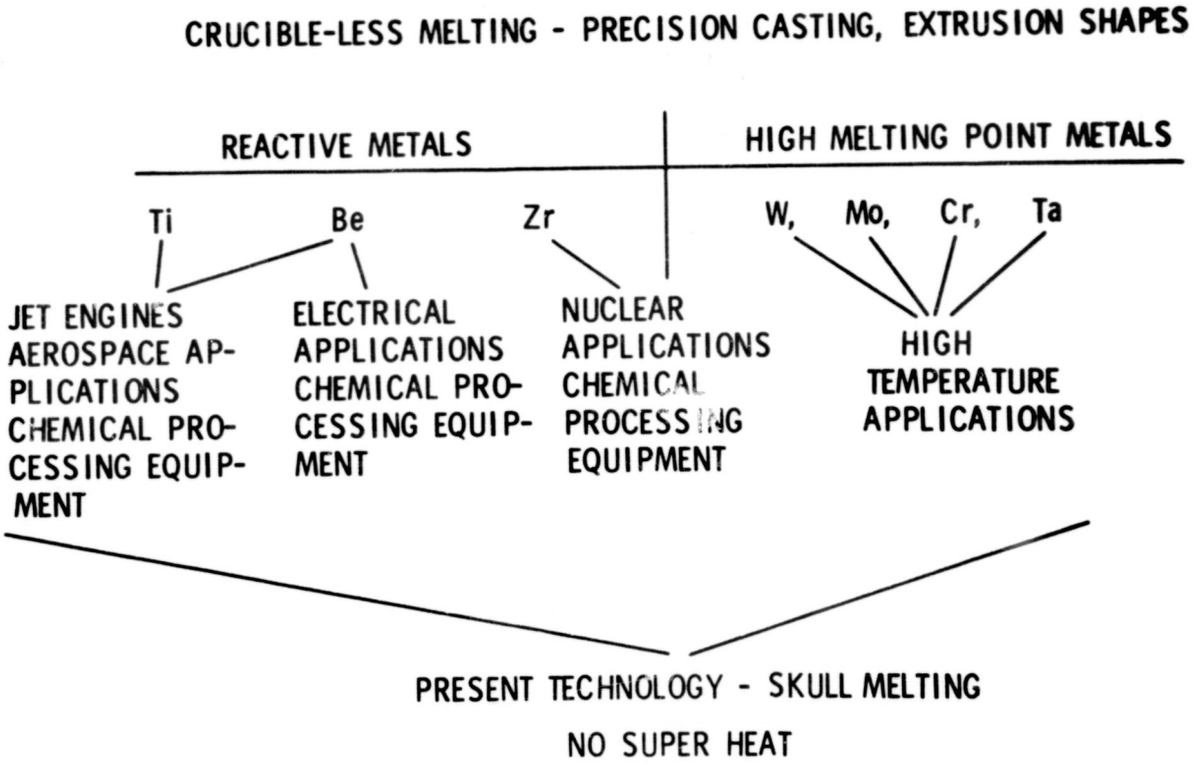


Figure 5

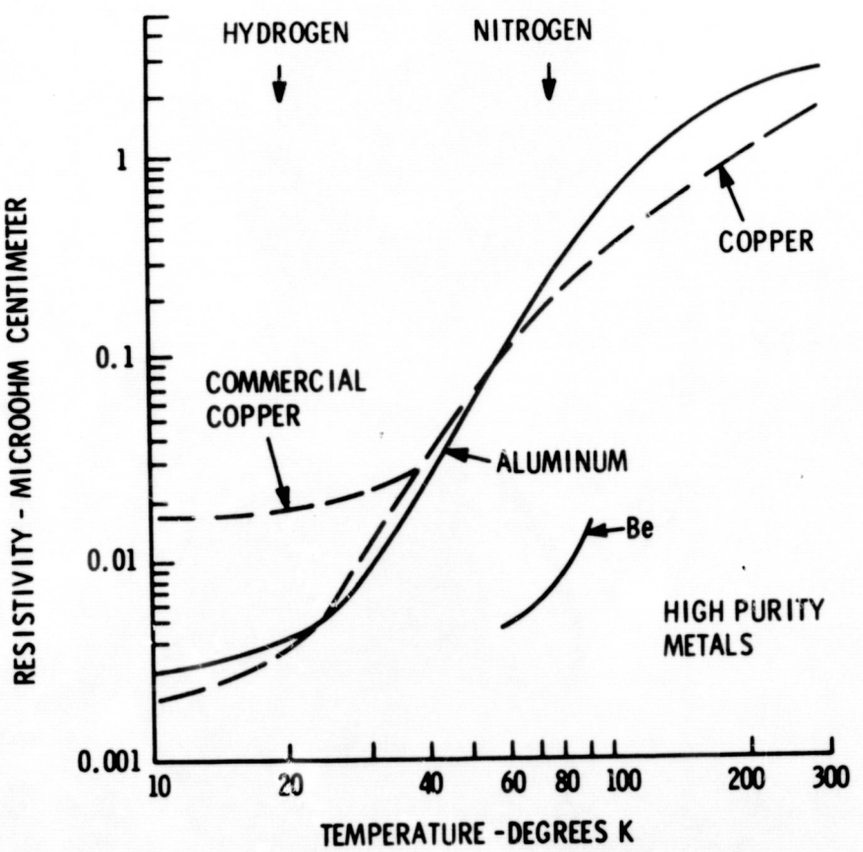


Figure 6

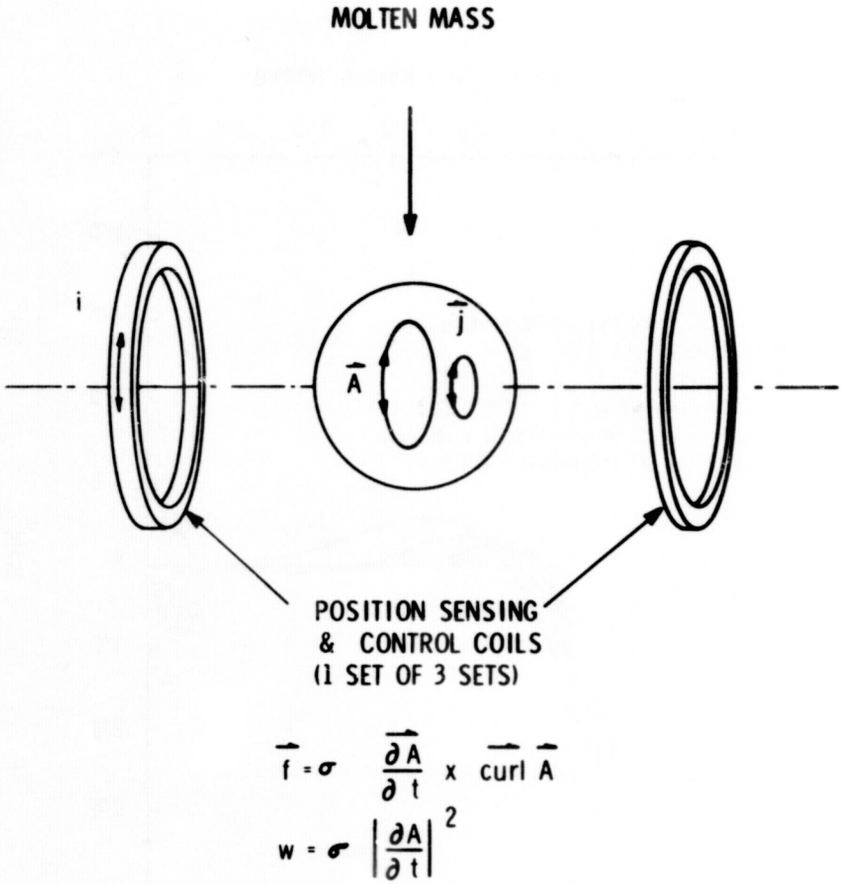


Figure 7

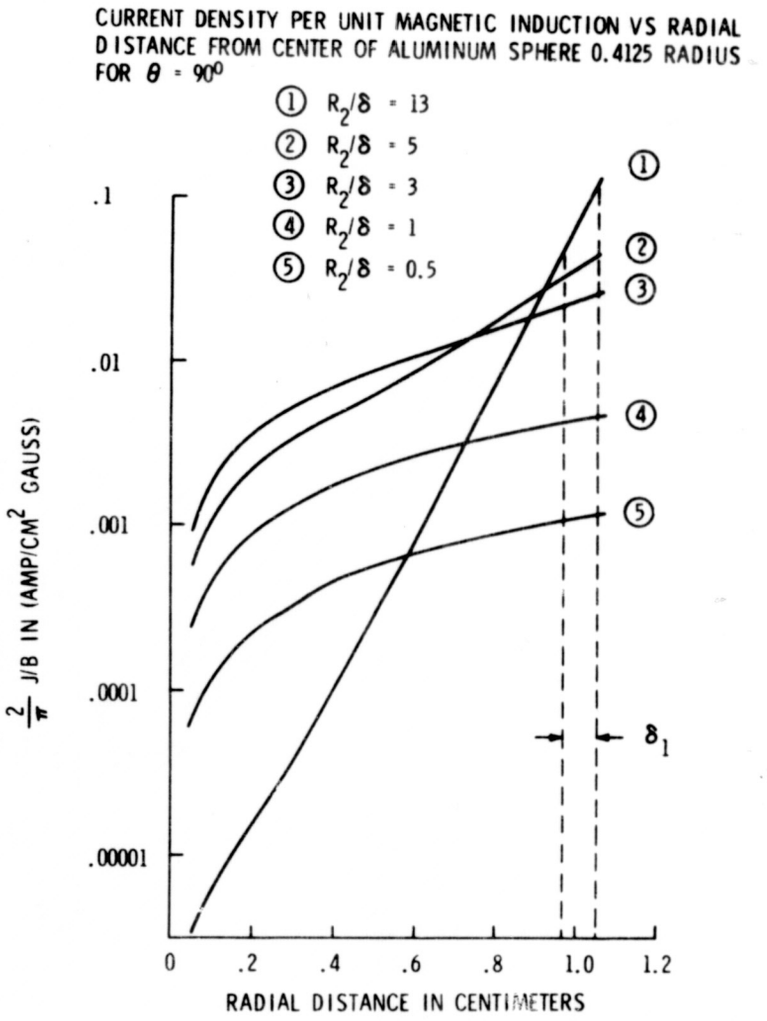


Figure 8

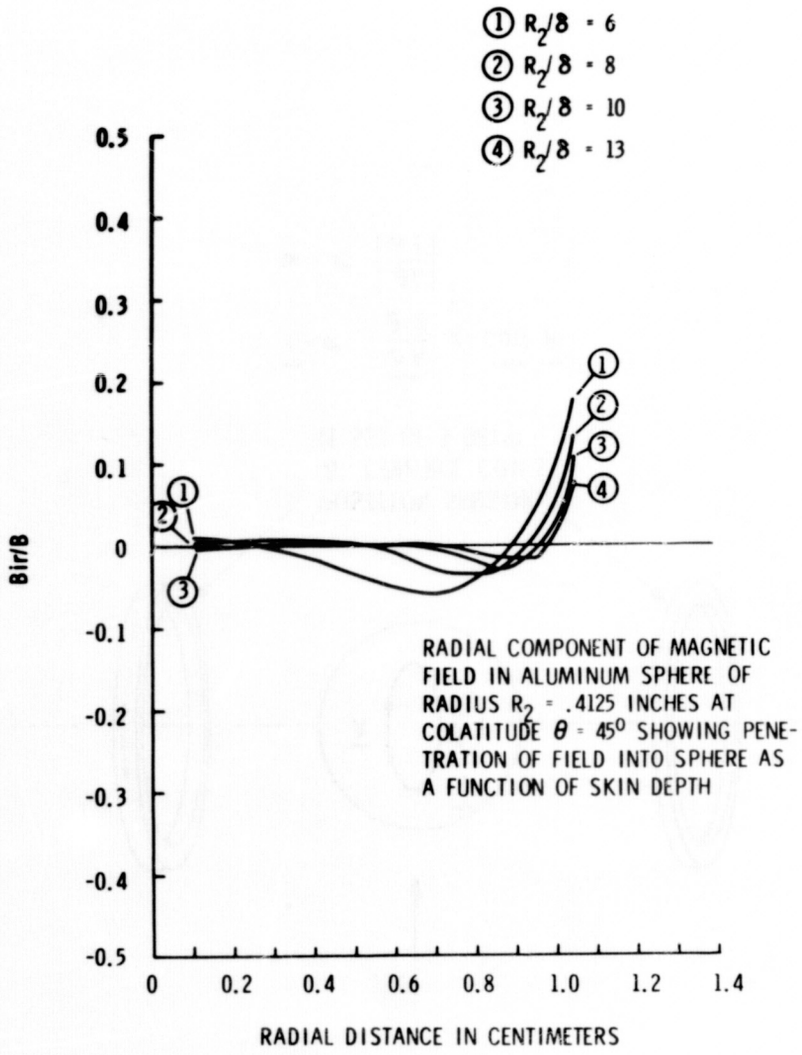


Figure 9

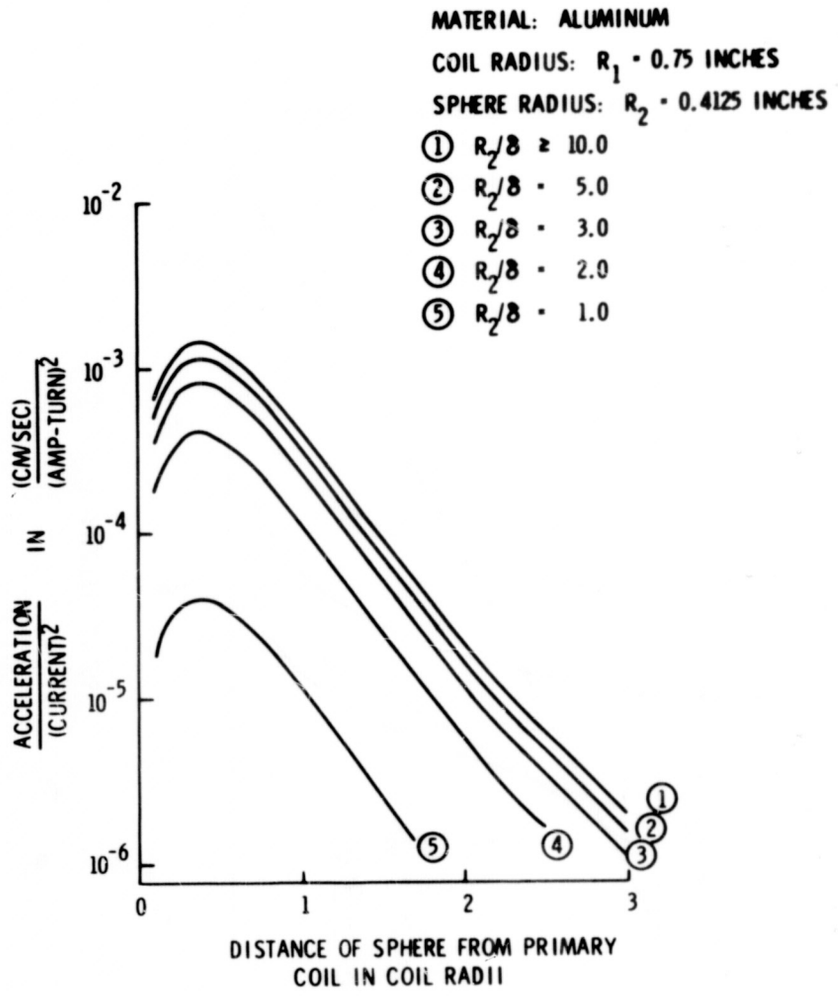


Figure 10

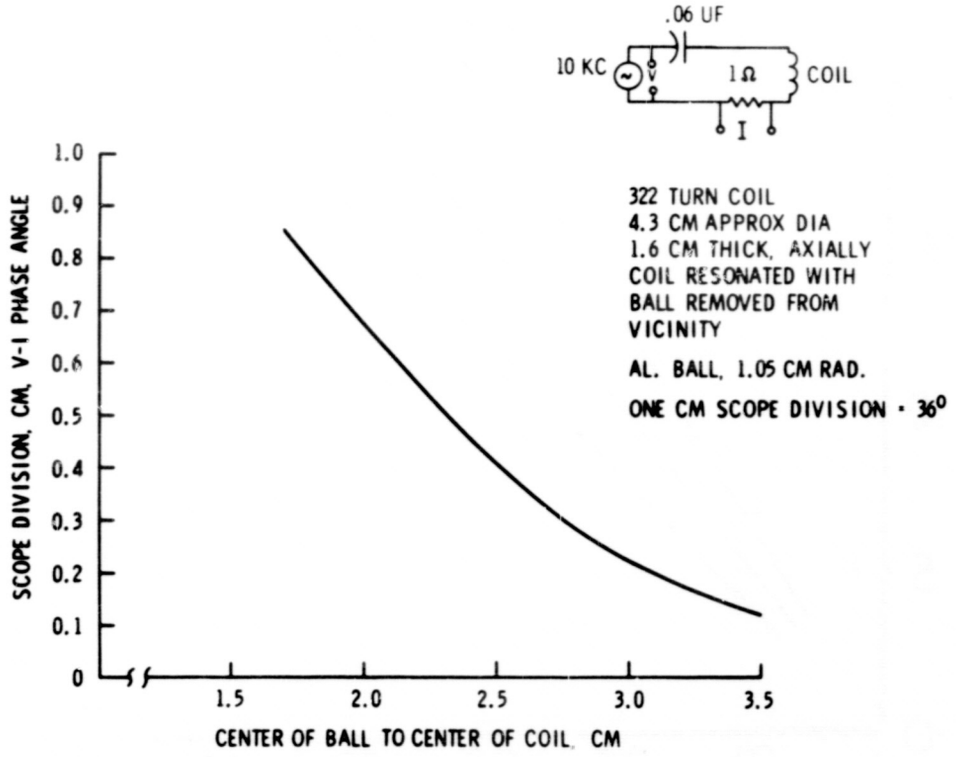


Figure 11

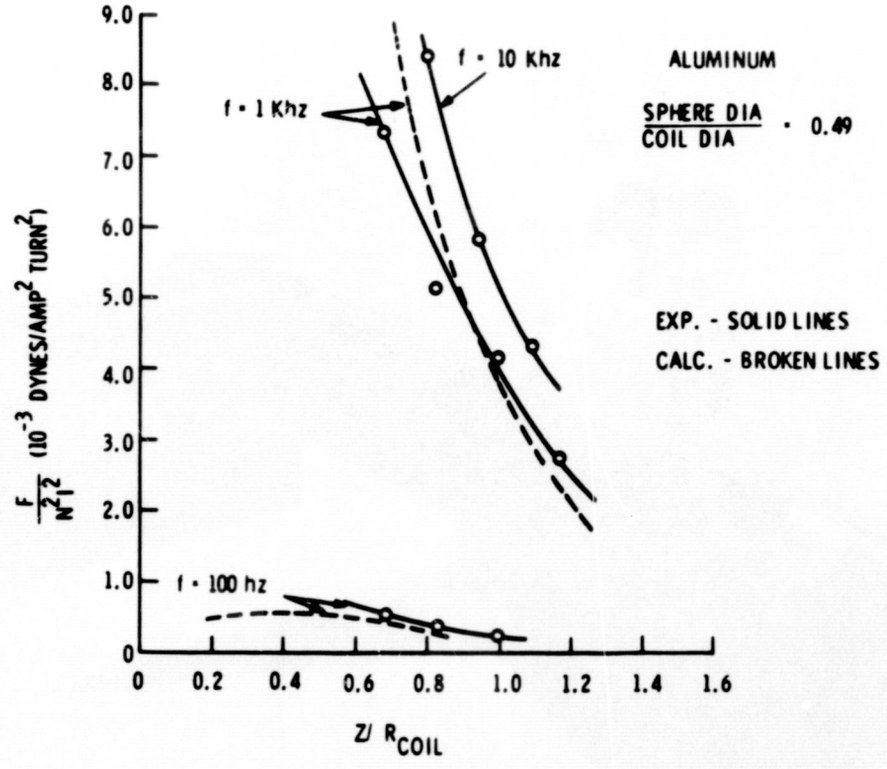


Figure 12

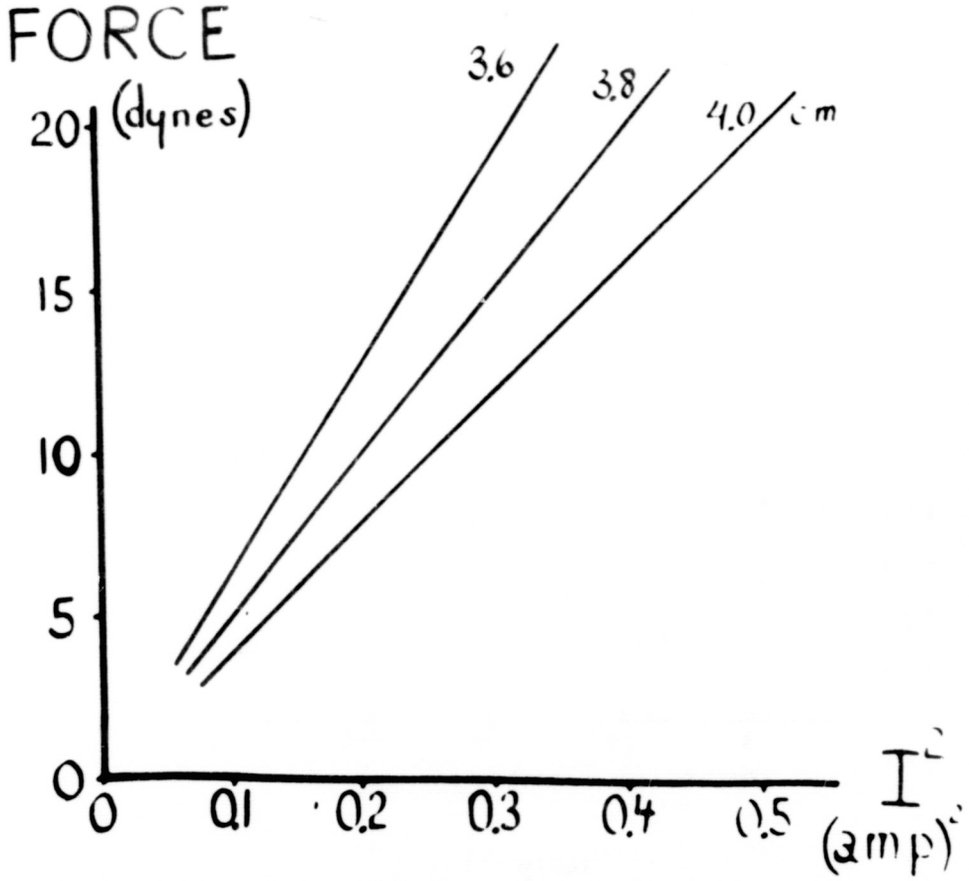


Figure 13

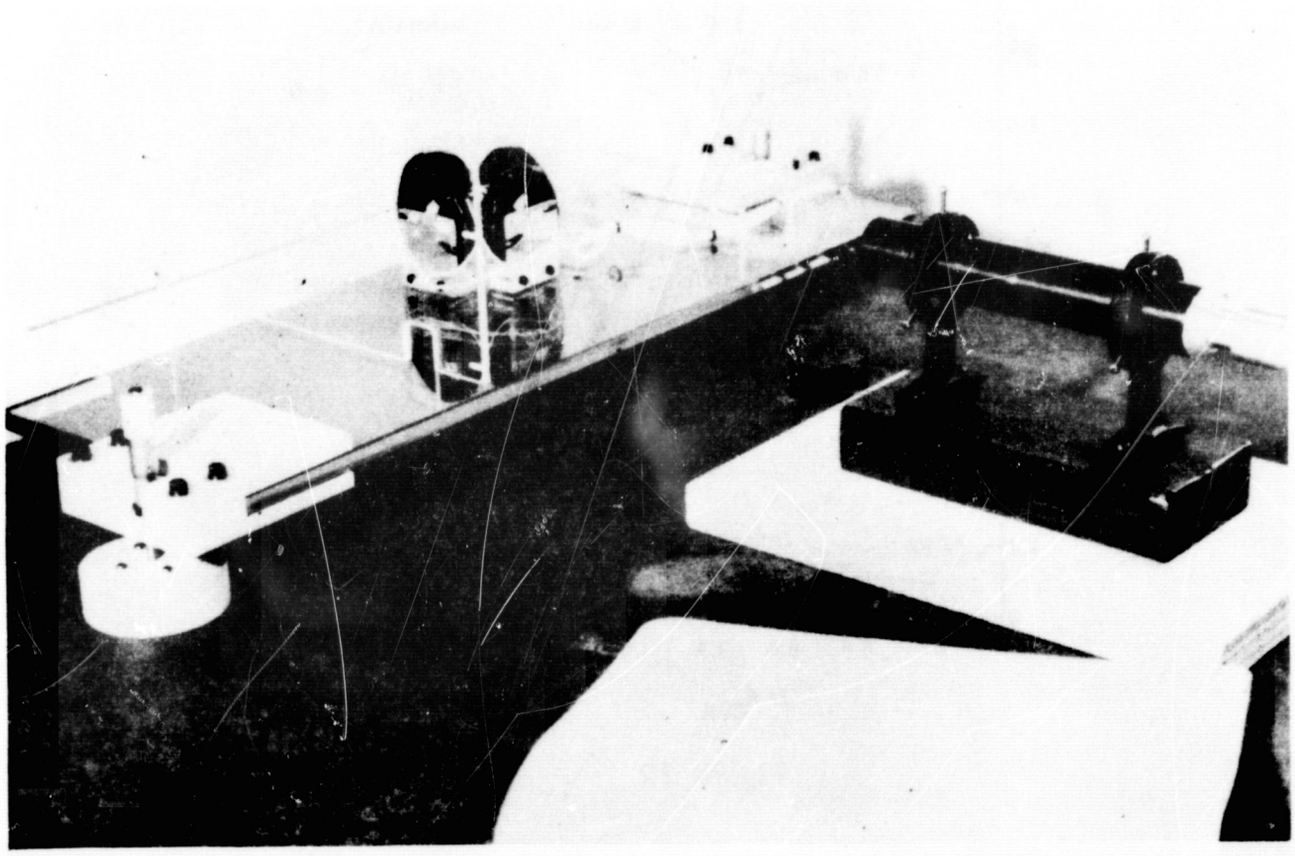


Figure 14

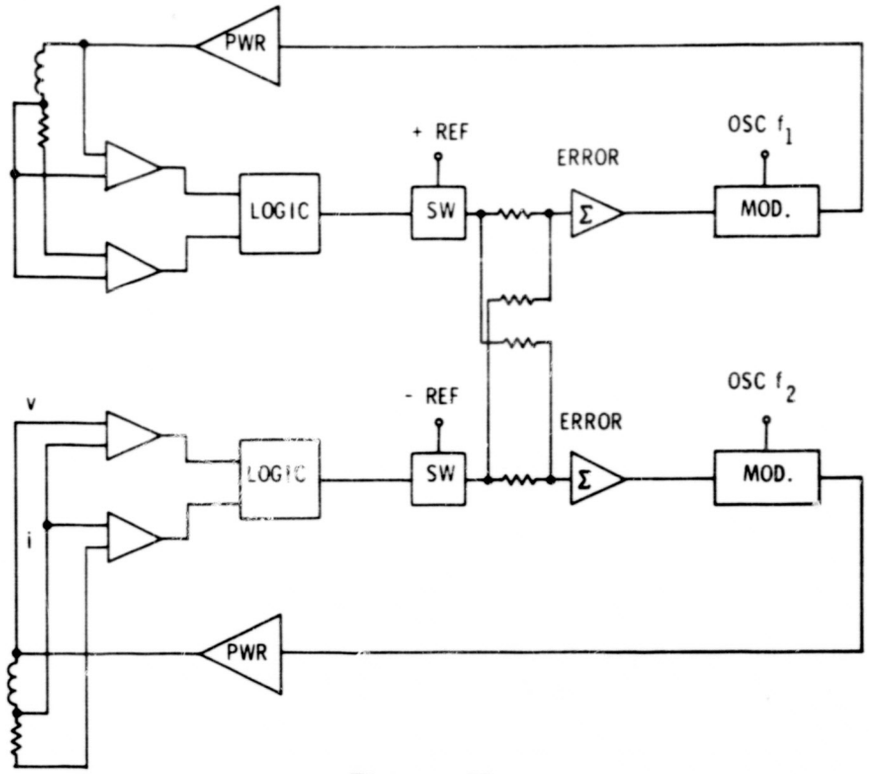


Figure 15

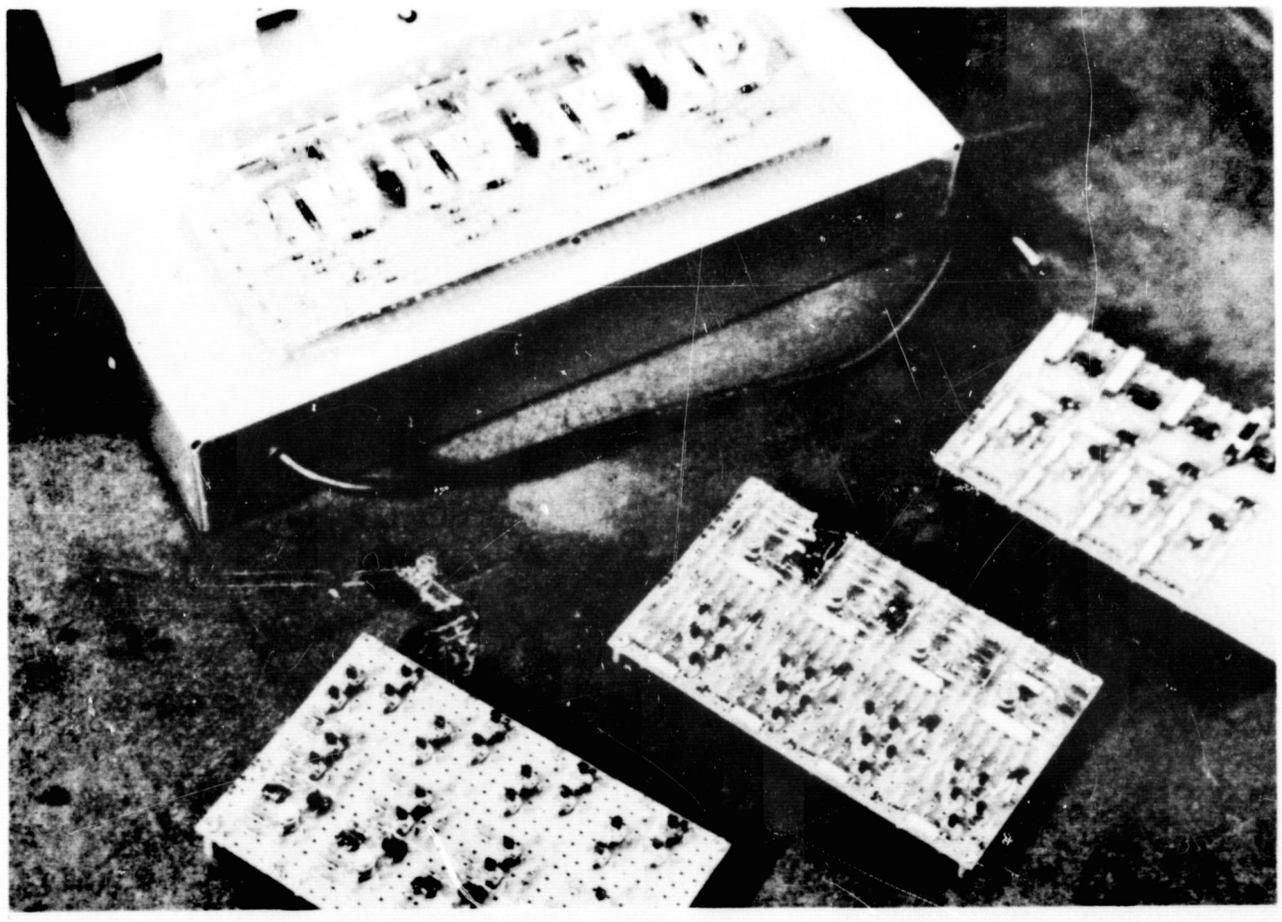
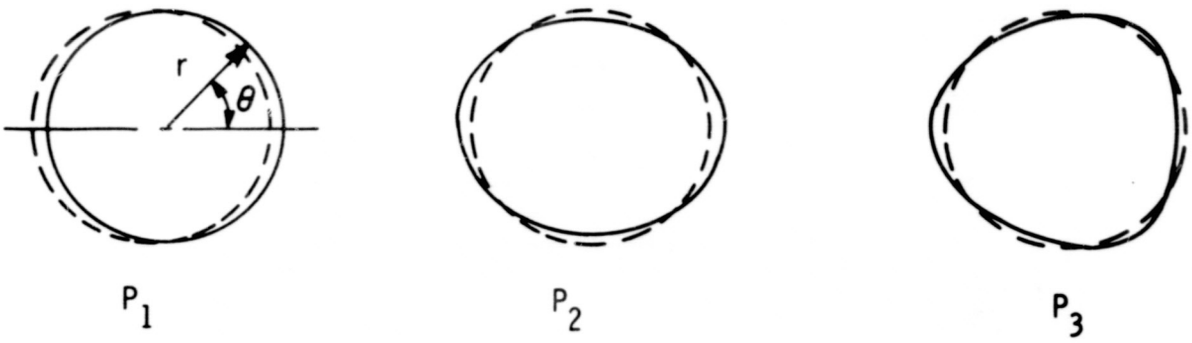


Figure 16

HYDRODYNAMIC MODES



$$r = a_{\ell} P_{\ell}(\cos \theta) \cos \omega_{\ell} t$$

Figure 17

FLUID CURRENTS DUE TO MAGNETOSTRICTION

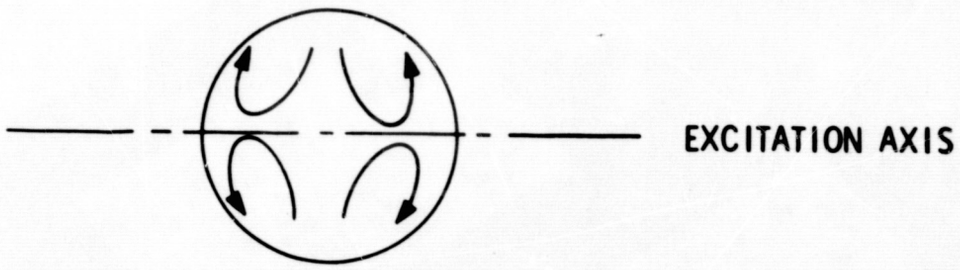


Figure 18

N70-20523

DIRECTIONAL SOLIDIFICATION OF MULTICOMPONENT SUPERCONDUCTING SYSTEMS UNDER ZERO G CONDITIONS

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ABSTRACT

Metallurgical microstructure plays a major role, through its influence on magnetic flux pinning, on the critical current density of superconducting materials It has been found in technological practice that the capabilities of superconducting materials, as measured in short length samples, are rarely realized when long lengths of the same material are wound in a solenoid. This degradation has been attributed to magnetically induced thermal instabilities. A method is proposed for the preparation of stable superconducting cables comprising a filamentary phase of one superconducting in a matrix of another This is to be achieved by directional solidification of appropriate superconducting systems under 0 g conditions.

Metallurgical microstructure plays a major role, through its influence on magnetic flux pinning, on the critical current density of superconducting materials. It is the purpose of this paper to outline the reasons for this relationship and indicate how, by taking account of recent theoretical and experimental advances, carefully chosen eutectics

*Paper presented by J. T. A. Pollock

solidified under conditions of 0 g would have major advantages over materials presently available.

First, consider only ideal homogeneous superconducting materials. These may be easily separated into two groups by their transition from the superconducting to the normal state in an increasing external magnetic field, H_e (Fig. 1). As the applied magnetic field is increased, type I (soft) superconductors have an abrupt transition at a single critical field (H_c), while type II (hard) superconductors undergo a gradual transition to the normal state between a lower critical field, H_{c1}, and an upper critical field, H_{c2}. Thermodynamic relationships hold for both reversible processes, and the work done in driving the material normal is given by the area under the curves. For type II material, an imaginary thermodynamic critical field, H_c, may be defined by assuming an abrupt transition enclosing an equal area (dashed line in Fig. 1b). The degree of type II behavior may then be described by the dimensionless Ginzberg-Landau parameter, $\kappa = H_{c2}/\sqrt{2}\, H_c$. Theory indicates that κ depends primarily on the superconducting critical temperature, T_c, the electron density of states at the Fermi level, $N(0)$, and the normal state resistivity, ρ_n. κ is, therefore, sensitive to alloy concentration. Its relationship with the resistivity is given by the following equation:

$$\kappa = \kappa_0 + 7.5 \times 10^{-3}\, \gamma^{\frac{1}{2}}\, \rho_n$$

where κ_0 is the κ value for the pure element or compound, and γ is the coefficient of electronic specific heat. Thus, while elements (with the exception of Nb) are known to be type I, solid solutions, other than the very dilute, are type II. Intermetallic superconducting compounds are also type II, because their high $N(0)$ values result in a large κ_0. Table I gives values of T_c for metals, alloys, and compounds, together with H_c or H_{c2} (listed as H_n) values at 4.2 °K. It is apparent that high field superconducting materials must have type II characteristics, i.e., they must be either alloys or compounds.

Between H_{c1} and H_{c2}, type II materials are described as being in a "mixed state." To be useful for high field applications, a superconducting material must not only have a high H_{c2}, but must be able to carry large resistanceless currents in this mixed state. As the applied field is increased above H_{c1}, partial field penetration occurs in the form of quantized magnetic flux threads which consist of a normal core supported by a vortex of shielding current. This flux lattice, representing an internal magnetic field, B, has been directly observed,[3,4] and a balance is reached between the mutual repulsion of the fluxoids and the applied field force. If a current (J) is passed through the conductor at right angles to the direction of the applied field, a Lorentz force given by the cross product of $\vec{J}$ and $\vec{B}$ acts on the

flux threads in a direction perpendicular to both the applied field and the impressed current. In a homogeneous material, the flux lines will move and resistance will appear if the drift rate is sufficiently high. Thus, ideal reversible type II superconductors are expected to have low critical currents (Fig. 2).

If, however, the flux motion can be impeded by imperfections in the superconductor, the Lorentz forces may be resisted and the material can carry large superconducting currents without reverting to the normal state. Inhomogeneities [5,6] such as nonuniform dislocation arrangements, coherent precipitates, finely dispersed second phase, and voids can all aid in raising the critical transport current density, J_c. A flux line will remain "pinned" at an inhomogeneity until the Lorentz force exerted on it exceeds the pinning strength. When, as a result of increasing applied field or impressed current, the Lorentz force exceeds the value of the local pinning forces, a change in the flux line gradient will occur. If a balance with local pinning forces in another part of the superconductor does not take place, the superconductor will transform to the normal state and a resistance to current flow will be observed. The greater the differences in free energy of the inhomogeneity and the superconducting matrix, the greater its effectiveness in raising J_c (or, the greater the difference in electronic properties, the greater the pinning force).

This resistance to the motion of magnetic flux lines under the influence of the Lorentz forces will also result in an altered magnetization curve. The presence of heterogeneities causes a resistance to field penetration in increasing fields and impedes the flux thread escape in decreasing fields. This means that the magnetization curves for high field, high transport current superconductors are irreversible. Fig. 2 is a schematic representation of the way magnetization characteristics and critical current densities are altered by deviations from ideal behavior produced by inhomogeneities. Note that the magnetic hysteresis resulting from the nonhomogeneous nature of the material is a measure of the resistance to flux motion and, hence, of critical current densities in the mixed state. A quantitative theory relating J_c and magnetization data is available. [7,8]

Thus, the ultimate critical current densities which can be carried are controlled by interaction between the metallurgical microstructure of the sample and the magnetic flux thread lattice present in the mixed state.

In practice, it has been found that the capabilities of superconducting materials, as measured in short length samples, are rarely realized when the same material is used in a solenoid. This degradation has been attributed to magnetically induced thermal instabilities and may

be explained as follows. Increasing temperature (T) results in a parabolic decrease in the critical field and critical current of a superconductor for $T < T_c$. The relationship for H_c is given by the equation

$$H_c(t) = H_0 (1 - t^2)$$

where $t = T/T_c$ is the reduced temperature, and H_0 is the critical field at 0 °K. The fact that J_c usually decreases at a faster rate than H_c is generally ascribed to thermally activated flux creep past barriers.[9] Local variations in the movement of flux past the pinning sites (e. g. , due to mechanical shock) can result in a local rise in temperature. Since dJ_c/dT is negative, the local J_c value is decreased, allowing more flux motion for a given applied field, H_e, and creating more temperature rise, etc. This is commonly known as a flux jump and can result in a premature transition to normality. As a result of the heat generated, severe damage to the device may occur. This has been a major problem in superconducting solenoids and the reason for the incorporation of large volumes of high conductivity copper (a non-superconductor) in magnet design.

Some experimental results reported by Livingston[10] indicate a possible solution to this problem. It is known that the precipitation of Sn from supersaturated Pb-In-Sn solid solutions (which are superconducting above 4. 2 °K) results in flux pinning and magnetic hysteresis as shown in magnetization measurements made at 4. 2 °K (Fig. 3, curve A). However, magnetization curves taken at 2. 0 °K (Fig. 3, curve B) indicate that, although H_{c2} increased as expected, a decrease in magnetic hysteresis and, hence, the critical current density, were also reported. These results can be explained on the basis of the different flux pinning ability of the Sn particles at the temperatures at which the data were taken. Sn is superconducting at temperatures below 3. 7 °K. The Sn precipitates act as preferred flux pinning sites for the fluxoids at 2 °K because, although the Sn particles are superconducting at this temperature, their order parameter (a measure of the proportion of available electrons which are superconducting) is smaller than that for the higher superconducting transition temperature Pb-In-Sn matrix. However, as the temperature increases, the Sn particles become normal at a faster rate than the matrix, and are normal at 4. 2 °K. During the temperature rise, their flux pinning ability increases with respect to the matrix and increases substantially when the transformation to normality occurs. Therefore, although H_{c2} (controlled by the matrix) decreases with increasing temperature, the magnetic hysteresis and J_c characteristics increase. Briefly, this means that within the range of applied magnetic field indicated in Fig. 3, dJ_c/dT is positive over the temperature range ~2. 0 to 4. 2 °K. This is significant, since it offers a method of controlling those magnetic (i. e. ,

transport current) instabilities in which a negative dJ_c/dT plays such an important role.

An examination of the commercial superconducting materials presently available indicates that although high pinning characteristics have been achieved through highly disordered structures and the introduction of the heterogeneities in the form of second phase particles, no attempt has been made to achieve positive dJ_c/dT characteristics. The nonsuitability of superconducting elements as useful materials except in specialized instances, e. g. , Nb for ac conduction, has been previously noted. Superconducting solid solutions and compounds are, therefore, of primary interest. The introduction of a second superconducting phase as a source of pinning sites leads us to consider ternary phase systems, since an examination of phase equilibria between the components of possible superconducting solid solutions and intermetallic compounds points to few binary systems which present favorable phase relationships for achieving positive dJ_c/dT. The behavior at low temperatures of mixtures of superconducting phases is dependent not only on the electronic properties of the phases at these temperatures but also on their distribution and relative proportion. In particular, it is essential that the primary superconducting phase be present in electrically connected networks if resistanceless operation in high magnetic fields is to be realized. The need to meet this condition of multiple connectedness suggests that directional solidification of continuous fibers of the primary superconducting phase in a superconducting matrix of the second superconductor would be the ideal method for preparing a material with positive dJ_c/dT characteristics.

Directional solidification of binary eutectics has been used to prepare in situ intermetallic compound fibers in a metal matrix, and successful results have been reported in such systems as Cu_2Al in Al[11] and Al_3Ni in Ni[12]. Several problems are, however, encountered in such systems mainly associated with the invariant nature of a eutectic reaction. Normally, no adjustments in fiber-matrix ratio can be made and no influence on the properties of the matrix can be exerted. This latter factor is a severe shortcoming, since control of the matrix composition is essential in optimizing any alloy system. Nevertheless, composite electronic materials have been prepared by directional solidification of binary eutectics and show interesting properties which have made possible their use as polarizers for infrared light[13] and armatures for miniature electric motors.[14]

Since the use of ternary systems is envisioned in the preparation of the proposed superconducting materials, another class of phase reactions presents itself which leads to the same final structure as that of invariant binary eutectics, yet offers a means of overcoming some of

their shortcomings. The class of reactions proposed consists of monovariant eutectics present in higher order systems. The usefulness of these monovariant reactions arises from the fact that the crystallized binary eutectic type structure obtained is actually a solid solution matrix and a eutectic precipitate. The structure forms essentially in the same way as a binary eutectic by the simultaneous precipitation of two crystallite types, one of which is a solid solution and may consist of an essentially infinite number of alloying elements. Also, in certain cases and within limits, the fiber-matrix ratio may be variable. However, the most important possibility offered by the use of monovariant eutectics is that of controlling the matrix composition. This will allow relative adjustment in the superconducting properties of the phases, primarily T_c, to produce an essentially two-phase material with positive dJ_c/dT characteristics It has also been demonstrated[15] that control of the matrix composition can be a method of changing the crystallization behavior of the fibers.

It will be relevant to consider, briefly, the properties of eutectic composition material, paying particular attention to their preparation under directional solidification conditions. As pointed out previously, a eutectic structure, when directionally solidified, can consist of one rodlike or lamellar component of very high length-diameter ratio embedded in a matrix of the other eutectic component. Generally, however, as has been discussed by several authors, [16] small temperature fluctuations which cause convection and attendant changes in supersaturation cannot be avoided. Thus, fibrous growth of one component is interrupted; the filaments, instead of being continuous, become discontinuous. In other words, since the eutectic is an invariant point in the thermodynamic description of the system, for ideal eutectic solidification, temperature and composition are fixed. Local compositional variations such as those induced by convection cause a disruption of ideal thermodynamic growth conditions. As a consequence, fibers become irregular, or cells develop and a much less than ideal composite is the result.

In the case of monovariant eutectic reactions in higher order systems, these difficulties are sharply amplified because the liquid from which the fibers are precipitated contains more than two species of atoms, and the probability of producing local compositional gradients is consequently much greater. It is therefore suggested that directional solidification of superconducting monovariant eutectics would greatly benefit from the absence of gravity segregation and thermal convection, and that substantial advances in superconducting technology might be realized by manufacturing in space.

At present, there is a paucity of information available on ternary phase systems. It would, therefore, be necessary to investigate the phase

equilibria in systems which are tentatively suggested in order to determine whether suitable eutectic reactions are present. The superconducting characteristics of the materials can, however, be determined during the initial investigation and will themselves yield valuable phase equilibria information. Nevertheless, several interesting possibilities based on Nb compounds and solid solutions present themselves. Nb based A-15 type intermetallic compounds have the highest T_c measured to date [$Nb_3(Al_{0.8}Ge_{0.2})$, $T_c = 20.05$ °K)]. We suggest that suitable monovariant eutectic reactions may be found among such ternary systems as Nb_3Al, Nb_3Ge, Nb_3Sn with V, Ti, Ta, etc. These ternary systems would allow, if successful, the directional solidification of a high T_c intermetallic compound in an Nb based solid solution which would, on the basis of information available,[17, 18, 19] also have a high T_c and excellent J_c characteristics.

Initially, feasibility experiments could be carried out by producing directionally solidified eutectics with the correct current density characteristics in a Pb based ternary material. Pb based compounds and alloys have superconducting transition temperatures well above 4.2 °K (boiling point of liquid He) and, because of their low melting points, the additional advantage of easy preparation. Also, there is some information on directional solidification of Pb alloys already available.[20] Meanwhile, phase diagram information could be generated in the more important transition metal systems which would have superior superconducting characteristics.

In summary, we have proposed a method of preparing superconducting material which would be stable in the presence of the flux jumps which can lead to a catastrophic transition to normality. The idea is based on three interconnected propositions:

1. The material should be multiphase. At least two phases should be superconducting and with electronic properties such that stability to flux jumps is possible.

2. To ensure continuity of the high current density superconducting path, directional solidification of eutectics under conditions of 0 g should be used to prepare the samples.

3. The use of multicomponent monovariant eutectic systems presents major advantages over invariant eutectics which have been successfully used to prepare composite materials. In particular, the ability to adjust the matrix composition is a tremendous advantage, since it allows proposition (1) to be more readily realized.

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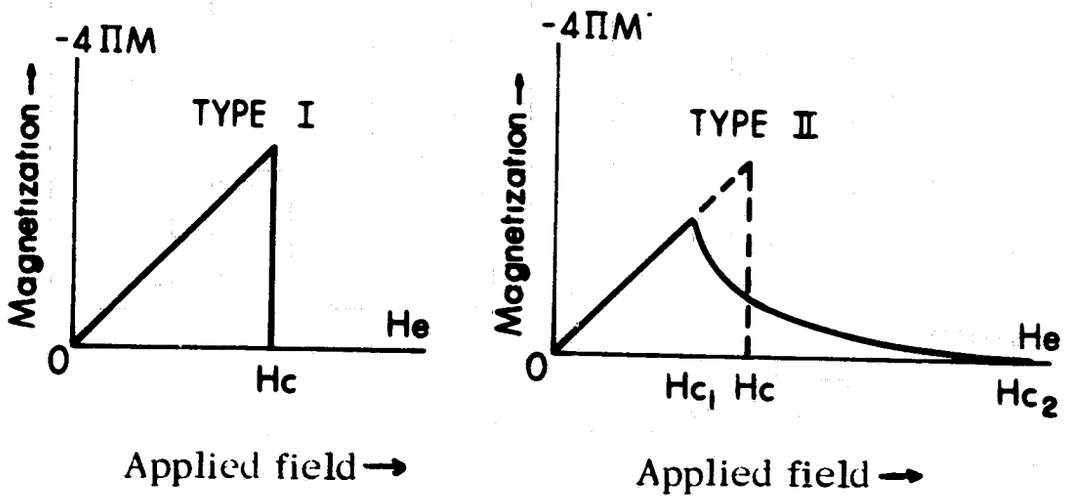


Fig. 1. Schematic magnetization curves for types I and II superconductors

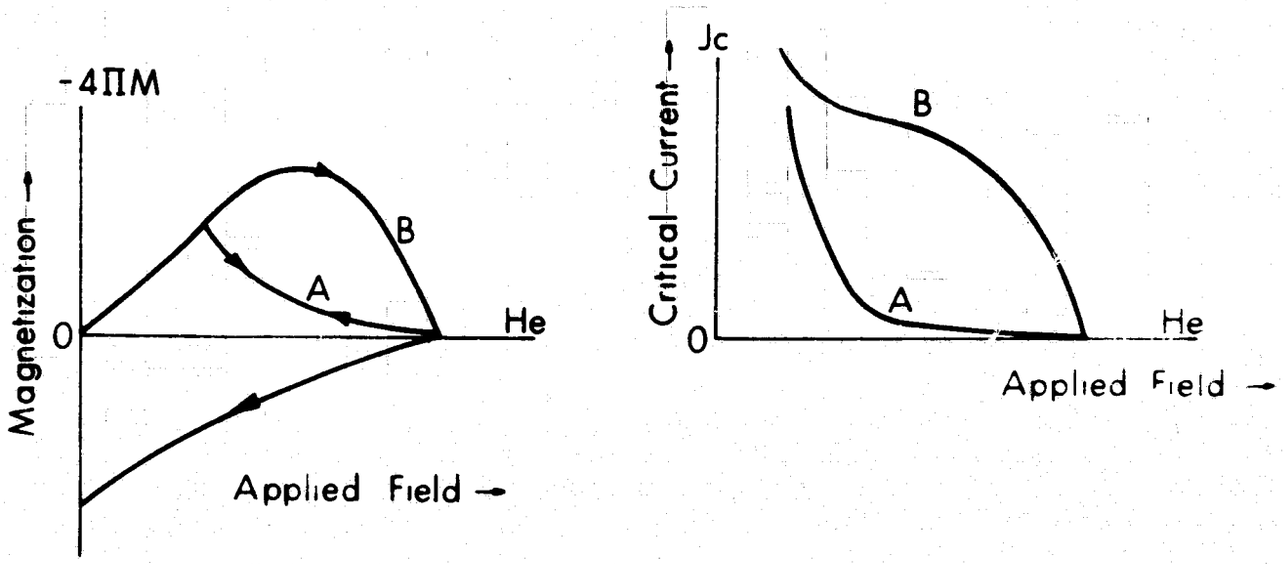


Fig. 2. Schematic magnetization and critical current density curves for type II superconductors (curve A = reversible magnetization curve and corresponding J_c curve; curve B = same material in, for example, a highly deformed condition — magnetic hysteresis is evident and a corresponding enhancement of J_c has occurred)

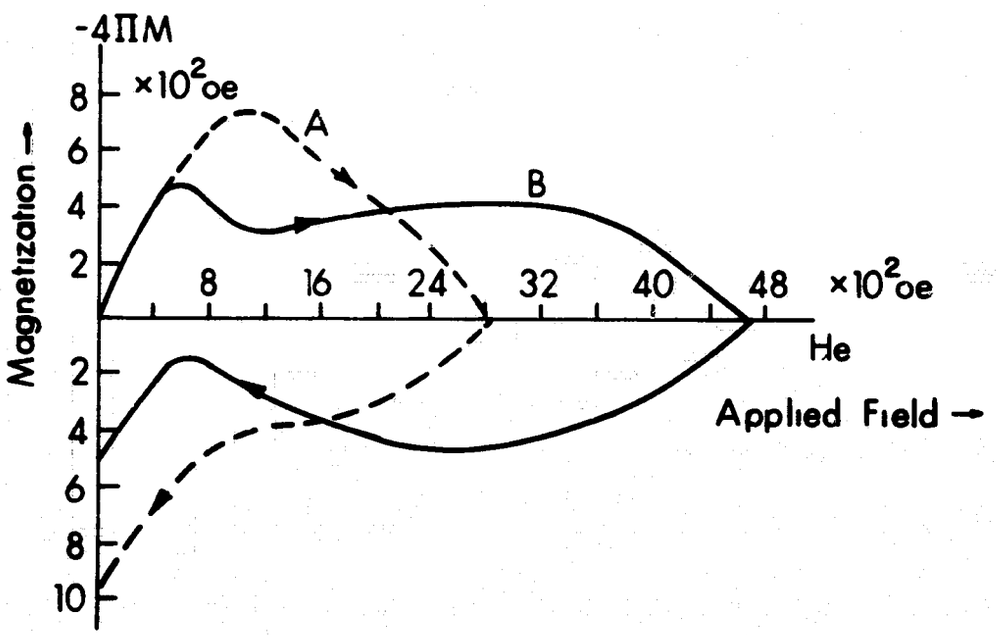


Fig. 3. Magnetization curves[10] for a Pb-22 a/o In-21 a/o Sn alloy aged 1 hr at room temperature after solution treatment (curve A = measurement at 4.2 °K; curve B = measurement at 2 °K)

Table I. T_c and H_n Values[1,2]

Element	T_c, °K	H_n (oe)
Al	1.18	99
Nb	9.13	1980
Pb	7.20	803
Sn	3.72	309
Ta	4.48	830
V	5.30	1020
Alloys		K (oe)
Nb-25a/o Zr	10.8	~100*
Nb-33a/o Ti	9.3	~100*
Ta-35 → 100 a/o Ti	4.4 — 7.8	14-138+
Mo-33 a/o Re	10.8	~28+
Compounds		
Nb_3Sn	18.05	350+
Nb_3Al	17.0	
V_3Si	17.0	300+
PbBi (ϵ phase)	8.8	~30‡

*Extrapolated linearly to 0 °K.

+Measured at 1.2 °K.

‡Measured at 1.9 °K.

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POSSIBILITIES FOR PRODUCING NEW GLASSES IN SPACE

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ABSTRACT

In July, 1968, Mr. Hans Wuenscher of the NASA Marshall Space Flight Center visited the Space Division of the North American Rockwell Corporation and discussed the many possibilities for manufacturing in the "zero gravity"[1] environment of space. Zero gravity conditions of earth orbit have been known for a long time, but, until recently, very little serious thought had been given to the possibilities for exploiting these conditions for technical and, ultimately, commercial purposes.

Many of the concepts that emerged from a preliminary study were concerned with the potentially significant advantages attending the melting of materials in space free of gravitational restrictions. While such feats have been performed on a limited scale on earth

> Zero gravity melting permits the elimination of a solid container during both the melting and cooling phases of glass production. The combination of superheating well above the melting temperature and cooling in the absence of most normal nucleation sites promises to permit the production of glasses from normally crystalline materials such as Al_2O_3, HfO_2, ZrO_2, etc. Such glasses should find immediate applications in refractive optics, where the unusual combinations of index of refraction and dispersion can be used to advantage in highly corrected multi-element lenses. The possibilities for returning supercooled liquids as glasses from orbit and growing single crystals on earth is discussed. Heating equipment and atmospheres for space melting of glasses are considered.

[1] "Zero gravity" is used here to describe the condition of equillibrium between earth's gravitational pull and the centrifugal forces of earth orbit, or in other words, a condition of perpetual free fall.

("levitation melting" of metals supported by an induction field), here appears to be an opportunity to melt almost any material without the restrictions imposed by a container. No longer need "levitation melting" be limited to only 15 to 20 grams of materials with high electrical conductivity. In zero gravity almost any inorganic material can be melted without requiring a container if a suitable atmosphere and heat source can be provided. The surface tension forces cause the liquid material to assume a spherical shape. Melting in space, therefore, has been dubbed "containerless melting" to distinguish it from "levitation melting", which term can be reserved for processes performed in a normal gravitational field.

Initial efforts at space melting can be justified only where the resultant product cannot be made on earth with today's state-of-the-art. Such an approach necessarily takes us into relatively unknown and quite possibly controversial territory. A corollary requirement is that the ultimately resultant product be sufficiently useful to justify the expense of the initial experimental work.

The balance of this paper deals with one of the many possible concepts involving containerless melting--that of producing new (inorganic) glasses in space. For purposes of this discussion, the definition of glass given in Shand (Reference 1) is appropriate--"An inorganic product of fusion which has been cooled to a rigid condition without crystallization." Most of the emphasis in the study to date has been on the possibilities for new glasses composed of metal oxides. Less emphasis has been placed on chalcogens. There are, no doubt, possibilities for producing glasses of other types of compounds, such as halides and nitrides, or for that matter, of metals, but time has permitted only superficial consideration of them to date.

To appreciate the possibilities for producing new glasses in space, it is necessary to explore further some of the really unique aspects of zero gravity melting. Not only is it theoretically possible to melt very high melting point substances without contamination from container materials but, of equal importance for the production of glass, it is also possible to cool the substance free of any contact with solid material. Thus many of the usual sites for nucleation of crystals can be eliminated. Is it possible that elimination of the easier nucleation sites could result in complete suppression of nucleation, and therefore of crystallization, of materials such as Al_2O_3, TiO_2, etc? This is a question that will be dealt with, if not fully answered, in more detail later. Another question that will be explored is--assuming glasses could be made from materials normally obtainable only in the crystalline state--would they be useful technologically?

Another appealing feature of the concept of glass-making in space is the relative simplicity of the operation, resulting in a spherical boule of optical glass. Such a shape is quite useful for the production of lens elements. The techniques for cutting, shaping, and figuring lens blanks into the final configuration are well known and need not be elaborated on further here. It is conceivable then that, given a well-engineered facility and a modest amount of special training, an astronaut can perform the necessary space operations. The more technically complex operations of selecting, refining, and preparing the starting materials and the highly skilled post-flight operations of property measurements, lens grinding, figuring, coating, etc., could be performed on earth with conventional techniques.

Assuming that unusual glasses can be made in a zero gravity environment, there are possibilities that single crystals might be grown from the glass boules after returning them from space.

GLASS APPLICATIONS

VISIBLE TRANSMITTERS

Most of the optical glasses used for refractive optics in the visible region of the spectrum are based on the dioxide of silicon, SiO_2. The large range of optical properties required for sophisticated, multi-element lenses are achieved commercially by incorporating other oxides, such as PbO, La_2O_3, Al_2O_3, CaO, etc., with the SiO_2 base. There are two other glass formers, B_2O_3 and P_2O_5, that in recent years have been employed as bases for the specialized optical glasses required for today's better optical devices. These three base oxides, SiO_2, B_2O_3, and P_2O_5, are all very viscous in the molten state, a property that reduces mobility sufficiently to prevent nucleation and crystallization on cooling so that a glass results. A glass, then, might be considered a supercooled liquid with very high viscosity. As such it is amorphous, or without the long range, repeatable structure found in the solid, crystalline state. While recent studies have shed much light on the nature of the "structure" of glass and have shown that it bears some resemblance to the crystalline state, the differences are of great significance in terms of the unique properties[1] that make glasses useful in refractive optical applications.

The principal characteristics of glasses that make them useful in refractive optical applications are:

1. Transparency
2. Hardness
3. Chemical durability
4. Index of refraction (n)
5. Dispersion ($dn/d\lambda$)
6. Optically isotropic

[1]For a more complete dissertation on the essential features of glass, the reader is referred to a clearly written artical by Dietz (Reference 2).

The last three characteristics are of prime importance in multi-element lenses. Since many crystalling materials are normally anisotropic and hence have more than one index of refraction, they are unsuitable for refractive optical applications. If, however these materials can be produced optically isotropic, they then become potentially useful for refractive optical applications. For example, crystalline SiO_2 is anisotropic, while glasses formed from SiO_2 are isotropic. In other words, the number of materials useful for refractive optics applications would be increased significantly if normally anisotropic materials can be produced with isotropic optical properties.

TABLE 1 lists some pertinent optical properties, taken from the published literature, in the visible range of the spectrum for a number of transparent oxides. The structure for which the data applies, where known, is noted. For those crystalline substances which are anisotropic and uniaxial, the data for both the ordinary ray (ω) and extraordinary ray (ϵ) are given. Of those substances listed only monoclinic ZrO_2 and HfO_2 are biaxial -- therefore three indices and dispersions are given. The data listed include the index of refraction at the sodium D (yellow) line and the inverse rate of change of index with wavelength. This latter property, given by the Abbe number, ν_D, is a function of the refractive indices of the blue hydrogen F line, yellow sodium D line, and red hydrogen C line (n_F, n_D, and n_C) and is given by the relationship $\nu_D = \frac{n_D - 1}{n_F - n_C}$

It should be borne in mind that the Abbe number is in inverse relationship to the dispersion -- low dispersion glasses having high Abbe numbers and vice versa. The index of refraction for all materials characteristically decreases with longer wavelength as is shown schematically in FIGURE 1. Low dispersion materials have flatter and high dispersion, steeper curves.

The data from TABLE 1 are plotted in FIGURE 2, the traditional $n - \nu$ diagram used in the optical glass industry. It should be noted that the data points for the anisotropic crystalline materials are the mean values as calculated by the formulas:

$$\text{mean} = \frac{2\omega + \epsilon}{3} \quad \text{or} \quad \frac{\alpha + \beta + \gamma}{3}$$

where $\omega, \epsilon, \alpha, \beta, \gamma$ stand for the ordinary and extraordinary ray of uniaxial crystals and the three rays of biaxial crystals, respectively.

The area shown in FIGURE 2 encloses the n, ν values for virtually all of the commercially available optical glasses. The development effort over the past 100 years or so has concentrated on filling

in the areas between the low index, low dispersion crown glasses and the higher index, high dispersion flint glasses. In recent years the trend has been to expand the available glasses in the higher index, lower dispersion direction. One of the present goals of some optical glass producers is to achieve the properties of spinel ($MgAl_2O_4$).

If it becomes possible to obtain some of the oxides shown as glasses by melting and cooling in zero gravity, a major expansion of optical glass properties could be achieved. Of particular interest are the oxides of aluminum and hafnium, both of which combine unusually low dispersions with high index of refraction.

It should be emphasized that we are talking about only the pure oxides which might be used as bases for new glasses. If the pure oxides could be obtained as glasses, it is logical to assume that mixtures could be produced to fill in the area needed on the n - ν curve to supply the optical designer with the selection of properties needed to create new, highly corrected lenses.

In recent years there has been increasing emphasis on producing highly corrected lenses of increasingly high aperture. In such lenses an error known as secondary spectrum becomes significant. The secondary spectrum can be defined as the residual chromatic aberration that remains after two wavelengths have been brought to a common focus using conventional achromizing techniques, and is determined by the partial dispersion ratios[1] of the optical materials used in the system.

In order to appreciate more fully the potentials for new glasses if they could be made in space, it is necessary to consider the role of partial dispersion. As the relationship $L = f\left(\frac{P_a - P_b}{\nu_a - \nu_b}\right)$ shows for a two-component achromat, the secondary spectrum (L) is a function of the focal length (f), the partial dispersion ratios of components a and b (P_a and P_b) and the Abbe numbers of the components. In order to minimize L the numerator should be small and the denominator large. Unfortunately, nature has apparently decreed that the P, ν points for glasses of a given base all fall on a single line, for example lines SS, BB, and PP of FIGURE 3.

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[1]The partial dispersion is essentially the ratio of the slope of a portion of the n vs. λ curve to that of a larger portion. A ratio sometimes used is $P_{FD} = \frac{n_F - n_D}{n_F - n_C}$ For a more complete discussion of the role of partial dispersion in the correction of secondary spectrum and the relationships to optical glasses. the reader is referred to a paper by Brewster, Hensler, Rood, and Weidel (Reference 10).

In order to correct secondary spectrum, it is necessary, then to choose glasses of more than one base for the individual elements of the lens. This consideration has prompted a leading producer of optical glasses and optical equipment to develop the non-cross-bred[1] borate and phosphate glasses to provide a useful range of Abbe numbers. The secondary spectrum correction possibilities are limited with conventional glasses, however, because the horizontal displacement of the three lines of FIGURE 3 is quite small.

Undoubtedly, if new bases for optical glasses could be found, new families of glasses with different P - ν lines could be created and the possibilities for secondary spectrum correction thereby significantly increased. Unfortunately, it is not possible to predict the location of the lines for such glasses at this time. Partial dispersion calculations require that the index of refraction be known to five or six significant figures. Even if data of such accuracy were available for the crystalline materials being considered in this report, the imprecise conversion of data from the crystalline to the glassy condition would render the exercise meaningless.

INFRARED TRANSMITTERS

In recent years the advancement of infrared technology has delineated requirements for materials which are transparent in the infrared portion of the spectrum. Good infrared transmission is, by and large, characteristic of many semiconductor materials, i.e., silicon and germanium amoung the elements and the chalcogenides among the compounds. The infrared transmitting chalcogenides[2] are composed of group IV-A and V-A elements, with sulfur, selenium, and tellurium of group VI-A.[3] Among the two-component chalcogens, the compound, As_2S_3, is a strong glass former. By rapid quenching from the molten state, glasses can be formed from certain As-Se, Ge-S, and Ge-Se compositions and a number of ternary and quaternary compositions. Unfortunately, the chalcogenide glasses obtained to date are soft

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[1] i.e., borates free of silicates and phosphates, etc.

[2] For a good discussion of the state-of-the-art of infrared transmitting glasses, the reader is referred to articles by A. Ray Hilton, and A. J. Worrall (References 11, 12).

[3] Oxygen, also in group VI-A, causes infrared absorption in the sulfide, selenide, and telluride glasses. Therefore strong efforts are made to exclude it.

and have low softening temperatures. Zero gravity melting and cooling may make it possible to obtain glasses with improved hardness and higher softening temperature from compositions with higher Si and/or Ge contents, or possibly even containing elements from groups other than IV-A and V-A.

Silicon and germanium have superior mechanical properties but are not suitable for infrared transmission at higher temperatures because of significant "holes" in the transmission spectrum. If they could be obtained as glasses, there is the possibility that the holes might disappear, rendering them among the most promising candidate materials for infrared transmitting applications. It appears that the chances for successfully melting and cooling any metal to a glass in space are significantly smaller than that for compounds, however.

GLASS MAKING FEASIBILITY

The discussion in the previous section was based upon the assumption that new glasses can be made in zero gravity. This section examines that assumption in terms of the possibilities for suppressing nucleation of crystals, atmospheres that might be used, and possible heating methods.

NUCLEATION AND CRYSTALLIZATION

Work by Duwez (Reference 13) and others demonstrate that crystallization can be suppressed in tellurium and some metal-based systems through the use of extremely high cooling rates from the liquid state. By using thermal conductance to obtain cooling rates on the order of 10^6 C per second, glasses have been formed from tellurium-based systems with low melting eutectic additions of Ga, In, Ge, Cu, and Cu-Au. Among the metal-based systems studied by Duwez and others, the low melting eutectic compositions of the systems Fe-P-C; Au-Si and -Si-Ge; Pd-Si, -Si-Fe, -Co, -Ni, -Ge; Pt-Si, -Ge, -Sb; and Rh-Ge have been obtained as glasses on a laboratory scale. It appears unlikely that the methods used to rapidly cool are capable of suppressing nucleation entirely, but they obviously are effective in preventing crystal growth, which is a time-dependent phenomenon. The main point here is that it has been shown to be possible to prevent detectable crystallization even in metal systems, with their very high heats of fusion and very low viscosity.

Are the conditions present in zero gravity melting and cooling, then, sufficient to prevent crystallization in oxides? While the cooling rates obtainable under the conditions anticipated in space, being dependent solely on radiation losses, are rapid, at least for the higher melting materials, they cannot approach the rates obtainable by conduction cooling of metals in the laboratory. Therefore, the basis for predicting that zero gravity melting and cooling can result in unusual glass formation appears to rest strongly on the possibilities for suppressing nucleation, at least for the first 600 degrees or so of cooling below the normal freezing point.

Assuming that all residual nuclei from the crystal state can be destroyed in the molten state, possibly by heating to 10 or 20 percent above the melting point, will the materials spontaneously

nucleate? This is a question that cannot be resolved without further study. It is possible that there may be no such thing as truly spontaneous nucleation in glasses. Ernsberger and Neely have pointed out that nucleation does not occur preferentially at bubble surfaces in plate glass (Reference 14) as was originally thought by many to be the case. Ernsberger (Reference 15) has also pointed out that invariably, in cases where spontaneous nucleation was thought to occur during devitrification of silicate glasses, closer examination has revealed other explanations. In one case, small pieces of undissolved platinum from the melting crucible were present in each crystallite examined. The platinum undoubtedly served as a nucleation site. In other instances evidence for "spontaneous" nucleation have been explained on the basis of chemical changes at the outer surfaces of a glass body or at crack surfaces. The "spontaneous" nucleation that apparently occurs in crystallized glasses, such as Cer-vit and Pyroceram, can be explained on the basis of a two-stage process involving separation into two liquid phases. Liquid-liquid nucleation is known to have a lower energy barrier than liquid-solid nucleation.

At any rate, it is anticipated that nucleation (and therefore crystallization) in zero gravity can be suppressed for the following reasons:

1. Oxides are excellent solvents for expected impurities. Therefore, the chances are very good that impurities that could serve as nucleators can be completely dissolved. The elimination of a solid container precludes the possibility of contamination from that source.

2. Because materials being considered can be superheated without contamination from a crucible, it appears possible that all of the residual nuclei from the crystalline starting material can be destroyed.

3. The cooling rates obtainable by radiation, especially for the higher melting temperature materials, can be very high. Since the materials are transparent, radiation can occur from within the bulk of the material as well as from the surface. Cooling rates therefore should be quite uniform. This should also reduce the tendency to fracture on cooling, even if the glasses formed have relatively high thermal expansion coefficients. Radiation cooling rates will be highest at the higher temperatures where rapid cooling is most important if nucleation is to be suppressed. If a sufficient amount of supercooling can be achieved, increasing viscosity should prevent nucleation and crystal formation at the lower temperatures, where cooling rates will decrease.

4. Many of the oxides being considered at this time have a tendency to be glass formers in spite of their never having been observed in the amorphous condition in the massive, pure form. It is the writer's understanding that Al_2O_3, for example, can be treated as a glass former in silicate glass research (Reference 16). Al_2O_3 base glasses free of SiO_2 , B_2O_3, or P_2O_5 are being produced commercially (for example, CaO-BaO-MgO-Al_2O_3) (Reference 12). Recent work in the Soviet Union has shown that there is a large glass forming area in the ternary system, TeO_2-V_2O_5-BaO, which extends into the three binary systems (Reference 17). None of the three pure oxides are glass formers under normal circumstances. In these instances, for example, zero gravity processing may provide the means for preserving the amorphous form on cooling even in the pure oxides. If this can be done, glasses can be formulated on the basis of obtaining desired optical properties without the restrictive necessity of choosing compositions with low mobility.

In summary, it is not possible to state with finality at this time that zero gravity processing will prevent nucleation per se. It does appear reasonable, however, that the combination of circumstances attending melting and cooling in zero gravity will permit the production of glasses from substances never before observed in other than the crystalline form.

ATMOSPHERES, EVAPORATION, AND DECOMPOSITION

While high vacuum and virtually infinite pumping capacity are available for the taking in space, it does not appear obvious that the high vacuum can be used to advantage for melting the materials being considered here. Several considerations appear to counter-indicate its use:

1. Evaporation and decomposition of the compounds being considered would be accelerated in a vacuum.

2. The transfer of condensible materials from the melt to cooler surfaces might be particularly troublesome in space.

3. There is a possibility that bubbles might form within the melt, being generated by outgassing products such as oxygen, metal, and oxide vapor. If this happens, the lack of gravity may prove to be a disadvantage. In the absence of gravity there can be no buoyancy effect--the principal means by which bubbles are removed from melts in conventional earth melting processes.

The most reliable information located to date on the melting and "boiling" points of some of the oxides being considered are listed in TABLE II. For comparison purposes, data for the three conventional glass formers are given at the bottom of the table. The melting and boiling points for MgO and SrO are quite close together at atmospheric pressure. For example, if one were to assume that MgO does not decompose on vaporizing, the Langmuir equation[1] can be used to calculate the evaporation rate. On this basis the evaporation rate for MgO at pressures less than about 10^{-5} torr is calculated at about 3000 cm/hr. at its melting point (2825C). In other words, a 10cm. diameter sphere of molten MgO, if suddenly subjected to the vacuum of space, would completely disappear by evaporation in about 6 seconds. Similar calculations for Al_2O_3, ZrO_2, and TiO_2 yield evaporation rates less than 1 cm./hr.[1] Such rates would not pose a serious problem in terms of material loss, but could be serious in terms of material transfer by evaporation and condensation. For example, the reflective surface of a solar furnace could become rapidly coated, or windows used for observation of the melting process in chambers could rapidly become clouded.

It must be emphasized at this point that the basic assumption leading to the calculations cited above is not, strictly speaking, a valid one. A cursory survey of the literature indicates that most of the oxides in TABLE II vaporize incongruently. Al_2O_3, HfO_2, La_2O_3, TiO_2, and SiO_2 all decompose to their constituent elements and/or to suboxides at the temperatures required for melting (References 18, 19, 22, 23, 24, 25) depending upon the ambient atmospheric composition and pressure. For example SiO_2 in vacuum at 2000 K will vaporize as Si, SiO, O, and O_2 at a total pressure of about 10^{-3} atmospheres, whereas in the presence of O_2 at 1 atmosphere the escaping species will be predominantly Si, SiO_2, and O_2 at a total pressure of about 10^{-6} atmospheres. The ambient atmosphere will have a much smaller influence on oxides which tend to vaproize congruently. For example, BeO tends to form polymeric vapor species as $(BeO)_n$, where n = 2,3,4,5,6. In this case even a very small partial pressure of O_2 will suppress incongruent vaporization.

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[1]The Langmuir equation was used in the form: $R = \frac{Kp}{d\sqrt{T/M}}$

where

R=rate of evaporation, cm./hr.
K=2.1 x 10^2
d=density, gm./cc.
T=temperature, °K
M=molecular weight
p=vapor pressure, mm. of Hg

For these calculations the vapor pressure at the melting point was assumed as:

4 x 10^2 for MgO
5 x 10^{-3} for Al_2O_3
1 x 10^{-1} for ZrO_2
6 x 10^{-3} for TiO_2

Another type of vaporization can occur if solids of varying stoichiometry may form, as for example, TiO_2. Careful control of oxygen pressures may prove essential in these cases.

It would appear that an oxygen atmosphere would be preferable to a vacuum for melting most of the oxides. Suitable pressures can be calculated for those oxides where reliable thermodynamic data are available. This has not been done to date, nor has any serious thought been given to compounds other than oxides.

Regarding consideration 3 listed earlier, it should not be assumed, without further study, that bubbles will indeed form during high vacuum space melting. There is a strong possibility that, at least for the gasses that evolve at lower pressures, the pressure of evaporation or decomposition will be found to be less than the internal pressure of the melt. If such turns out to be the case, the mechanism for evaporation might consist of diffusion to the surface of the melt, and evaporation from the surface. In that event, bubble formation would not occur. It should be possible to pretreat the starting material by vacuum heating to eliminate the more volatile gasses while the bulk of the material is solid. This should leave only those gas formers whose pressures are less than the internal pressure of the melt. In any event, the internal pressure in the melt can be raised by increasing the atmospheric pressure surrounding the melt, a condition readily accomplished in a chamber.

HEAT SOURCES

In the present study a number of possible heat sources for melting the materials of interest have been considered:

1. Chemical reactions
2. Plasma
3. Electron beam
4. Induction
5. The sun (solar furnace)

One of the more obvious problems that must be handled in the design of equipment for space melting is the propulsion effect. Such an effect is present in varying degrees in the first three heating methods. Perhaps this effect could be turned to advantage by simultaneously directing four torches, electron beams, etc., at the melt. This could be arranged by aiming the "torches" at the melt

from directions normal to the faces of an imaginary equilateral triangular pyramid (the melt being in the center of the pyramid). Special consideration would have to be given also to removal of the products of combustion in the case of the first two methods.

The first four methods above all share a significant drawback for space melting of large sized heats. The power requirements should exceed anything attempted in space to date by a significantly large margin. This naturally leads to the last heat source listed above, the sun. It would appear logical to directly utilize in space the unlimited energy available from the sun. The maximum temperature available by solar heating, approximately 5700 K[1], is more than ample for any of the materials of interest.

An example of solar furnace that might be utilized in space is pictured in FIGURE 4. The furnace shown is conceived as essentially an unmanned spacecraft incorporating a sun sensor which keeps the optical axis pointing toward the sun. Also incorporated are three detectors, which serve to keep the focus of the parabolic mirror centered on the melt (small sphere near the furnace). All sensors are servoed electronically to attitude control jets located on the periphery of the furnace. The antenna shown permits manual override of the automatic functions by personnel in the orbiting workshop (upper right background). Such a design should permit the furnace to "chase" the melt as it moves with respect to the orbiting workshop. By incorporating a radiation pyrometer, possibly as one of the melt sensors, it should be possible to automatically hold a pre-set temperature by focusing and defocusing with respect to the melt. The flat ring around the parabolic reflector holds solar cells used to provide secondary power. Not shown in the rendition is a pressure vessel with a suitable window for permitting entry of solar energy. Such a vessel could be attached to the solar furnace and would contain the melting atmosphere. It could be sized to permit reasonable movements of the melt without contact with the vessel walls.

Large parabolic mirrors of suitable quality for the purpose can be made by the spin-casting process. The orbit of the workshop, of course, would have to be chosen to provide sufficiently long duty cycles in the sun. Such high inclination orbits should not be a serious problem for missions whose prime purpose is melting of materials.

Perhaps induction furnaces are more appropriate for initial, small scale flight experiments where suitable orbits may not be chosen because of conflicts with other experiments and because of a desire to keep astronaut extravehicular activity to a minimum.

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[1]The apparent black body temperature of the sun.

A discussion of induction units for space melting of metals has been presented by Frost (Reference 26). Induction heating appears possible for the materials being considered, most of which are poor conductors at ordinary temperatures. The effect of temperature on the electrical resistivity of a number of oxides is shown in FIGURE 5. The curve for graphite, a known good susceptor, is shown for comparison purposes. It is also known that zirconium dioxide is a satisfactory susceptor, with resistivity values in the 10^{-1} to 10 ohm-cm range. With the possible exception of alumina and magnesia, all of the oxides shown fall into this range or below it at temperatures well below their melting points. It is therefore apparent that most of the oxides shown could be induction heated without a susceptor provided they were preheated, perhaps in a resistance furnace. In the event AL_2O_3, and MgO are found to be too high in resistivity to permit induction melting, it might be possible to dope them with small additions of other materials to lower their resistivity without seriously affecting their optical properties as glasses.

In FIGURE 6 are shown several possible schematic arrangements for a space induction melting concept which might be suitable for initial flight experiments on a small scale. FIGURES 6A, B, and C show different methods for transferring the material from the preheating furnace to the induction field, and after cooling, to the retrieval device. In FIGURE 6C the preheating furnace, induction furnace, and retrieval device are all fixed with respect to the chamber. The different locations of the melt are accomplished by shifting the chamber on a track to different positions which register with the desired positions with respect to the melt. In an alternate arrangement (not shown) the preheating furnace, induction furnace, and retrieval mechanism might all be attached to a track within the chamber and moved by a remote control mechamism.

As Frost (Reference 26) has pointed out, a centering force will be required to maintain the position of the melt while the workshop shifts with respect to the melt position, due to astronaut motions and orbit eccentricities. It appears likely that the small forces required could be provided by suitably utilizing the forces of the induction field. By the same token the arrangement suggested for the "nozzles" in the chemical, plasma, and electron beam concepts could provide the restorative force necessary.

CRYSTALLIZATION OF SPACE GLASSES

If we presume that experiments to produce supercooled glasses are successful, then another prospect of material production becomes evident. This additional prospect is that of producing single crystals of material either than cannot be produced otherwise or that would have improved physical properties. The proposed procedure would seem to have its principal merit with those materials that are polymorphic or those that are incongruently melting, for the reasons to be described later.

Suppose we consider the glasses that might be produced in a space station. The special feature of glass production in space is the lack of a crucible for containing a molten mass. In the absence of contact with any other solid material, the prospects for heterogeneous nucleation are eliminated, so that (it is theorized) it will be possible to produce substantial supercooling in materials that readily crystallize when heterogeneous nucleation is not avoided. Presuming that the supercooled material has been brought to a temperature low enough to prevent devitrification, we can now contemplate the prospect of controlled crystallization from a single point in the glass body.

An apparatus for accomplishing this is shown in Figure 7. The glass body is more or less balanced on the point of a seed crystal, with further balancing provided by air jets (air bearings). The air jets are to be precisely adjustable so that they can come very close to the surface of the glass but are kept out of actual contact by air pumped through the jet tips. Now, whereas the glass body requires the special provision of zero-G environment, the crystallization experiment takes advantage of terrestrial gravitational field in order to maintain a firm contact between the glass body and the seed crystal.

The phenomenon we wish to promote is that of controlled crystallization of the glass body, with crystallization initiating at the seed contact, and progressing slowly through the glass body. It probably will be necessary to maintain the system at an elevated temperature in order to permit crystallization to progress at acceptable rates.

A potentially troublesome aspect of the proposed procedure can arise from release of heat during crystallization. If the heat generated cannot be conducted away from the crystallizing front rapidly, both temperature and crystallization velocity will increase with

time, and this may lead to uncontrolled heating and crystallization. Experience certainly has demonstrated that material supercooled some few tens of degrees below the normal freezing temperature will crystallize very rapidly with a flash of luminescence when a seed is introduced. At much lower temperatures crystallization kinetics will be much slower, and presumably at some appropriate temperature crystallization rates will be controllable.

In a number of materials, certain physical properties prevent their being prepared in single crystal form. For example, ZrO_2 melts at a very high temperature, which makes it impractical to produce ZrO_2 by normal Czochralski techniques. Furthermore, ZrO_2 suffers a destructive phase change at 1100-1200°C. If ZrO_2 could be produced as a glass in an orbiting laboratory, we could contemplate conversion of the glass to crystalline form at a temperature below 1100°C, and thereby avoid the polymorphic transition. Beryllium oxide also suffers a polymorphic transition about 500°C below the melting temperature. There would be a real advantage, therefore, to be able to crystallize BeO from a glass body at a temperature below the transition temperature.

This crystallization process may be of value also in the formation of crystals whose composition melts incongruently. An example of this is beryllium silicate ($2BeO{:}SiO_2$, phenacite) whose decomposition point is about 1550°C. Crystals of this composition, therefore, are not amenable to being produced by Czochralski techniques. However, by crystallization from glass of the same composition, it may be feasible to prepare large crystals of compounds that exhibit incongruent melting. Another example is zircon ($ZrO_2{:}SiO_2$).

Throughout this discussion, no attempt has been made to identify materials that would have special economic or technological value. Such identification necessarily will require a more thorough investigation than has been done to date. The discussion, however, does point out some possible materials processes that potentially can expand the value of new glasses made in space.

CONCLUSIONS

Tentative conclusions based on the study conducted to date are:

1. There is a strong possibility that oxides such as Al_2O_3, ZrO_2, HfO_2, TiO_2, and others might be obtainable as glasses through space melting and cooling.

2. Glasses produced from such oxide bases would have optical properties not obtainable in the conventional silicate, borate, and phosphate-based glasses.

3. The combination of optical properties obtainable in such glasses should make them suitable for use in advanced optical systems, especially high resolution multi-element lens systems.

4. The spherical shape of glass boules that would result naturally from space production is quite suitable for the making of lenses and windows.

5. The production of glass, given a well-engineering space facility, should be well within the capabilities of astronauts after a suitable training period.

6. It may be possible to grow single crystals from glasses of suitable composition.

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It is not to be implied that by acknowledging the contributions of the people listed that any of them necessarily concurs with all the statements and conclusions drawn here.

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Table 1. Optical Properties of Some Oxides

Oxide	Structure	Ray	n_D	ν_D (calculated)	Source of Data
Al_2O_3	Rhombohedral (corundum)	ω ϵ	1.7686 1.7604	71.8 73.1	(Reference 3) (Reference 3)
CeO_2	Cubic (film, polycryst)		2.148	8-10	(Reference 4)
HfO_2	Monoclinic	α β, γ	2.070 2.146	37 44	(Reference 5) (Reference 5)
$MgAl_2O_4$	Cubic		1.72	63	(Reference 6)
MgO	Cubic		1.73790	54.3	(Reference 7)
Nb_2O_5	Unknown (film data)		2.258	8	(Reference 8)
Ta_2O_5	Unknown (film data)		2.091	23	(Reference 8)
TiO_2	Tetragonal (rutile)	ω ϵ	2.6124 2.8993	10.5 9.3	(Reference 3) (Reference 3)
	Unknown (film data)		2.657	9	(Reference 8)
ZnO	Hexagonal (zincite)	ω ϵ	2.013 2.029	15.8 14.9	(Reference 3)
ZrO_2	Monoclinic	α β γ	2.13 2.19 2.20	~5	(Reference 9)

Table II. Melting and "Boiling Points" of Some Oxides

Oxide	Melting Point, °C(T_m)	Boiling Point, °C(T_b)	Source of Information***** T_m	T_b
Al_2O_3	2050	2980	(18)	
BeO	2547	3787*	(18)	(18)
HfO_2	2897	~5400	(19)	
La_2O_3	2207	~2590**	(19)	(19)
MgO	2825	3260***		(18)
Nb_2O_5	1485-1512		(20, 21)	
SrO	2430	~3000		
Ta_2O_5	1875		(20, 21)	
TiO_2	1870	2500-3000	(18)	
ZnO	>1800	Subl. 1800		
ZrO_2	2675	4275****	(18)	(18)
SiO_2	1610	3273	(18)	(18)
B_2O_3	450	1500		
P_2O_5	570	Subl. 300		

*Listed T_b is temperature at which some of partial pressures of species in the vapor = 1 atm
**By extrapolation of the vapor pressure vs. temperature curve for the reaction, $La_2O_3 \rightarrow LaO+O_2$
***Temperature at which $\Delta F \rightleftharpoons O$ for $MgO(l) = MgO(g)$
****Temperature at which $\Delta F \rightleftharpoons O$ for $ZrO_2(l) = ZrO_2(g)$
*****References not listed are from The Handbook of Chemistry and Physics, various editions.

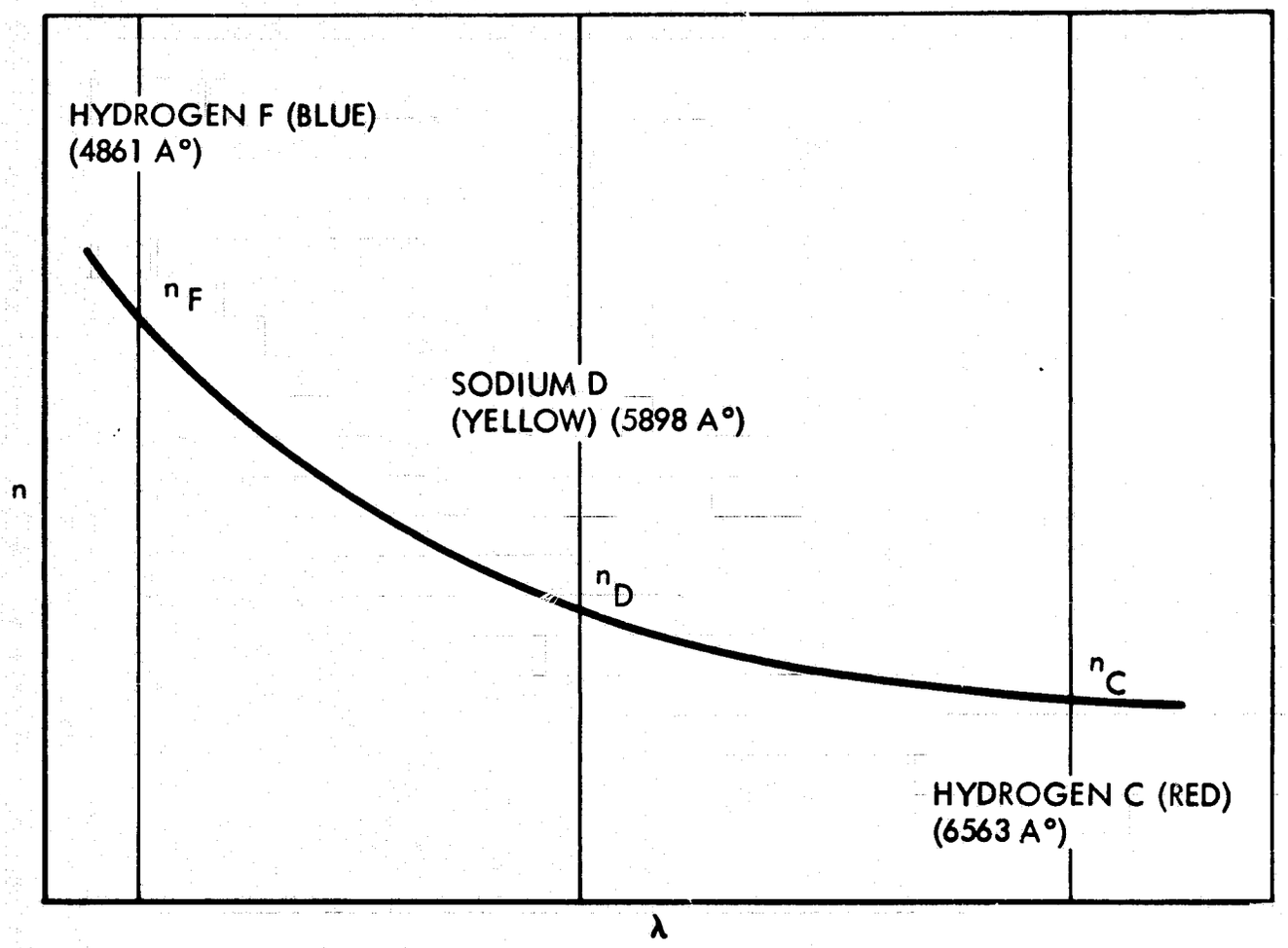


Figure 1. Schematic of a Typical n Vs. λ Curve

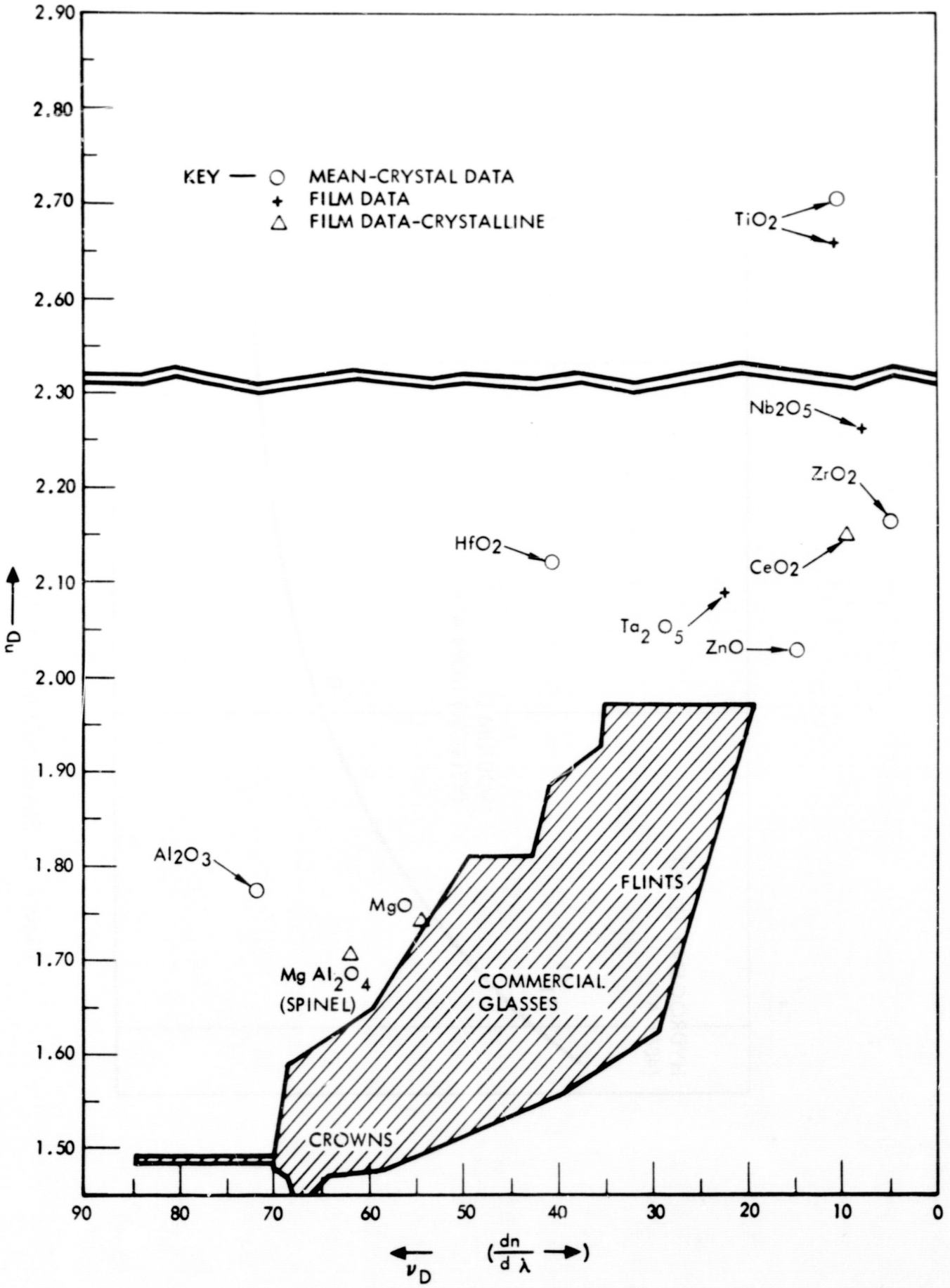


Figure 2. Refractive Index Vs. ABBE Numbers for Oxides

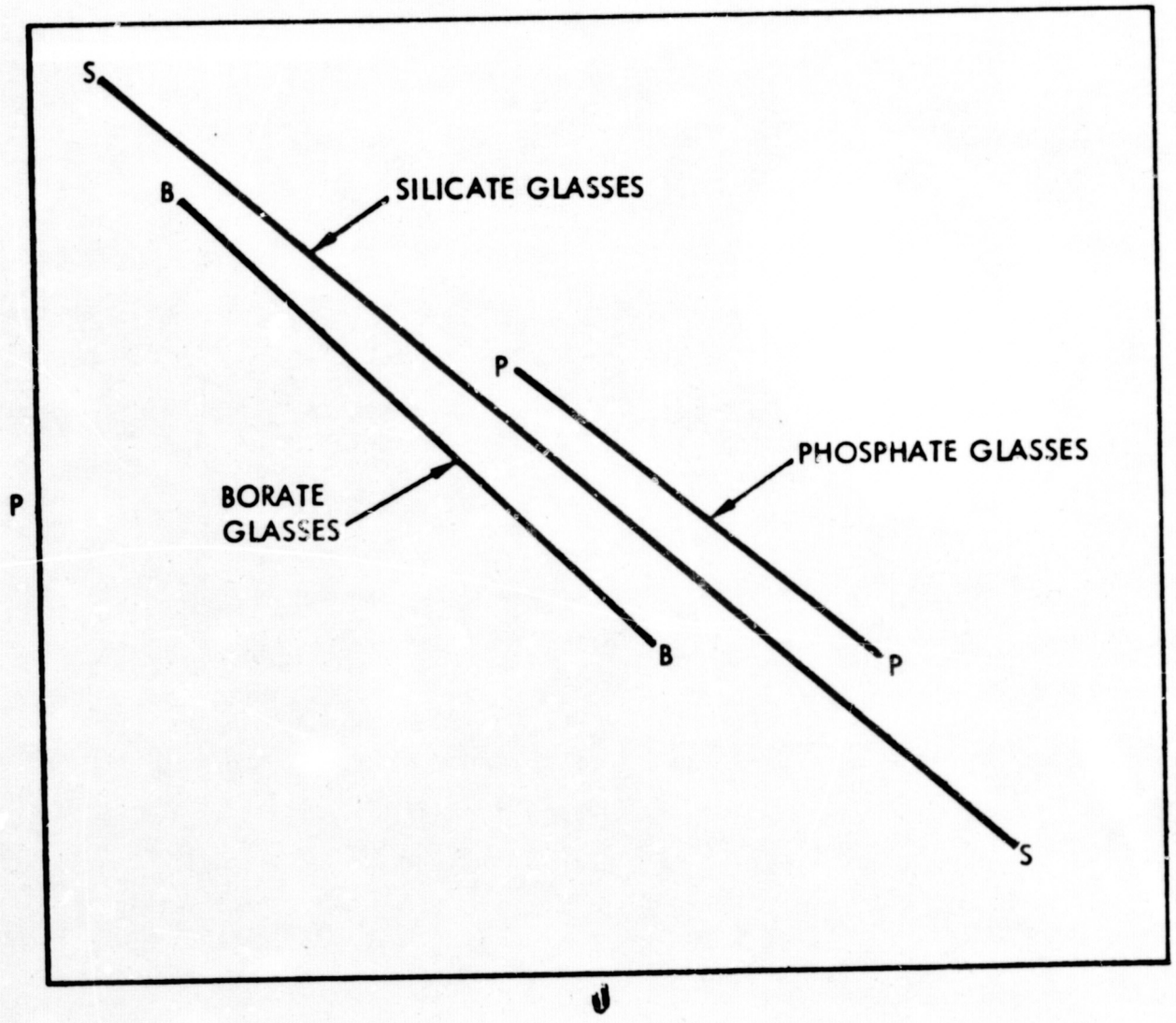


Figure 3. Schematic of a Partial Dispersion Vs. ABBE Number for Borate, Silicate and Phosphate Glasses

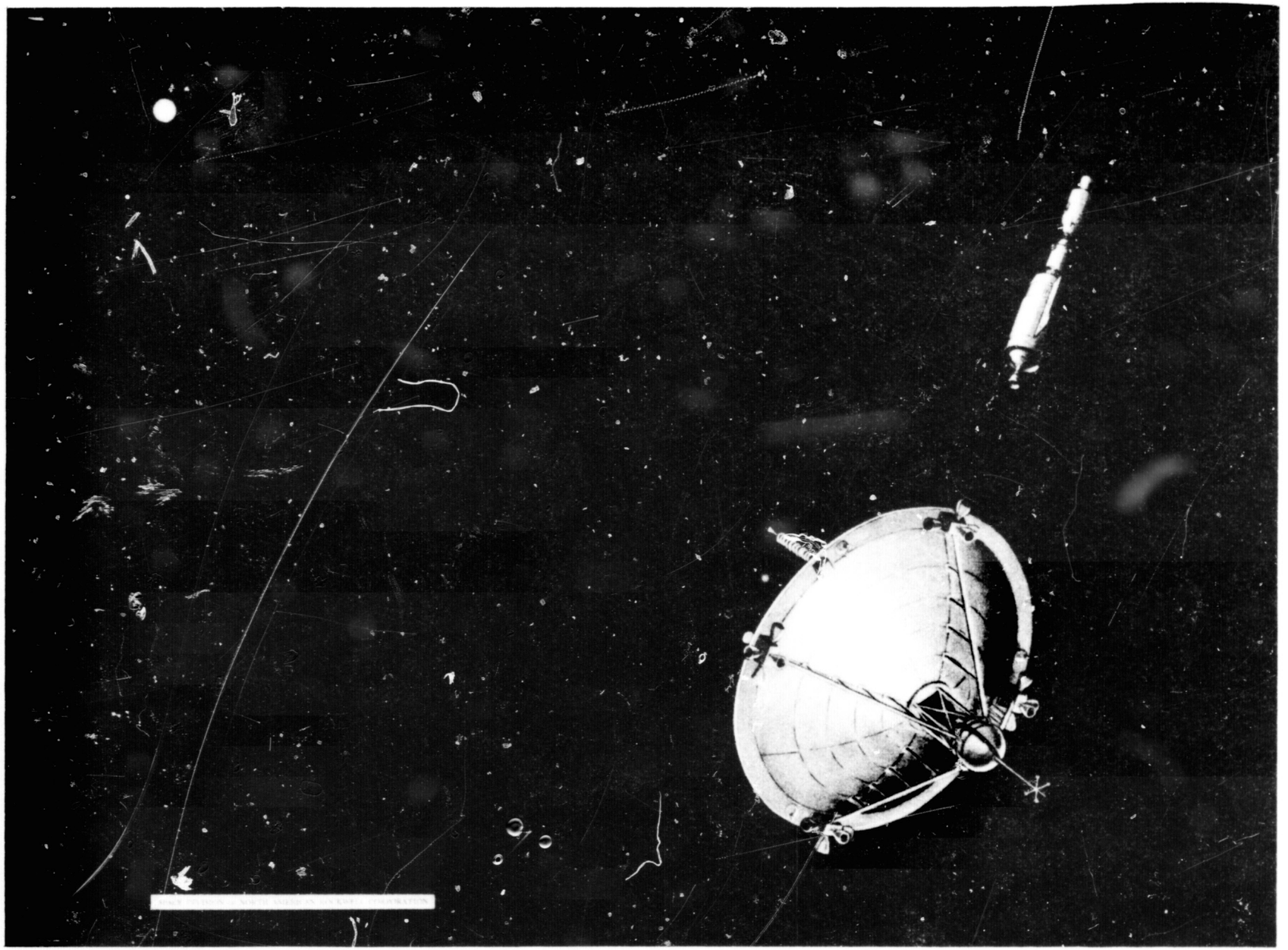


Figure 4. Concept of a Space Solar Furnace

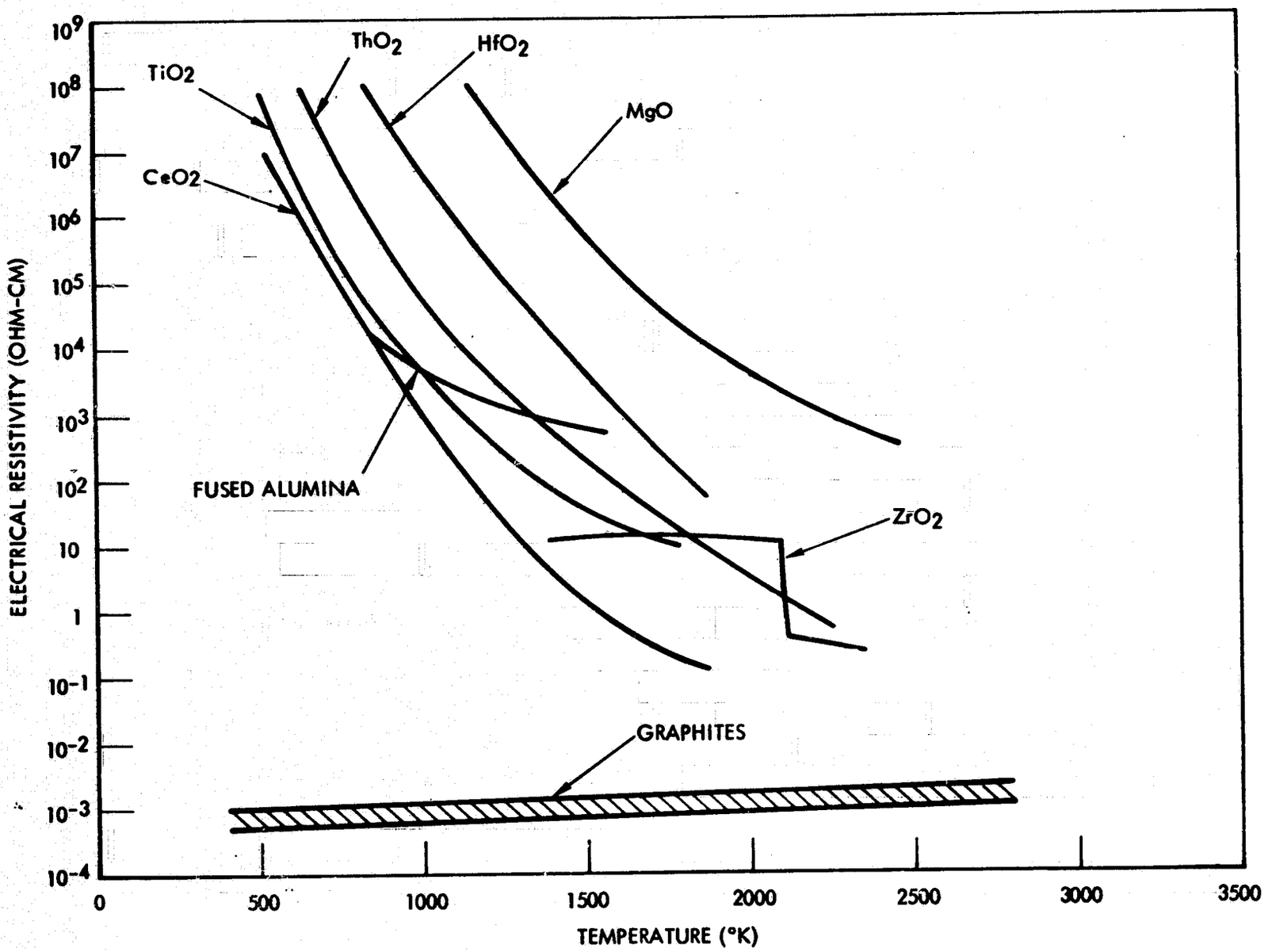


Figure 5. Electrical Resistivity as a Function of Temperature for Some Oxides and Graphite

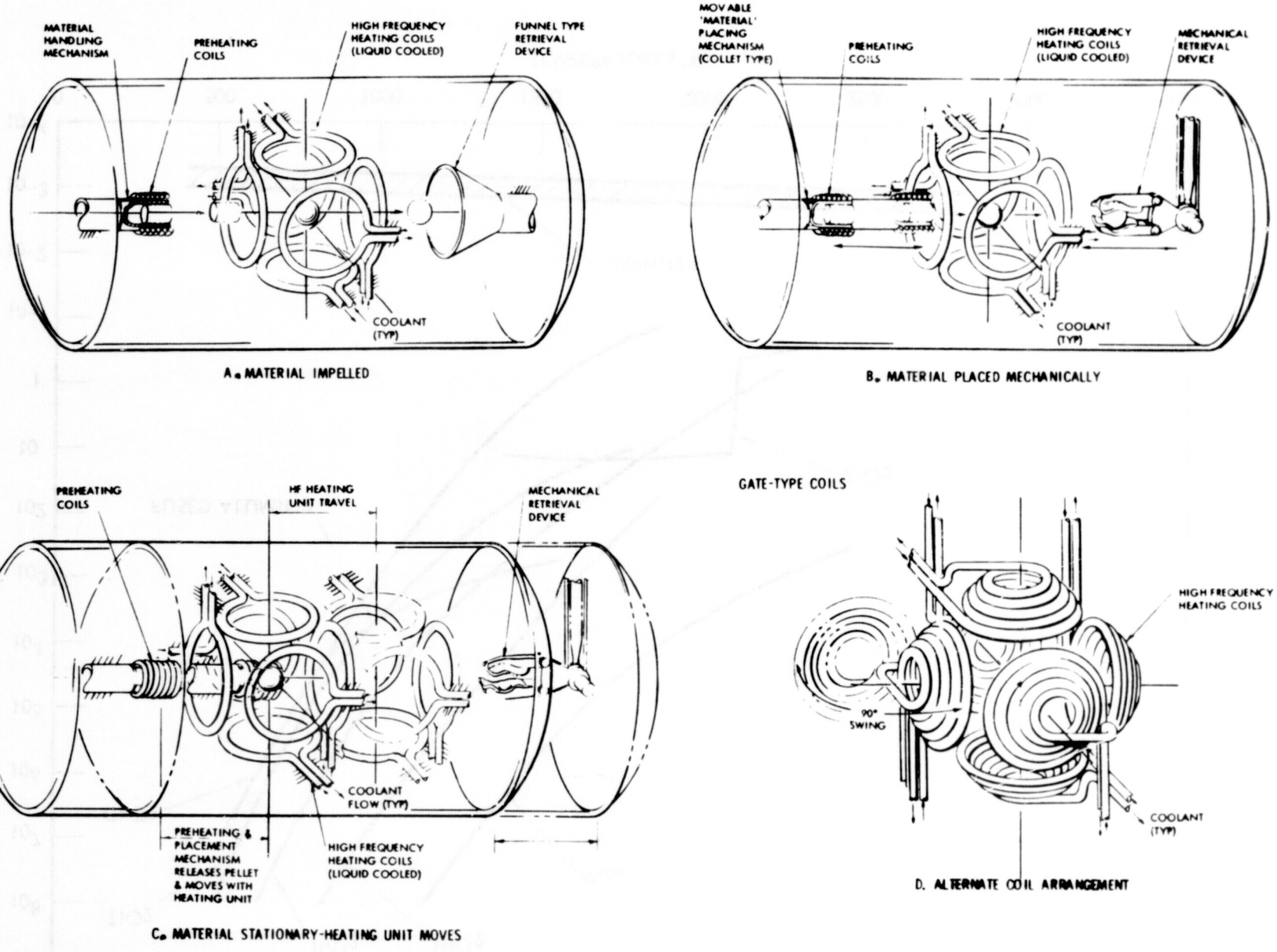
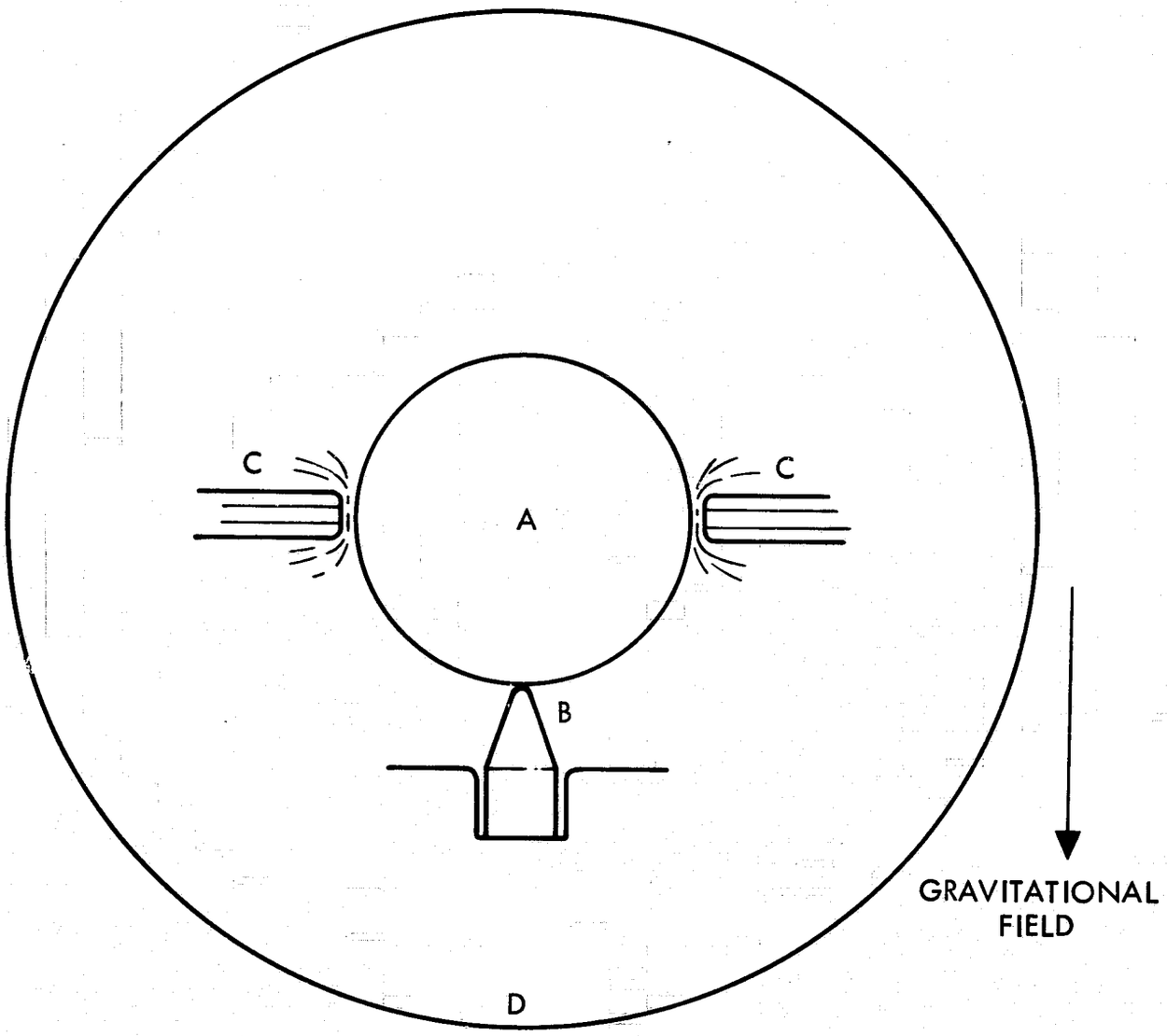


Figure 6. Zero G Induction Melting Concept



A GLASS BODY (SPHERE)

B SEED CRYSTAL

C AIR BEARINGS

D ISOTHERMAL ENCLOSURE

Figure 7. Shcematic of Apparatus for Growing Crystals from Glass

N70-20525

ALUMINUM AND ALUMINUM OXIDE IN ZERO GRAVITY

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ABSTRACT

An experiment is described to test the feasibility of using absence of gravity to mix immiscible materials. The mixing of aluminum oxide into molten aluminum has been chosen, as representative of the dispersing of immiscible solids into liquids. The equipment planned consists of a small self-contained furnace burning a Thermit mixture, which can handle some 100 grs. of metal. A gas operated stirrer will provide the mixing. One of two results is expected: 1. Mixing is successful. 2. Freezing produces separation. In either case, industrial exploitation is to be expected.

Since the beginning of time, men have tried to do things that are impossible. An idealist would call this the eternal striving of mankind toward a brighter future, a more down to earth person would see into it only man's basic inability to comprehend the laws of nature, but the fact remains that, given an insoluble problem, there is always some stubborn fool that will spend his lifetime on it and occasionally solve it in some fashion! One of these insoluble problems is mixing insoluble substances, that is, substances that are immiscible even in the liquid state. Probably the problem first arose when the ancient Greeks tried to make a salad dressing by mixing oil and vinegar, but through the ages the problem has remained unsolved: one still has to shake the bottle vigorously immediately before use.

Metallurgists have also encountered the problem: there are many metals that show interesting properties, when combined, but that are practically immiscible in the liquid state. An obvious example is lead, which imparts good machinability to most metals, but mixes only in limited amounts in them. When it comes to mixing nonmetallic compounds into metals the situation is even worse: the solubility of oxides, nitrides, etc., into metals often is measured in ppm. With vigorous stirring mixing can be accomplished, but it is not lasting. Within minutes or even seconds there is separation due to differences in specific gravity. Yet many products composed of mixtures of metals and compounds have outstanding (and unmatched) properties: dispersion strengthened metals, graphite-containing bearings, carbide cutting tools are some products of this type.

Some means have been found around the obstacle. Thus, we have powder metallurgy which avoids the liquid phase and relies upon mechanically mixed powders, and ultrasonic vibration to disperse solids in the liquids and keep them dispersed during freezing. Both methods are fairly successful for small size, but when large pieces have to be made, the equipment and power needs become impossible: one Kw of power can ultrasonically mix few grams of steel, but the equipment and power requirements to shake a 50-ton ladle of steel would dwarf a rocket to Mars.

This is the reason for the experiments planned. In absence of gravity there is no reason for two immiscible substances not to remain dispersed into each other once they have been thoroughly mixed. Most of us have seen pictures taken within spaceships showing droplets of liquid hanging in air. Why should not the same be true if the air is replaced by another liquid? If the two (or more) dispersed liquids are frozen, a solid should result with a free dispersion of one material into the other. This, of course, assumes that when the liquids freeze there is no pronounced segregation. Since most metals under normal conditions freeze dendritically, there is good reason to expect the dispersion to survive the freezing.

If for some unforeseen reason separation is achieved during the relatively rapid freezing that is planned, some very interesting possibilities appear. Separation of solids from liquids is a problem in the metallurgical industry, but much more so in the chemical industry. If filtration can be achieved just by freezing the liquid, decantation basins, filter presses and all similar equipment could be eliminated. It would be the equivalent of a zone refining operation in which the freezing front moves at the rate of feet per minute instead of the present inches per hour or per day! One outstanding feature of these two possibilities is that no matter how the experiment turns out, not only can we claim that it has been highly successful, but we can take pride in the fact that it worked exactly according to predictions!

The experiment planned involves the mixing of an insoluble solid into a liquid. The substances chosen are molten aluminum as liquid and Al_2O_3 as insoluble solid.

There are many reasons for this choice. First of all, Al_2O_3 is not wetted by aluminum even in vacuum so that we have a truly immiscible mixture. Aluminum is one of the few materials that has a relatively low melting point and very high boiling point so that when melted in the vacuum of space it does not evaporate into it: the oxide also has a very low vapor pressure and very high melting point so that even if the temperature control is far from accurate, there is no danger of melting it. No extra reaction can take place: the Al_2O_3 is very stable, whereas the suboxides Al_2O and AlO are unstable, as shown in Table 1 in which heats of formation are listed.

Table 1. Heats of Formation of Oxides

		Reference
Al_2O_3	400 kcal/gr. mole	(1)
Al_2O	250 kcal/gr. mole	(2)
AlO	97 kcal/gr. mole	(3)
	138 kcal/gr. mole	(2)
Fe_2O_3	196 kcal/gr. mole	(1)

(1) L. S. Darken, R. W. Gurry, Physical Chemistry of Metals, McGraw Hill, 1953.

(2) L. Brewer, A. W. Searcy, J. Am. Chem. Soc., 1951, 73, 5308.

(3) E. Zintl and Coll., Z. Anorg. Allg. Chem., 1940, 245, 8.

Aluminum can be melted in graphite crucibles without contamination, and Al_2O_3 does not react to any appreciable extent with graphite at temperatures below 900°C. Thus no reactions with crucible material are to be expected and the crucible will not volatilize. Both aluminum and aluminum oxide have low density, thus reducing the weight of the experiment. Last, but not least, Revere is in the aluminum business and I have worked with it most of my life.

Fig. 1 shows a section through the planned set-up. As can be seen, there is a crucible with cover containing the metal to be melted and an area around it in which the fuel will be burned. As fuel a Thermit mixture will be used, to be ignited by a resistance. An insulating brick shell will surround the fuel zone to reverberate as much of the heat as possible to the crucible. Some preliminary calculations based on heats of reaction and fusion indicate that an amount of fuel of the same weight as the metal to be melted will be more than sufficient. This, however, is a very rough calculation with a figure for the heat transfer efficiency of 20%, which was picked out of thin air.

Before the actual experiment goes in space some trials will be run in vacuum and from the actual temperature reached in the metal, fuel quantity will be adjusted so that the metal inside the crucible melts for the few minutes required to stir the oxide into the melt before it freezes.

Above the crucible and its covers is the stirrer to rotate the stirring rod when the metal is molten. A gas stirrer has been chosen for several reasons: It is much lighter than an electric motor, it operates out of any compressed gas and is a standard item off the shelf. The most important reason for the choice, however, is that perfect timing is not needed. The gas can be turned on when ignition is started and even if it is on when the metal is frozen there will be no damage. If the stirring rod is not free, the stirrer does not rotate, but does not burn out or break the rod as would be the case for an electric motor. Actually it is planned to stop the stirring before freezing starts, either by turning off the gas or by supplying only the amount of gas sufficient for few minutes stirring. However, since the timing that applies on earth may not be valid in space, some extra safety is valuable.

One spot which may be critical and on which suggestions are welcome is the hole where the stirring rod enters the crucible. The amount of metal in the crucible will be such that the crucible is completely full with melt and oxide so as to reduce the formation of metal shot. Under gravity conditions the metal can be trusted to stay into the crucible, but in zero gravity it will be necessary to have a close fit between the rod and the graphite cover to insure against leakage. We are now building the whole assembly and plan to test it upside down in the hope

that the melt will not flow around the graphite stirrer, freeze against the steel shell and gum up the works. Around the crucible and the insulations there is a stainless steel shell with clamped on cover and everything will be inside a closed container of stainless steel so that even if something goes wrong and molten metal escapes from the crucible, it does not float out into the module and burn something.

As can be seen the experiment is relatively simple and does not need elaborate equipment. However, a great wealth of information can be expected from it. As mentioned before, if the mixing is successful a wide range of possibilities is open: many materials that today are used only in small articles because they are not avilable in large quantities may become commonplace. For example, the mixtures of aluminum and aluminum oxide have outstanding high temperature properties, but since they have to be fabricated by mixing aluminum powder and extruding it, they are available only as small rods or plates. If a 10-ton ingot of the mixture could be cast in space and then rolled on earth, a good part of the titanium sheet in supersonic planes could be replaced by aluminum with a decided saving in weight.

Fiber reinforced metals are another type of product which has outstanding possibilities and for which zero gravity may make an enormous difference. On earth, production of three dimensional structures is almost impossible, but in zero gravity it is no problem to build a three dimensional lattice of reinforcing fibers and then pour the bonding metal around and let it freeze. This experiment will also give information on the feasibility of this process. If it is found that little or no displacement of the immiscible solid takes place during freezing of the liquid, the making of fiber reinforced parts with tridimensional reinforcement becomes a relatively simple process. There are many more examples that can be mentioned. Moreover, if the process becomes commercial, many more applications will be found, that at present we cannot even imagine.

In addition to the main goal of establishing whether immiscible materials can be dispersed into each other in zero gravity or whether zero gravity can be used for separation, other information can be expected from this experiment. Solidification of metals on earth is always affected by convection currents that mix metal. What pattern of freezing and segregation can be expected in the absence of convection currents? Will segregation be more pronounced, will the mode of freezing be drastically altered, will the grain size be much different? I understand that other people have experiments on these questions; it will be interesting to compare results and see how many different interpretations can be given to the experimental data.

After this experiment is completed the next step depends a great deal on what the results are. If mixing is successful, then the obvious next steps are other immiscible materials and a larger size one to yield a casting that can be worked to sheet or rod and fabricated into experimental products. The large experiment should make a 5-10 lb. casting. The smaller experiments should be of the same size as the present one and planned to test one or more of the following products: fiber reinforced materials, graphite or lead-containing metal, hard particles dispersed into ductile metal, metal bonded fiberglass. Probably other combinations may become interesting. If instead of mixing, separation is achieved, the limits of the process should be explored. Several small experiments with different materials and conditions should be tried. This would require at least four or five separate experiments, all small scale.

In all these experiments the main limitation would be space available and weight. The other limitation: heat, is basically one of weight: given enough fuel it is no problem to melt not only the metal for the experiment, but the orbital workship itself. Some tricky engineering may also be needed to design the equipment for the experiments, but I am sure that this is not an unsurmountable problem.

Altogether, I am looking forward to the day when this experiment will come back from space and I am very hopeful that this and other research will be successful, so that the program of space can continue at full speed. I feel that the work done here is among the most important for mankind, not because of the improved products that may come from this research program, but because only in space we will find a frontier.

I definitely think that when we can open space to colonization most of the present unrest and conflict will subside and that many people will be able to find in other planets the satisfaction and happiness that they cannot find in their present environment. In my opinion space exploration is more important to world peace than all the disarmament conferences and I hope that my modest contribution to the program can be of help.

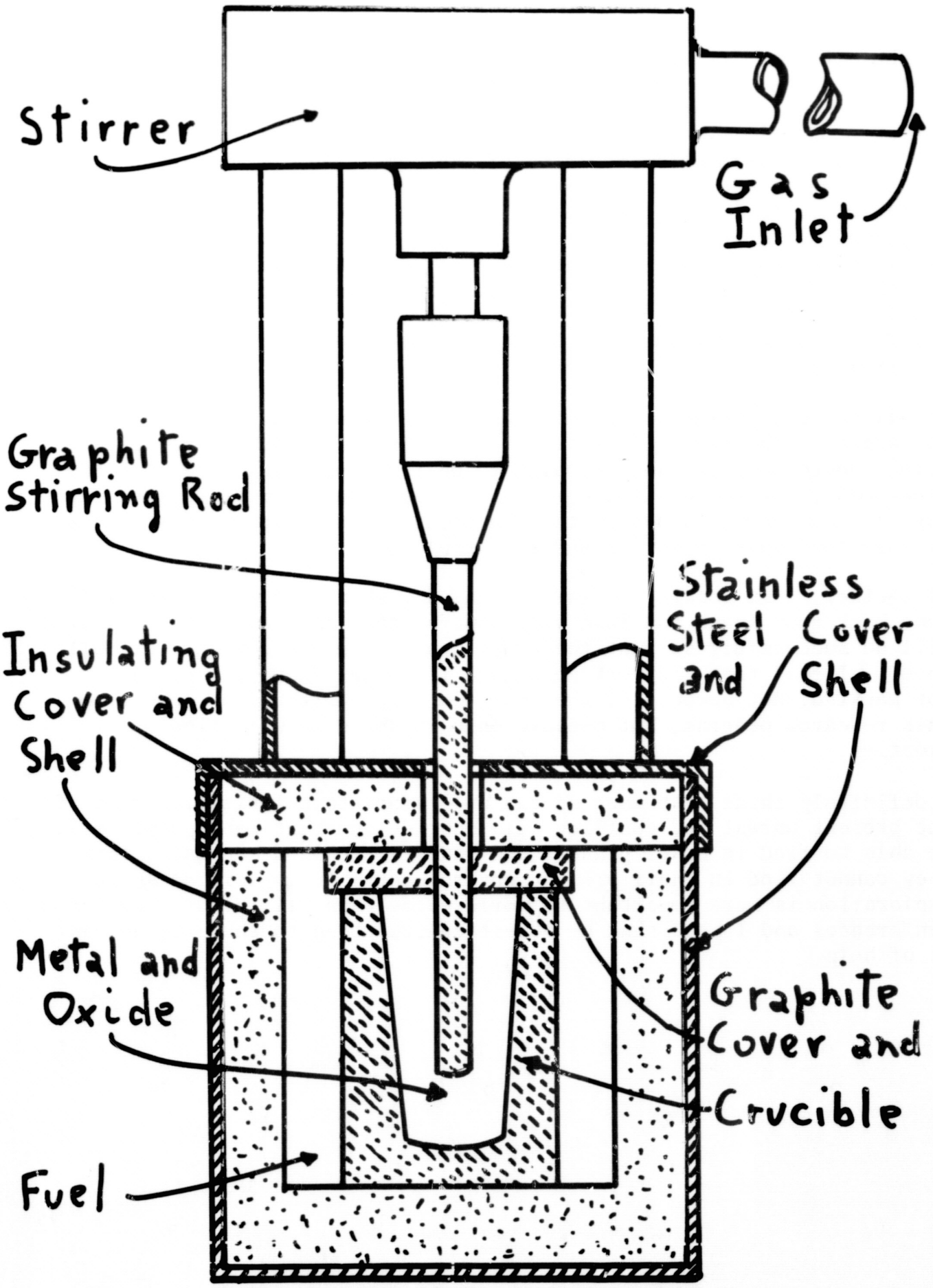

Stirrer
Gas Inlet
Graphite Stirring Rod
Stainless Steel Cover and Shell
Insulating Cover and Shell
Metal and Oxide
Graphite Cover and Crucible
Fuel

Figure 1

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REDUCED GRAVITY PROCESSING OF HOMOGENIZED IMMISCIBLE METAL ALLOYS

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ABSTRACT

Reduced gravity material experiments to process and prepare unique metal alloy systems from normally immiscible liquid phase melts are described. The study of this previously unclassified group of materials is considered from several aspects. The effects of low gravity environment on the observed immiscibility limits of two phase liquid combinations are considered. Included are discussions of homogenized alloy processing covering production of materials with unique physical and electrical properties, consideration of basic solidification processes, and the potential application of homogenized alloys in the preparation of composite materials.

Potential experiment performance limitations, requirements and interface criteria are identified. These considerations will include both phenomenological materials behavior and the practical experiment software, hardware and astronaut interfaces. Requirements for experiment development and pre and post orbital test are also considered.

INTRODUCTION

The logical starting point in the study and development of any alloy system is the establishment and utilization of the equilibrium phase diagram. Excluding the high temperature metastable phases, most binary and pseudobinary systems can be represented schematically by three general types of phase diagrams: complete solid solubility, Figure 1; partial solid solubility, Figure 2; and formation of an intermediate

phase, Figure 3. The high temperature metastable phases, often used in specialized alloys, are usually achieved by cooling the alloy at a high enough rate to retain the metastable phase at lower temperatures, thus allowing subsequent heat treatment to modify the alloy and achieve the desired physical properties. Some of these techniques, and their potential applicability to these experiments will be described later.

Almost no attention has been given to the study and development of alloys based upon components which exhibit a liquid phase immiscibility. This is directly a reflection of the inability to form alloys from these systems. Figure 4 illustrates a typical two component system which exhibits a liquid phase miscibility gap, and Table 1 is a partial list of such binary systems showing liquid phase immiscibility. The phase line separating the homogeneous single liquid from the two phase liquid region is defined as the consulate temperature line and indicates the variation of composition with temperature. Above the consulate temperature line, T_c, the liquid phase consists of a single homogeneous solution of components A and B. The function W_a, "Work of adhesion" is defined as $W_a=\sigma A+\sigma B-\sigma AB$ (reference 1) where σ_A is the surface tension of liquid A, σ_B is the surface tension of liquid B, and σ_{AB} is the interfacial tension between the mutually saturated liquids A and B. This function is used in an attempt to define the structure of phase boundries. If W_a is large, σ_{AB} is small and the liquids are miscible. For small values of W_a, σ_{AB} is large and the liquids are immiscible. Since the surface tension of a pure liquid is a function of the temperature, and decreases with increase in temperature, then at some elevated temperature, the surface tensions of the two components will become approximately equal and the liquids will be miscible. For a number of actual systems, however, this temperature is sufficiently high such that one (or both) of the components have an appreciable vapor pressure which can lead to compositional variations or void formation in the alloy after solidification.

Conversely, alloy compositions having a consulate temperature in the liquid state with little or no vapor present will still segregate into two immiscible liquids as the melt is cooled. Thus in both cases, the alloy composition will traverse the immiscibility region during cooling. Further lowering of the temperature produces a liquid-solid mixture and ultimately a complete solid mixture of saturated components A and B. Due to any density difference between A and B, separation of phases of the liquid mixture is enhanced, and the solid mixture is thus segregated and of little value as an alloy. The major effects which dominate the solidification of immiscible liquid mixtures of this type are the surface tension and interfacial energy, and the gravitational separation of phases due to density differences. If these interactions could be modified, or sufficiently reduced, a new class of alloys could potentially be produced.

This can be demonstrated by examination of the Bond number for two immiscible liquids, obtained by a variation of the equations derived by Reynolds and Satterlee (reference 2). The Bond number compares the relative magnitudes of gravitational and capillary or surface tension forces, and is used as the parameter for delineating capillary-dominating or gravity dominating hydrostatics. For two immiscible fluids, the Bond number Bo approximates $Bo \simeq \frac{(\rho_A - \rho_B)\, r^2\, g}{2\, \sigma_{AB}}$

where: ρ = density of liquid A or B
r = radius of curvature between liquid A and liquid B
g = local acceleration in the gravitational field
σ_{AB} = interfacial tension between liquid A and liquid B

For values of Bo greater than 1, the gravitational force predominates, and for Bo less than 1, the capillary (or surface tension) forces predominate. Thus in a near zero gravity environment, the Bond number is less than one, and the system will be dominated by surface energy considerations. Depending upon the kinetics of the surface driving force to cause phase separation, it may be possible in a variety of immiscible alloy systems to produce homogenized alloys from the melt.

REDUCED GRAVITY PROCESSING OF HOMOGENIZED ALLOYS

The previous discussion dealt with equilibrium phase diagrams as measured in the earth's gravitational field. In the absence of the gravitational field, the phase diagrams possessing a liquid miscibility gap may change in that the position of the upper consulate line and the position of the solvous lines are sensitive to gravitational effects. The change in head pressure due to the near zero gravity conditions may effect the consulate temperature (reference 3), thus the original assumption that the surface tension forces will predominate as the driving force for phase separation appears to be valid. As the melt traverses the immiscibility region, appearance of the two components will occur, and the resultant surface tension dominated two phase liquid may take the form of a continuum liquid of the component having the lower surface tension with the other component finely dispersed throughout. For the melt to be stable in this region, the dispersed phase must be finely divided so that droplet growth will not occur (reference 4). Thus the melt should be in the form of an emulsion, and subsequent cooling will result in a fine grain homogenized alloy which may be crystalline or amorphous. If the alloy processing is initiated within the immiscibility region, rather than above the consulate line, then the requirement for homogenization in the solid phase region is that the melted component having the highest surface tension must be dispersed throughout the remaining component liquid phase in the form of finely divided liquid

droplets. With the assumption that these homogenized alloys are feasible to produce in a near-zero gravity environment, such alloys may offer a large area of potential usefulness in terms of their unique behavior, as discussed by the following examples.

Potential Extrinsic Semiconductor Alloy

Gallium arsenide, produced on earth, is a III-V compound semiconductor. It is finding usage as light emitting diodes, and is being developed for solid state microwave sources such as Gunn effect avalanche diodes or LSA (limited space charge accumulation) devices. The system gallium bismuth exhibits a liquid miscibility gap, and homogeneous alloys of these elements cannot be produced on earth. Since bismuth is in the same period as arsenic, a homogenized alloy of GaBi might exhibit extrinsic compound semiconducting qualities similar to gallium arsenide if it could be prepared in a manner to promote compound formation. An example of immiscible liquids which result in intermetallic compound formation at lower temperatures is found in the iron-tin system; it may therefore be possible to process an immiscible combination such as gallium and bismuth into atomically homogenized alloys, thereby promoting the interatomic bonding exhibited by the III-V semiconductor compound class.

Solid Lubricants

Copper-lead alloys have become commercially important as aircraft and automotive bearing materials. Although the copper-lead system has a liquid immiscibility gap, alloys of copper and lead containing up to about 30 weight percent lead can be produced without crossing the region of temperature and composition where the phase immiscibility occurs. The lubricating qualities of these alloys, however, increases with the lead content and therefore alloy compositions with a lead concentration of greater than 30 weight percent may be quite important. In the near-zero gravity environment, homogenized alloys containing almost any concentration of lead should be possible to be produced.

Directionally Solidified Composites

Directionally solidified composites as manufactured on earth are actually a binary eutectic reaction involving the transformation of a single liquid phase into two solid phases at a constant temperature. The reaction is invarient because it occurs in a system only when each of the three phases has a specific composition and at only one temperature. Thus, the "classical" type of directionally solidified eutectic composites would not benefit from a near-zero g environment. However, if one utilizes the homogeneous alloy concept, and maintained a unidirectional thermal gradient during solidification, the system is no longer invarient and the process can occur over a range of compositions within the immiscible region of the system. An example would

be the iron-lead system. If the molten iron-lead mixture is allowed to directionally solidify, it may be possible to produce single crystal fibers of iron directionally solidified in lead. Such a composite should have unique magnetic properties, as is the case with the directionally solidified Fe-FeS eutectic composite. Additionally, since the compositional range of the system can be varied, it should be possible to produce composite material having an extremely uniform microstructure phase spacing and alloy compositions which are not possible with eutectic alloy systems.

Alloys of Metals With Other Non-metallic Species

The homogenized alloy process is not necessarily limited to all metal systems. Any binary or pseudobinary system which exhibit a liquid miscibility gap should be capable of forming a homogenized alloy. Thus, mixtures of metals with metal oxides, carbides, nitrides, etc. are potential candidates for the homogenized alloy concept. Such alloys have the potential of producing unique cermet-like materials with structural and electronic applications.

In summary, the concept of homogenized alloys provides a basis for not only creating potentially unique materials, but will also contribute to the basic general understanding of gravitation effects on both liquid and solid alloy phases.

EXPERIMENTAL CRITERIA

The potential opportunity and possible types of homogenized alloys that may be processed in space in a near zero gravity environment has been outlined in the previous discussions. While these suggestions provide a basis for optimism in ultimately developing rewarding achievements, it is clear that a carefully designed experimental program to explore and develop these space manufacturing experiments will be required. Since the Orbital Workship is a closed ecological environment, and many types of experiments are planned, consideration of the interactions of the proposed homogenized alloy processing experiments with respect to the other experiments and the Orbital Workshop itself is necessary. These considerations consist of:

- Experiment Definition and Development
- Logistics Support Requirements for the Experiment Implementation
- Manned Interfaces

Experiment Definition and Development

This phase of the experimental criteria will consist of preorbital tests, astronaut interface considerations, and post orbital tests.

The preorbital tests should include a quantitative examination of the role of gravity (reduced gravity) on the phenomenological behavior of materials in the liquid state, and experimental attempts to produce small samples of homogenized alloys. The examination of the role of gravity should be based on both theoretical considerations, and modeling experiments with pairs of fluids having varying degrees of immiscibility and density gradients with respect to one another. In this manner, the interactions of density, surface tension and gravity can be estimated and correlated to the actual processing procedures necessary for the orbital experiments.

The preorbital experimental attempts to produce homogenized alloys should utilize the present procedures for obtaining metastable phases of alloys: rapid quenching from the liquid state ("splat cooling") (reference 5), and plasma-arc spraying or codeposition from the vapor phase onto a cooled substrate (reference 6). The splat cooling technique, particularly the levitation melt-shock tube ejection apparatus (reference 7), appears to be the most logical experimental method, since cooling rates on the order of 10^{6}°C/sec from the liquid to the solid state are achievable by this technique, thereby minimizing gravitational interactions during the liquid-solid transition. Although these methods produce relatively small samples, preliminary information can be obtained from examination of the types of materials likely to be obtained from the space manufacturing processes.

Consideration of the astronaut interface includes both the degree of involvement of the astronaut during the experiment, and the amount of subjective and/or objective judgment necessary for the astronaut to conclude if the experiment was a success or should be repeated, either under the same conditions or by varying experimental parameters. The interface should be minimal in all respects, in that the preorbital tests should delineate the processing parameters (temperatures, cooling rates, etc.), and the actual astronaut participation during the experiment be compatible with the other experiments on board, i.e., about the same involvement as would be required to cast a sphere or produce single crystals or glassy melts.

The post orbital alloy evaluation tests would be carried out on earth, and would consist of those measurements germane to the homogenized alloy produced: comprehensive metallurgical examination coupled with more detailed tests such as physical or electrical measurements. The results of these tests would then be correlated with the preorbital tests and the observations of the astronaut, and an evaluation of the feasibility of further homogenized alloy processing in space could then be carried out.

Logistics Support Requirements for the Experiment Implementation

The primary consideration of the logistics support requirements are that they are compatible with other processing experiments on board the Orbital Workshop. The compatibility requirements are power, thermal-temperature considerations, volume-weight considerations, and commonality of the processing hardware.

The basic process requirements for production of homogenized alloys are that the binary mixture be heated into the liquid state, held for a period of time at temperature, and then cooled to the solid state at some rate of cooling. The ancillary requirements are position control, thermal transfer or heating or cooling from the melt, and atmospheric control within the basic heating facility.

All of these requirements are common to the processing experiments which involve bulk melting of materials. The power requirement is dependent upon the sensible heat required to raise the materials to the melting point(s), the latent heats of fusion, and the excess energy to bring the melt to the proper liquidus temperature. Since relatively small quantities (0.1 to 1.0 kg) of bulk homogenized alloy, returned to earth, would be sufficient for laboratory examination and correlation of previous preorbital investigations, then the total logistics support requirements for the space manufacturing experiment package for processing homogenized alloys could be modeled to be compatible with the facility designed for the other experiments involving melting and/or casting processes. Assuming that the original processing experiments were successful, these same requirements would hold for successively larger amounts of homogenized alloys produced in larger Orbital Workshop space stations scheduled for future flights.

One exception to the above discussion would be the production of directionally solidified composites of homogenized alloys. In this particular process experiment, there is a need for a directional thermal gradient and the potential need for controlled nucleation sites. Thus, while the main logistics support is similar for the other processes, additional constraints are added in that the thermal control during solidification must be modified such that a thermal gradient force is imposed, and the solidification process will probably occur with the melt in contact with a solid support surface to provide directional nucleation growth sites for the homogenous composite. These facilities may be available for certain submerged liquid crystallization processes, and thus the commonality of the facilities is preserved. If such facilities are not available, the preorbital tests of nucleation processes as demonstrated by Linde (reference 8) and Duwez, et al (reference 9) should give an indication of the facilities and process conditions necessary for combinations of these experiments in future space flights.

Manned Interfaces

This aspect of the space manufacturing of homogenized alloys is based upon the evaluation of the design of the equipment and procedures to support the astronaut worker in terms of human factors requirements and safety.

The human factors requirements for the process should be evaluated in terms of the design of equipment and procedures. Weight, complexity, and development status of such support equipment should be evaluated against frequency of usage and operating feasibility. Since a number of the proposed space manufacturing processes utilize similar facilities, the equipment must be based on standardization and generalization principles, with multipurpose tools and equipment favored over highly specialized ones, and provisions for restraint and locomotion during the processing periods to be given priority. Since a number of manufacturing processes have commonality, the design of such equipment and procedures should be compatible with the homogenized alloy process concept.

The safety aspect of space manufacturing processes must be evaluated in terms of safety to the astronaut under "worst case" conditions. This applies to all space manufacturing processes, and as such, each process must be analyzed and developed such that all equipment and processes will at all times be oriented toward maximum operating reliability and safety. Again, because of the commonality of the homogenized alloy process with other experiments, this consideration should be amenable to solution by evaluation of the various process requirements, and thus be a basis for evaluation and design of all equipment and facilities for these processes.

CONCLUSION

This paper has described the concept of processing homogenized alloy systems. An essential portion of this proposed program is to clearly identify the interactions between the materials experiment definition, the processing equipment/facility to implement the experiment, and the astronaut/worker requirements to obtain an experimental process result. Each of these interactions are summarized below.

Preliminary Experiment Definition

The preliminary experiment definition requires the utilization of preorbital tests in order to supplement theoretical considerations of near zero gravity processing of homogenized alloys. These evaluations include model immiscible liquid studies to evaluate density, surface tension, and thermodynamic limitations, in order to determine those which may be of value to pursue further in a near zero g environment and rapid quench cooling studies to establish physical properties of meritorious interest.

Examination of post orbital evaluation techniques are also necessary in order to determine if the near zero gravity processing has produced a unique and potentially valuable material. These evaluations will include both conventional and phenomenological behavioral characterizations to establish the uniqueness of the materials produced.

Implementation of the Processing Equipment and Facility

The development of the processing equipment and the facility must be coordinated with the overall experimental processing program in the Orbital Workshop. This development requires a close coupling of the materials science definition activity to the engineering constraints of equipment performance capabilities and process scheduling. If a homogenized alloy process, for example, requires a high temperature capability, then this requirement must be assessed against the total experimental processes to be performed, the available equipment, and the relative value of the potential returns to be gained by the experiment.

Astronaut/Worker Requirements

Pertinent consideration must be given to the astronaut skills and training requirements. Orbital process work schedules and real time evaluation criteria must be established. Overall care must be taken to assure safety in the materials selection, process schedules and facility design.

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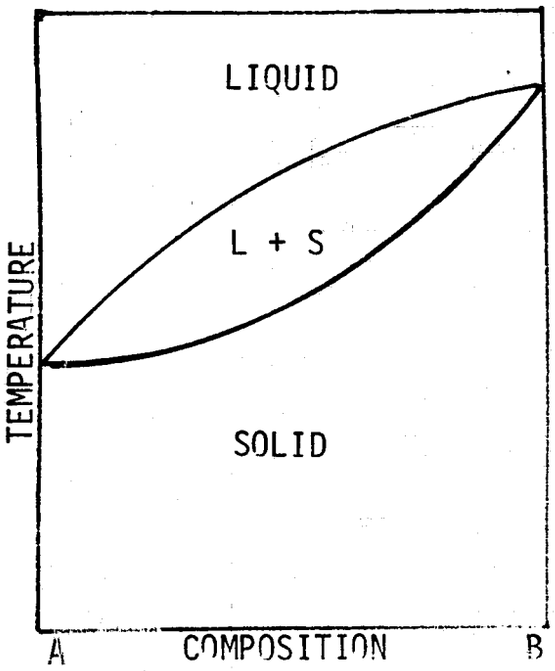


Figure 1
Complete Solid
Solubility

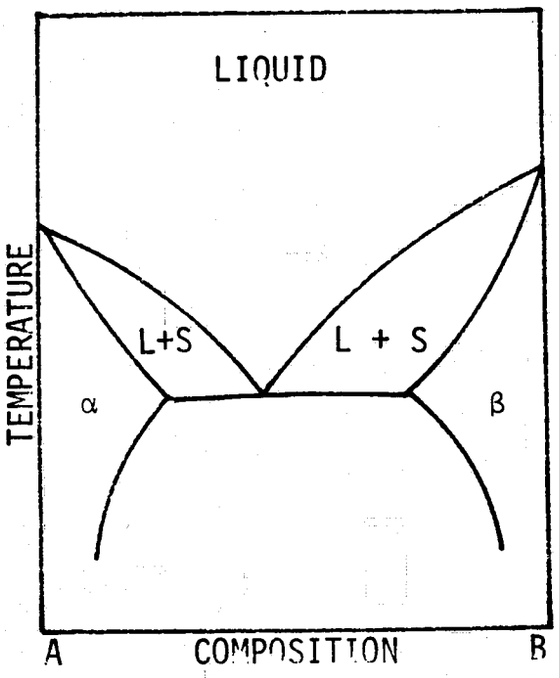


Figure 2
Partial Solid
Solubility

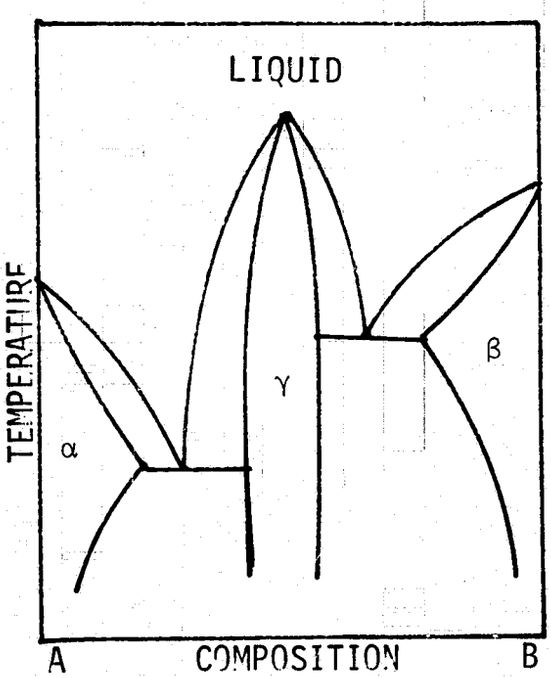


Figure 3
Presence of an
Intermediate Phase

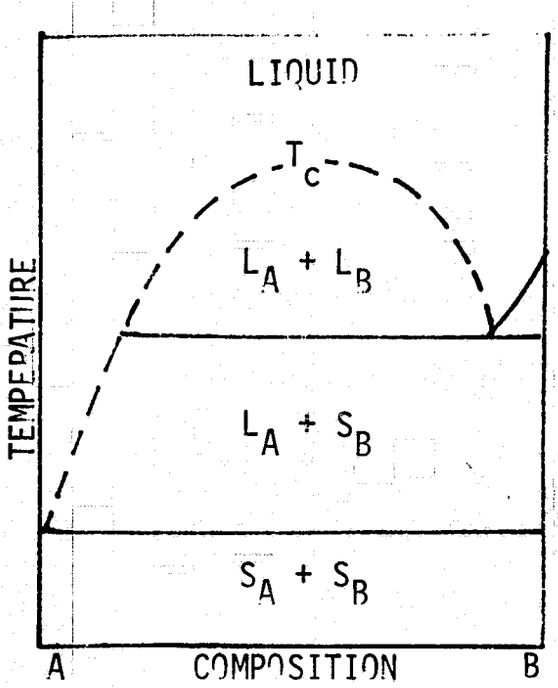


Figure 4
Presence of a Miscibility
Gap in the Liquid Phase

TABLE 1. Some Binary Alloy Systems Which Exhibit Liquid Phase Immiscibility

AgCr	BeGa	CoPb	GaHg	NaZn
AgMn	BeIn	CoSe	GaK	
AgNi	BeSn		GaPb	NiPb
AgRh		CrCu	GaTl	NiTl
AgS	BiCo	CrGd		
AgSe	BiCr	CrLa	InS	PbSi
AgTe	BiFe	CrPb		PbU
AgU	BiGa	CrS	KPb	PbZn
AgW	BiMn	CrSn	KZn	
	BiSi			PPt
AlBi	BiU	CuPb	LaMn	PTl
AlCd		CuS	LaPu	PSn
AlIn	CaCd	CuSe	LaV	
AlK	CaLa	CuTe		SSb
AlNa		CuTl	LiNa	SSn
AlPb	CbCe	CuU		STl
AlS	CbY	CuW	MgNa	
AlTl			MgPu	SeSn
	CdGa	ErV	MgU	SeSb
AsTl	CdK			SeTl
		FePb	MnPb	ThU
AuRh	CeMn	FeS	MnTl	ZnU
	CeU	FeSn	MnS	VY

THE INTERACTION OF LIVING SYSTEMS WITH THE SPACE ENVIRONMENT

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ABSTRACT

The successful launch and recovery of Biosatellite II and III was clearly a very rewarding endeavor. Thirteen experiments were flown in Biosatellite II for two days in September 1967. All of the 13 experiments were concerned with the role of gravity in living systems. Six experiments sought to determine the effects of weightlessness alone. Seven investigated the combined effects of radiation and weightlessness.

It was found that weightlessness altered the orientation as well as the growth of plants (pepper and wheat seedlings). The studies expanded the scientific knowledge of several mechanisms of plant function and growth that are regulated by gravity.

Bacteria, insects and plants exposed to gamma radiation while weightless confirmed that neutralization of gravity does change the effects of radiation on the cellular elements that control heredity. The effects were significantly selective. Greater damage occurred to unpaired chromosomes such as the "X" or male chromosome.

The primate in Biosatellite III showed physiologic deterioration attributed, mainly, to 8 1/2 days of

weightlessness. Changes occurred in central nervous system function, cardiovascular performance, fluid and electrolyte metabolism and circadian rhythms.

In general, positive effects of space flight in Biosatellites II and III were observed in cell division and differentiation, growth and development, chromosome aberrations and mechanics, mutations, biochemical interaction, and decrement physiologic function in organs and systems.

Living organisms, from microbial forms to man, are extremely responsive to their environment. The history of science shows that living systems have successfully adapted their life forms and life cycles to an inconceivable variety of Earth biologic environments. The space environment provides still another variety of unique environments to which living Earth systems are being exposed.

Looking back, the Space Science Board of the National Academy of Sciences, during its 1962 Summer Study, recommended "..... an exploitation of special features of the space environment as unique situations for the general analysis of the organism-environment relationships including, especially, the role environmental inputs play in the establishment and maintenance of normal organization (and function) in the living system."

Subsequently, in response to a NASA request, the scientific community enthusiastically submitted more than 185 experiment proposals for the Biosatellite late in 1962 and early in 1963. These were evaluated by panels of specialists and were submitted with recommendations to the Bioscience Subcommittee of the NASA Space Science Steering Committee during the fall of 1963. At the same time, the NASA Ames Research Center was selected to manage the Biosatellite Project, and began development of the recommended experiments. In early 1964 the General Electric Company was awarded the contract to design, fabricate, and test six spacecraft and associated ground equipment.

The Biosatellite is an Earth-orbiting satellite containing biologic experiments to study the effects of the space environment on living organisms. The specific factors studied were weightlessness, weightlessness combined with gamma radiation, and removal from the Earth's rotation. Originally, there were three Biosatellite missions, each with a back-up flight: a three-day mission, a 30-day mission, and

and a 21-day mission. In fiscal year 1969, the 21-day mission was cancelled and in fiscal year 1970 the second 30-day mission primate flight was dropped.

Although Biosatellite I was lost, the successful launch and recovery of Biosatellites II and III was clearly a very rewarding scientific endeavor. In Biosatellite II, the back-up of Biosatellite I, thirteen experiments were flown for two days in September 1967. All of the experiments were concerned primarily with the role of gravity in living systems. Six experiments sought to determine the effects of weightlessness alone. Seven investigated the combined effects of radiation and weightlessness.

The recent flight of Biosatellite III with a male pig-tailed monkey (Macaca nemestrina) included as its goals a comprehensive evaluation of central nervous, cardiovascular and metabolic effects of prolonged weightlessness on the primate. The flight lasted only 8 1/2 of the planned 30-days mission.

In Biosatellite II, the seven radiation-weightlessness experiments in the forward section (figure 1) were carried out with Tradescantia sp (clone 02), Habrobracon junglandis, Neurospora crassa, Tribolium confusum, larvae and adults of Drosophila melanogaster, and lysogenic bacteria (Escherichia coli and Salmonella typhimurium). Six weightlessness experiments in the after compartment (figure 2) were performed on pepper plants, wheat seedlings, fertilized frog eggs, and multinucleated amoebae. In addition, there were non-irradiated, weightless controls for each experiment in the forward section.

The effects studied by the experimenters included cell division and differentiation, development and growth, chromosome damage and mechanics, genetic mutations and biochemical regulation of cell nutrition and metabolism.

All experiment 'packages' including live specimens had experienced exposure to expected flight conditions with the exception of weightlessness prior to flight to give background data on possible responses to vibration, linear acceleration, temperature excursion, and other factors. Several sets of earth controls were run simultaneously with the flight period for comparison with flight specimens.

I will not detail all thirteen experiments since they have been documented previously. Rather, I will discuss those in which significant changes occurred. For instance it was that weightlessness altered the orientation as well as the growth of plants. In the pepper plant, Capsicum annuum, epinasty was observed in the leaves and stems by time lapse photography in the orbiting plants (figure 3)

compared to plants prior to flight. Although the degree of curvature was similar to that in clinostat control plants on Earth, no leaf motion was seen in weightless plants as occurred in both erect and clinostat controls. Return to normal Earth position of the leaves was delayed following recovery of the Biosatellite. There was no significant difference in amino acid and carbohydrate mobility in leaves and stems between the on-orbit plants and Earth clinostat controls. Both groups were significantly disoriented when compared to erect Earth controls.

When compared to Earth clinostat controls, the wheat seedlings, Triticum vulgare, germinating in the Biosatellite showed no significant difference in growth, development, morphology, energetics and auxin production and distribution. Disorientation of roots and coleoptiles was present in the weightless seedlings (figure 4) and the clinostat controls, when compared to seedlings grown erect to gravity in the Earth control laboratory.

The specific activity of peroxidase, glucose-6-phosphate dehydrogenase, and glyceraldehyde-3-phosphate dehydrogenase was higher in the tissues of flight plants than in earth clinostat and erect seedlings. Malic dehydrogenase, transminase and cytochrome-C reductase activities were not significantly different in any of the seedlings. No alterations were observed in carbohydrate, amino acid, and nitrogen content.

There was no significant difference in germination or coleoptile length. The ratio of roots to shoot were greater in the orbited seedlings as compared to earth clinostat and erect controls. Both the weightless and clinostat root tips and coleoptile tips showed a random distribution of statolith granules.

No significant effects attributable to weightlessness were observed in the developing frog eggs (figure 5) or the amoeba (figure 6).

In the weightless environment of the orbiting Biosatellite II, the radiation effects observed depended on the nature of the organism. In some cases the effects of radiation combined with weightlessness were greater than those observed in Earth-based controls and in some cases, the effects were less.

Seven hundred twenty pupae flour beetle, Tribolium confusum, (pre-irradiated with 1350 R of 180 keV x-rays) were orbitied in the Biosatellite, half in the presence of 85-strontium and half shielded from it. Identical Earth controls were maintained. Of the earth irradiated controls and the shielded flight pupae, 29.9% developed wing abnormalities (figure 7) whereas the abnormality occurred in

44.8% of the adults from flight irradiated pupae, which received an additional 100-150 R on orbit. Dominant lethality occurred in 78±6% of the offspring of flight irradiated female oocytes, compared to 27±5% in the Earth-irradiated controls.

In the vinegar gnat adults, Drosophila melanogaster, the deformed thorax and missing wing (figure 8) in Biosatellite II organisms was twice that of Earth controls. The interaction of weightlessness and gamma radiation induced premature aging and chromosome translocations and non-disjunction (extra Y's and missing Y's and IV's). Chromosome breaks were significantly increased.

The blue flower, Tradescantia, and the parasitic wasp, Habrobracon, showed cases of antagonism and enchancement of radiation-induced damage as well as no significant changes in certain parameters. The orange bread mold, Neurospora crassa, showed no changes. Antagonism of radiation by weightlessness was obvious, but not pronounced, in the lysogenic bacteria.

The experiment results of Biosatellite II showed convincingly that there is an interaction between radiation and one or more other factors encountered in flight. This interaction varied between increasing the effects of radiation fourfold to decreasing the effect slightly but significantly.

The plant experiments for study of the biologic effects of weightlessness alone showed a close correspondence to results obtained by exposure to rotation on the clinostat. The clinostat exposure, in its simplest form, consists of rotating a plant in horizontal position (normal to the direction of the force of gravity) at a rate of rotation sufficient to prevent the plant from responding normally to gravity in any one direction.

The physiologic deterioration of the primate flown in Biosatellite III is mainly attributed to the effects of weightlessness. The details are in press in SCIENCE. In summary, the monkey was in excellent condition at the time of launch and was fully adapted to restraint in his flight couch and long periods of isolation. All physiologic sensors functioned perfectly during flight and following recovery (figures 9-12).

Preliminary examination of these data indicate that the monkey remained alert in his waking periods until the eighth day. Much new information has been gathered on cycles of sleep and wakefulness in weightlessness. From brain wave records, heart rate and respiration, brain and body temperatures, and from spacecraft data on carbon dioxide excretion, it is clear that the animal lost normal circadian

or 24-hour rhythm and was no longer synchronized to the capsule day-night cycle. This longer period gave a progressive phase displacement of 8 hours in the daily peak of his metabolic and brain wave activities so that by the eighth day he slept late into the morning period. No such changes were seen prior to launch in the flight monkey nor in numerous control animals.

For the first time in any space flight of man or animals, the occurrence of rapid-eye-movement (REM) sleep was confirmed. This sleep constitutes about 20 per cent of normal sleep on earth and in man is associated with dreaming. It is essential in full amounts for continued behavioral well-being.

However, important signs of patho-physiology first appeared in early days of the flight. For the first time in man or animals, pendular eye movements were recorded in the first three days of weightlessness and indicate a vestibular-ocular disturbance. The eyes swung slowly and rhythmically from side to side about once per second with progressively increasing amplitude.

The animal's condition deteriorated sharply on the eighth day. Food and water were no longer taken during this period and the heart rate slowed to 70 beats per minute with an accompanying sharp drop in blood pressure. Brain wave records showed increased slow waves but were consistent with a sleeping rather than a comatose condition. This situation occurred at the end of a period in which the only telemetered signs of a progressive decline in general condition was a slow fall in brain temperature to 35°C compared with 38.2°C at launch, and a drop in central venous pressure (measured in the right atrium) to below 0 in the last 3 days of flight. Photographic records have confirmed that the animal was alert and active until the eighth day. Immediately prior to de-orbit the heart rate had fallen to 39 beats per minute.

The fluid loss approximating 20 per cent of body weight has been closely investigated, both from physiological data, and data on water condensed in the spacecraft. The following account of circumstances leading to the animal's collapse implicates weightlessness as a prime factor and is relevant to environmental constraints, task requirements and mission durations.

Spacecraft data clearly indicate an early and profound loss of fluid by insensible perspiration. After the fourth day this mechanism was no longer as severe. The urine output increased steadily to almost diuretic levels by the eighth day of flight making it difficult to measure calcium, creatine and creatinine excretion by virtue of a

high dilution (figures 13 and 14). As nearly as can be determined, the net negative fluid balance over the 8 day period was 1250 to 1280 milliliters. A primary mechanism of the continued loss of water in the later stages of flight appears to relate to a redistribution of blood volume in the thorax as a consequence of weightlessness.

The critical measurements from this study is the finding of a high fluid loss, even in a sedentary resting state, related to shifts in blood volume and its distribution. This involves perturbations in body fluid balance, electrolyte metabolism of sodium and potassium, and ultimately, the stability of the cardiovascular system.

In general then, the significant effects of space on the Biosatellite II experiments were observed in: (1) young and actively dividing cells **and tissues; (2) rapidly dividing** cells with a high metabolic rate; and (3) cells such as sperm and eggs after meiosis. Mature cells were least affected. Positive effects were observed in cell division and differentiation, growth and development, chromosome aberrations and mechanics, mutations, biochemical processes and population dynamics.

The Biosatellite III preliminary findings indicate positive effects of weightlessness on the central nervous system, cardiovascular system, fluid and electrolyte metabolism and altered circadian or 24-hour rhythmic cycles.

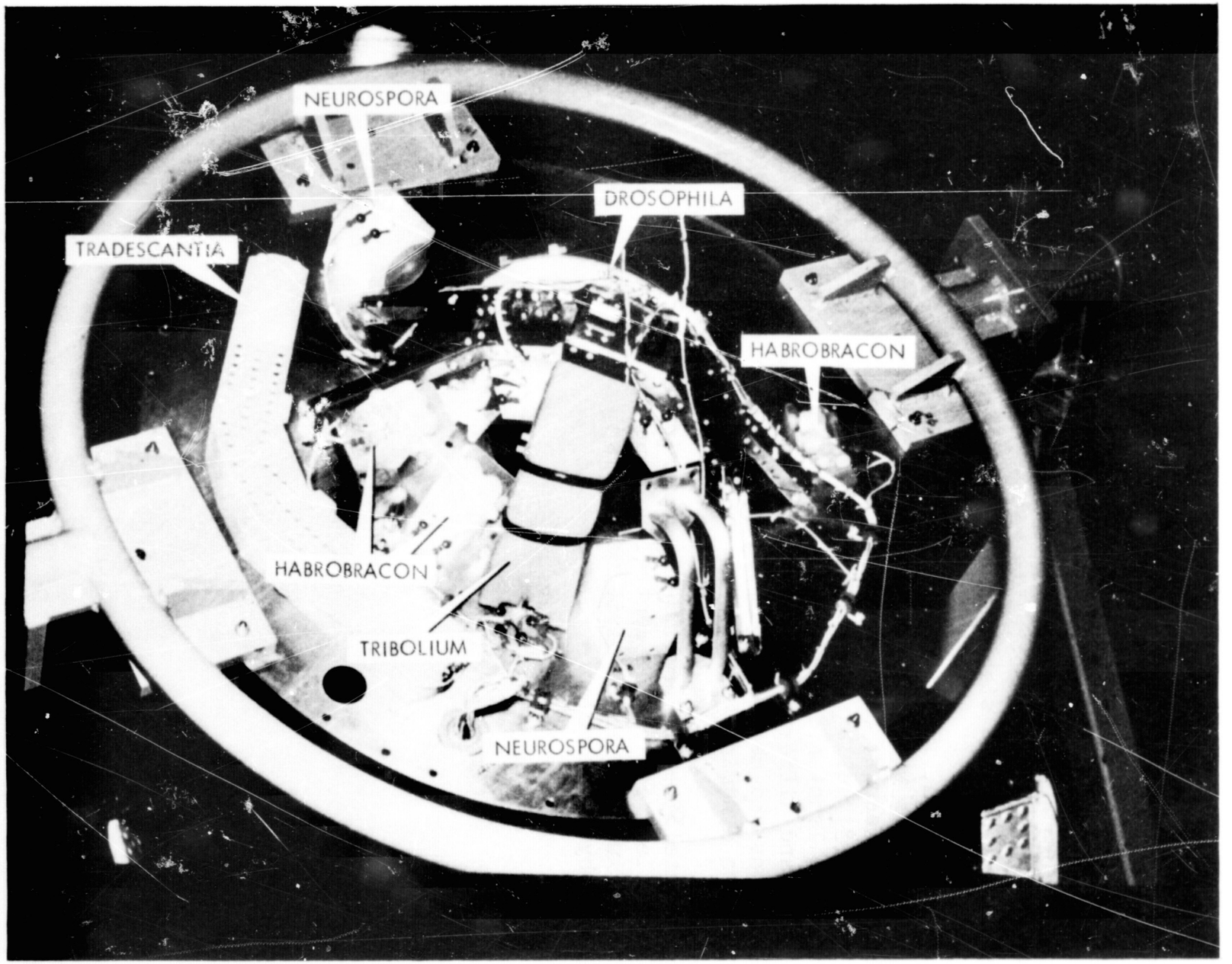


Figure 1. Biosatellite Experiments Payload Assembly (Located Around Radiation Source)

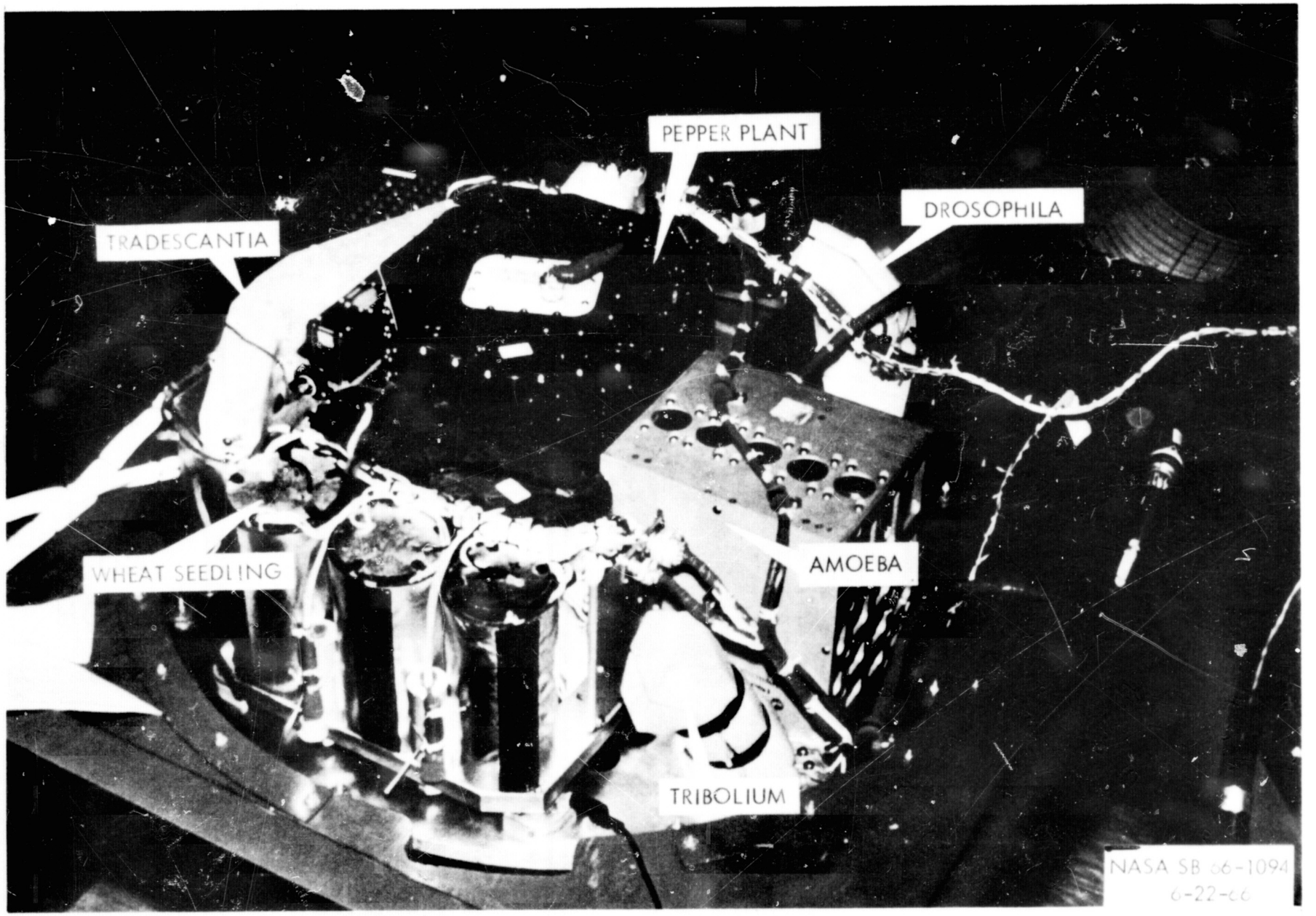


Figure 2. Biosatellite Experiments Payload Assembly (Behind Radiation Shield)

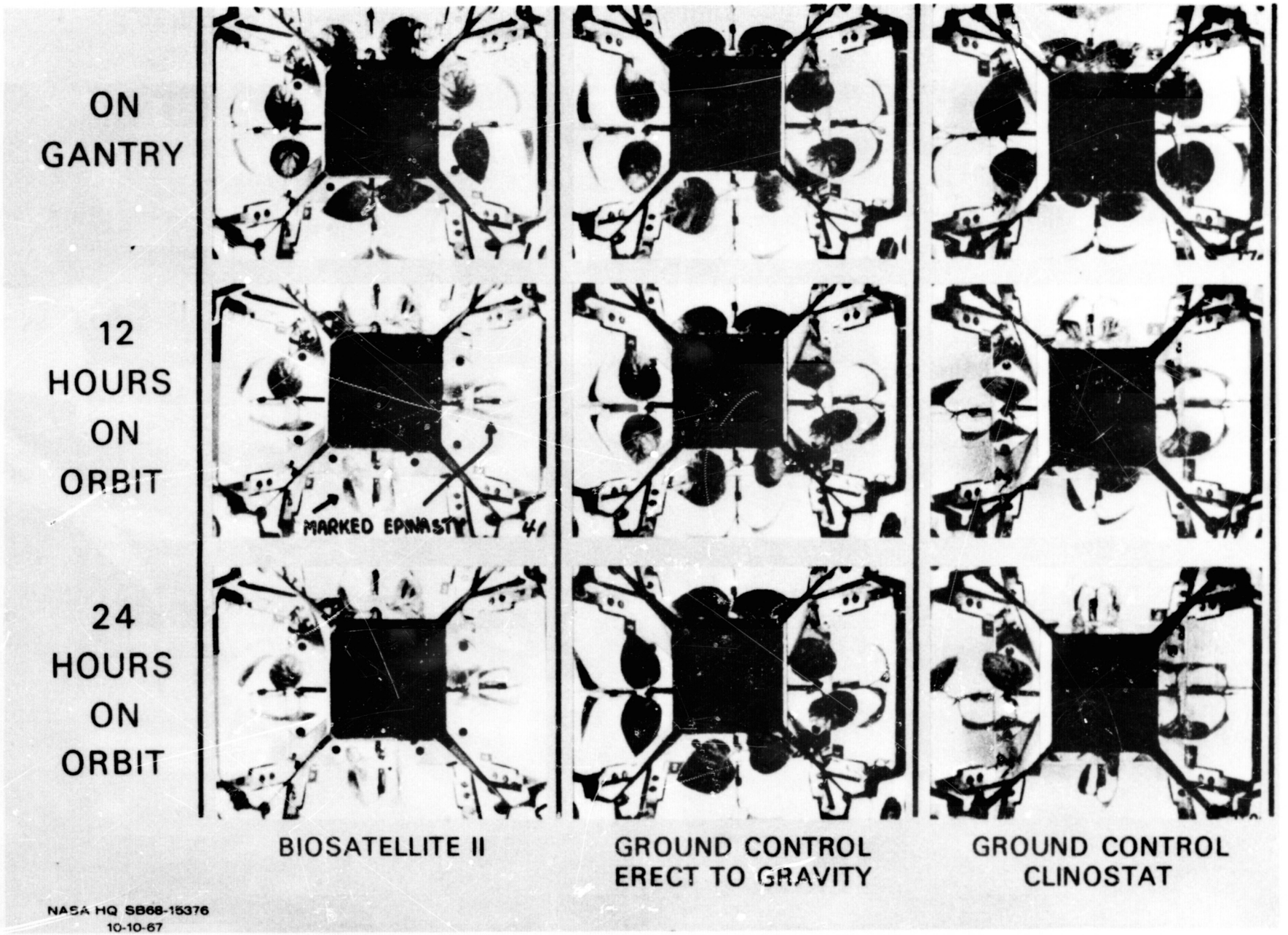


Figure 3. Biosatellite II: Effect of Weightlessness on Pepper Plant

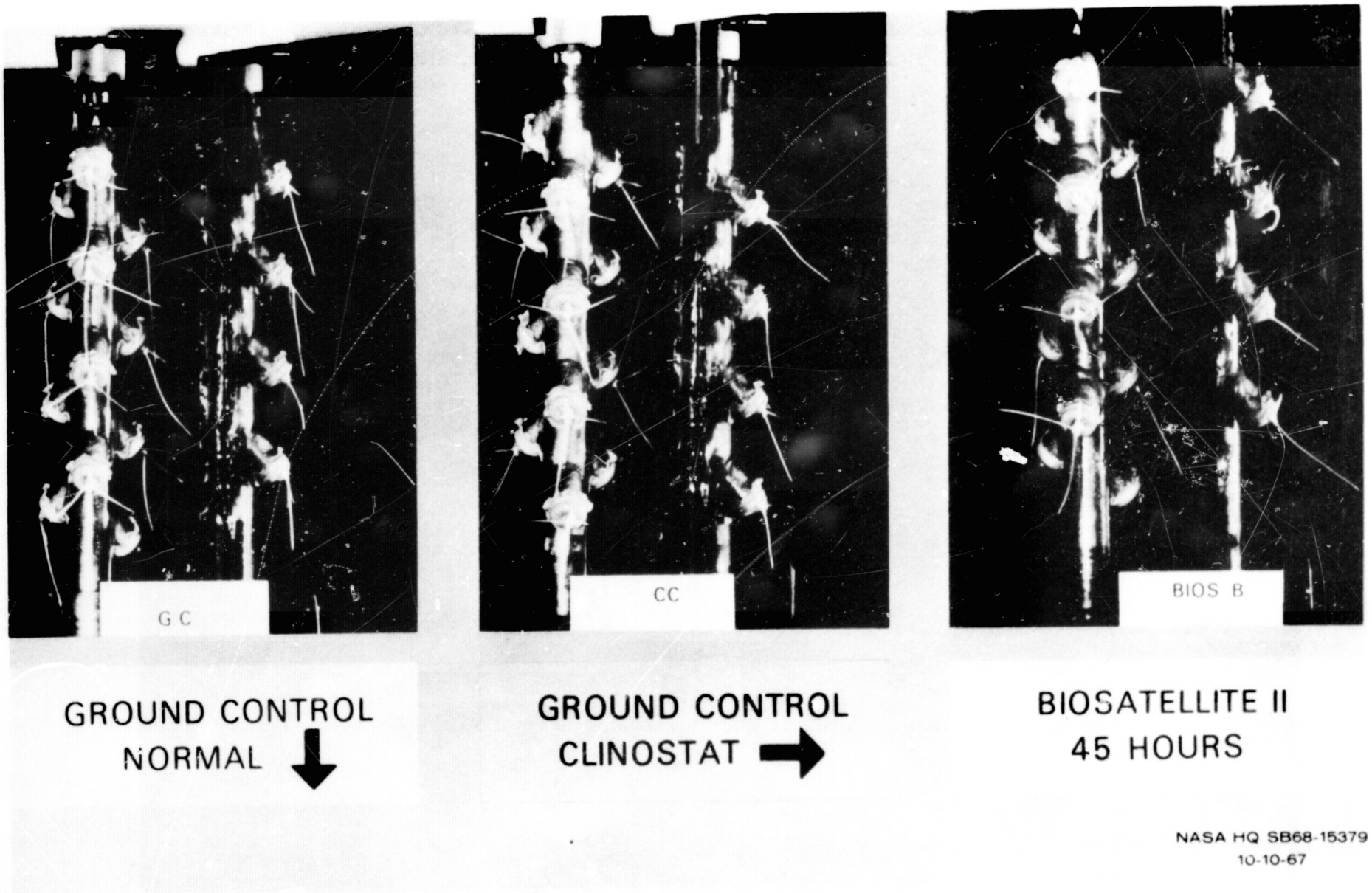


Figure 4. Biosatellite II: Effect of Weightlessness on Developing Wheat Seeds

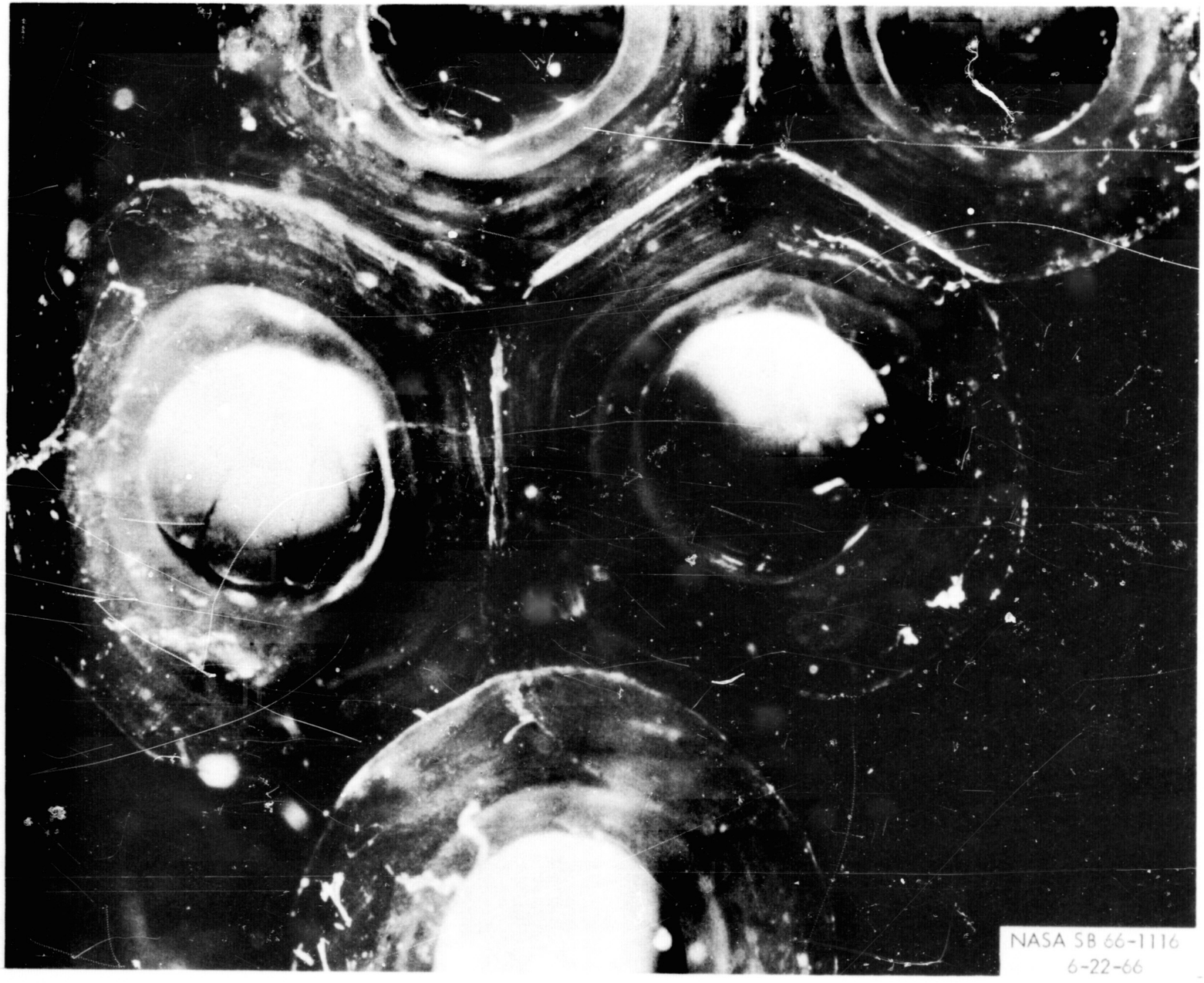


Figure 5. Frog Eggs With Eight Cells After 2.5 Hours of Weightlessness

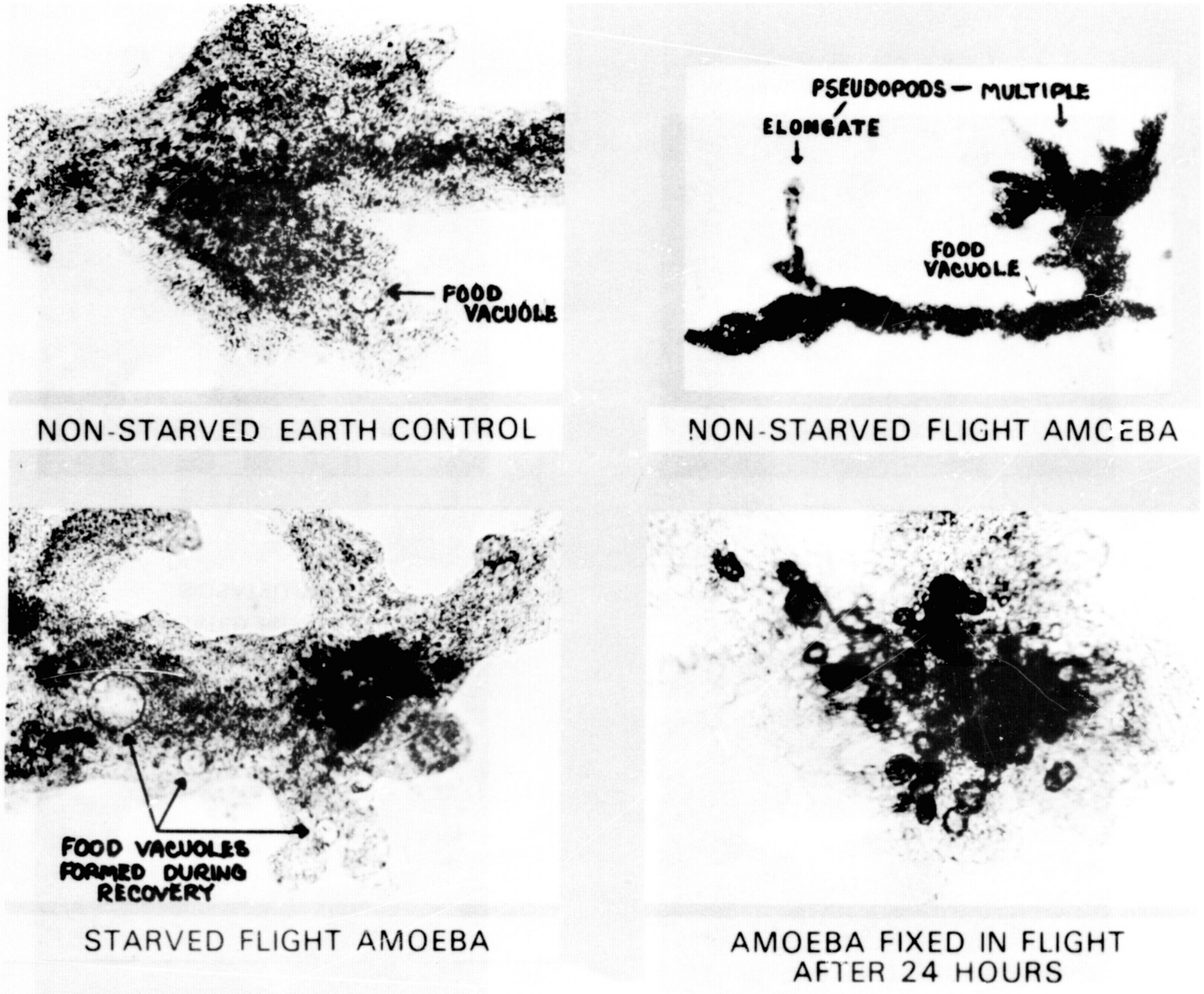
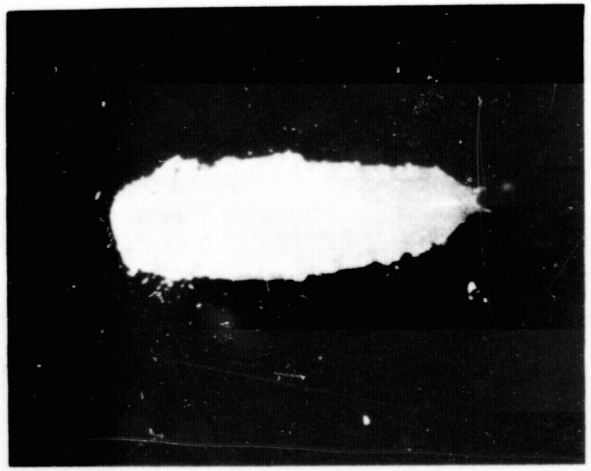
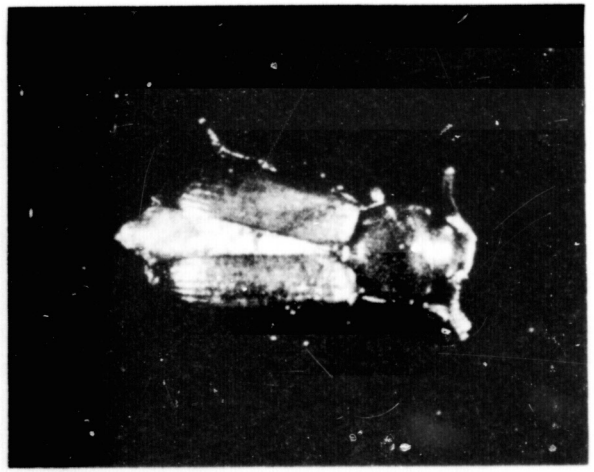


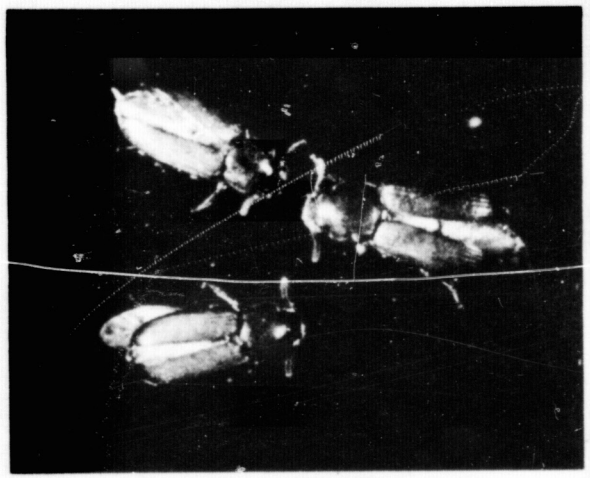
Figure 6. Biosatellite II: Effect of Weightlessness on the Amoeba



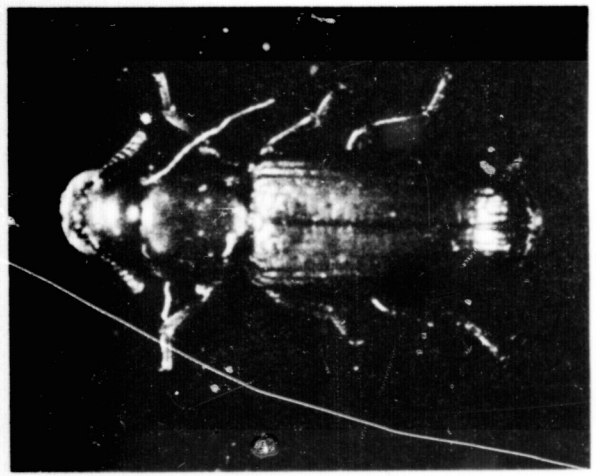
PRE-IRRADIATED PUPA FLOWN IN
BIOSATELLITE II



ADULT FROM BIOSATELLITE
IRRADIATED PUPA WITH SPLIT WING



SPLIT WINGS AND PROTRUSION
OF MEMBRANOUS WING



NORMAL EARTH CONTROL ADULT

Figure 7. Biosatellite II: Effects of Weightlessness and Radiation on Tribolium

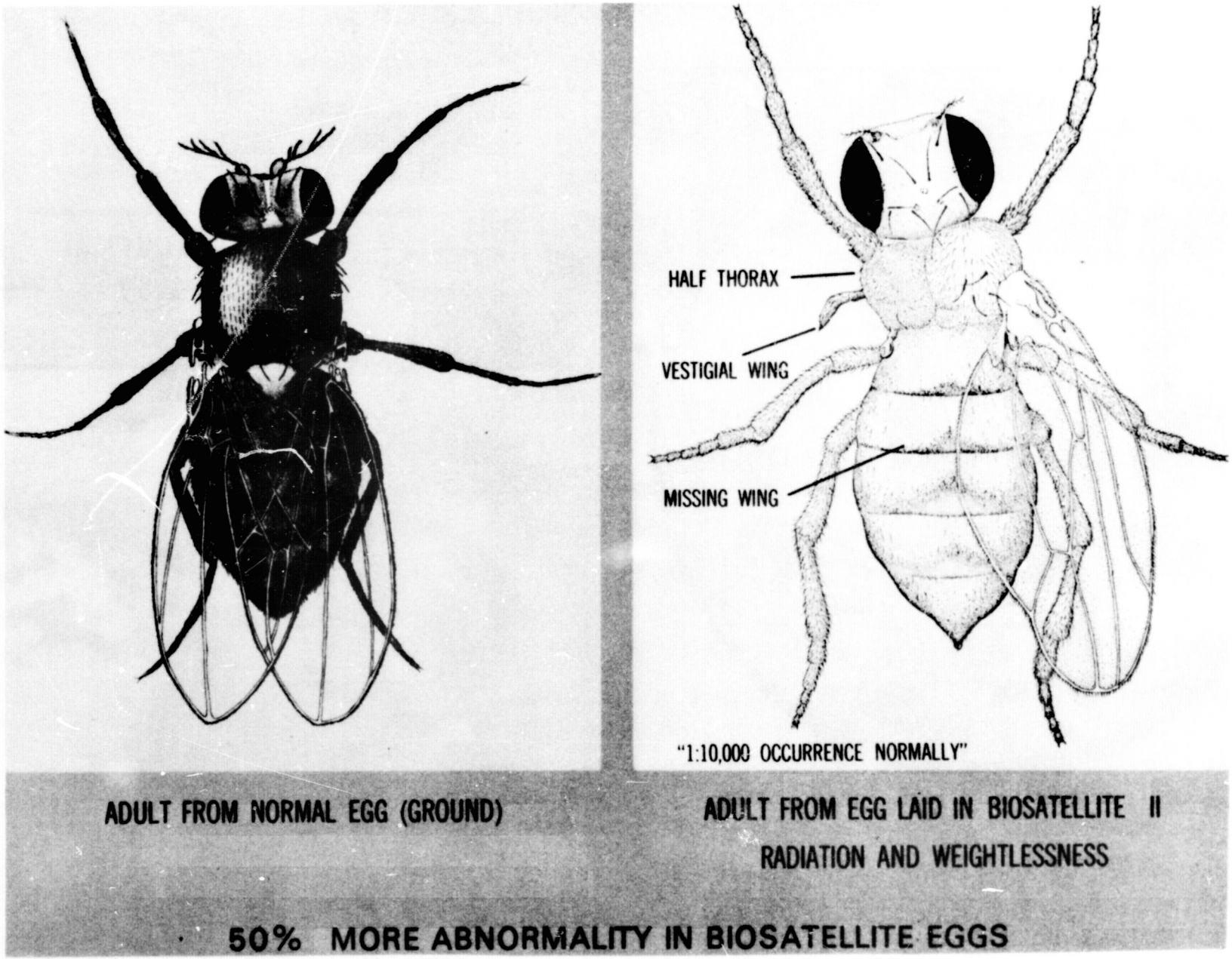


Figure 8. Biosatellite II: Effects of Radiation and Weightlessness on Drosophila (Vinegar Gnat)

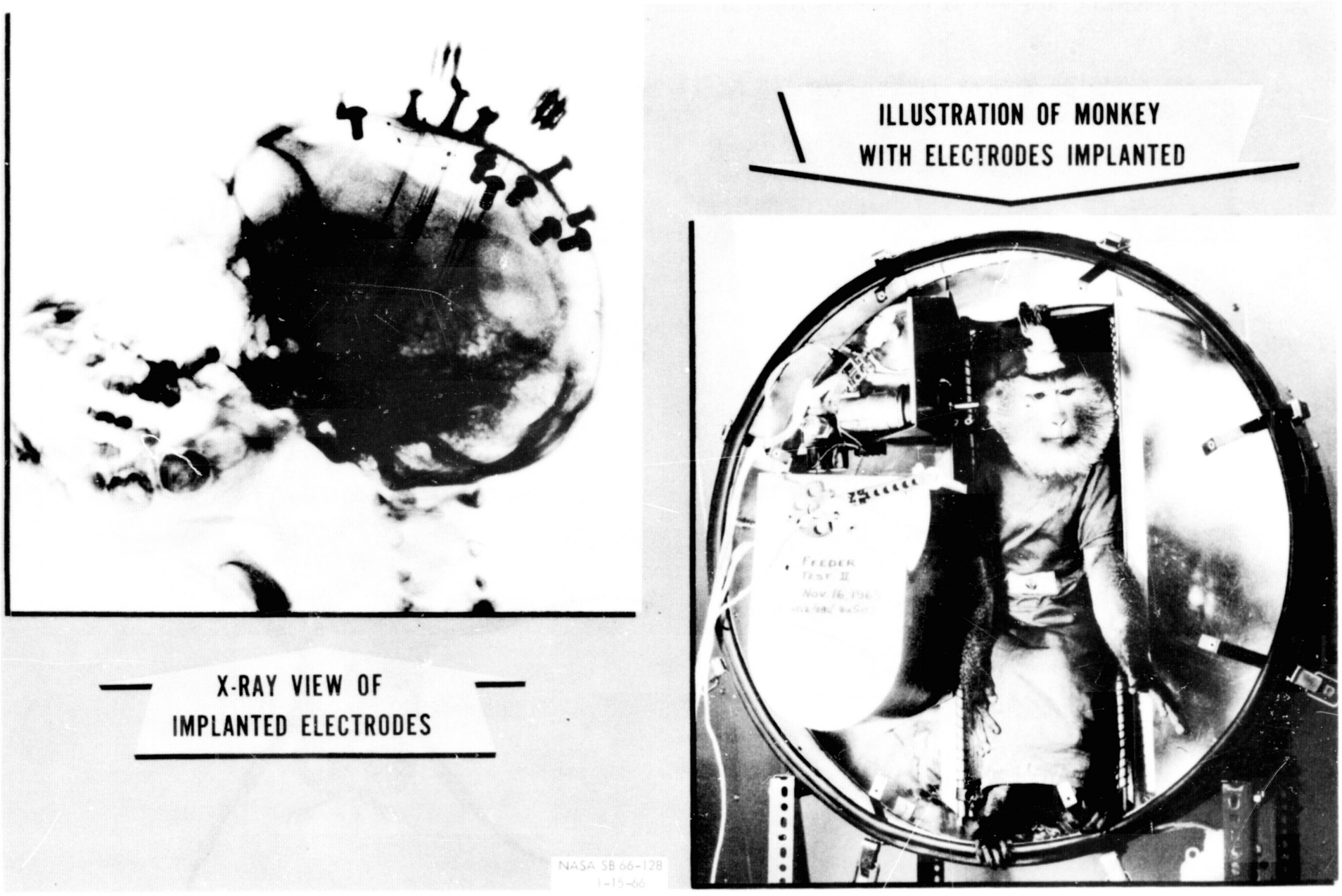


Figure 9. Brain Electrodes in Primate

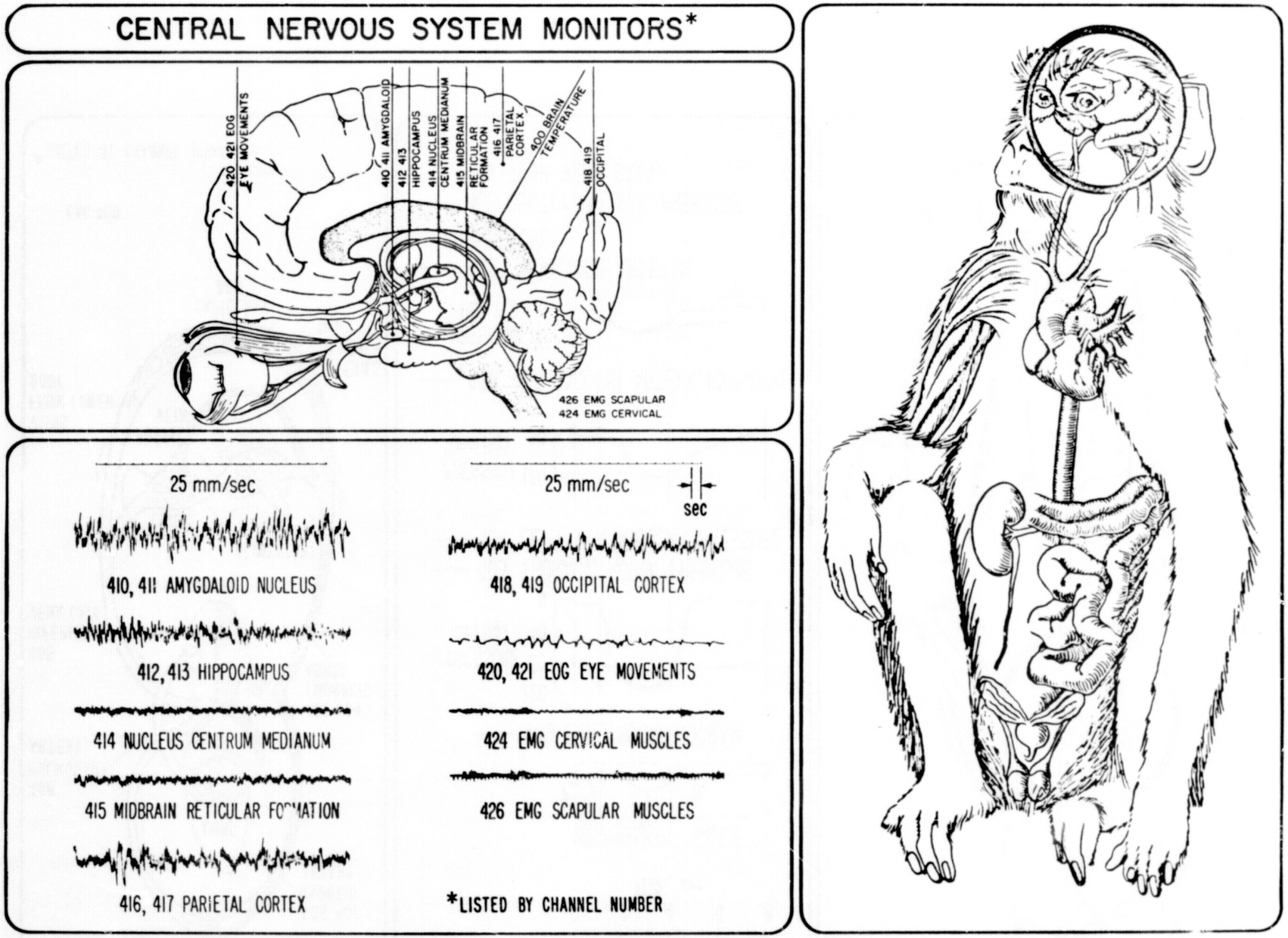

CENTRAL NERVOUS SYSTEM MONITORS*
420 421 EOG EYE MOVEMENTS
410 411 AMYGDALOID
412 413 HIPPOCAMPUS
414 NUCLEUS CENTRUM MEDIANUM
415 MIDBRAIN RETICULAR FORMATION
416 417 PARIETAL CORTEX
400 BRAIN TEMPERATURE
418 419 OCCIPITAL
426 EMG SCAPULAR
424 EMG CERVICAL
25 mm/sec
410, 411 AMYGDALOID NUCLEUS
412, 413 HIPPOCAMPUS
414 NUCLEUS CENTRUM MEDIANUM
415 MIDBRAIN RETICULAR FORMATION
416, 417 PARIETAL CORTEX
25 mm/sec
sec
418, 419 OCCIPITAL CORTEX
420, 421 EOG EYE MOVEMENTS
424 EMG CERVICAL MUSCLES
426 EMG SCAPULAR MUSCLES
*LISTED BY CHANNEL NUMBER

Figure 10

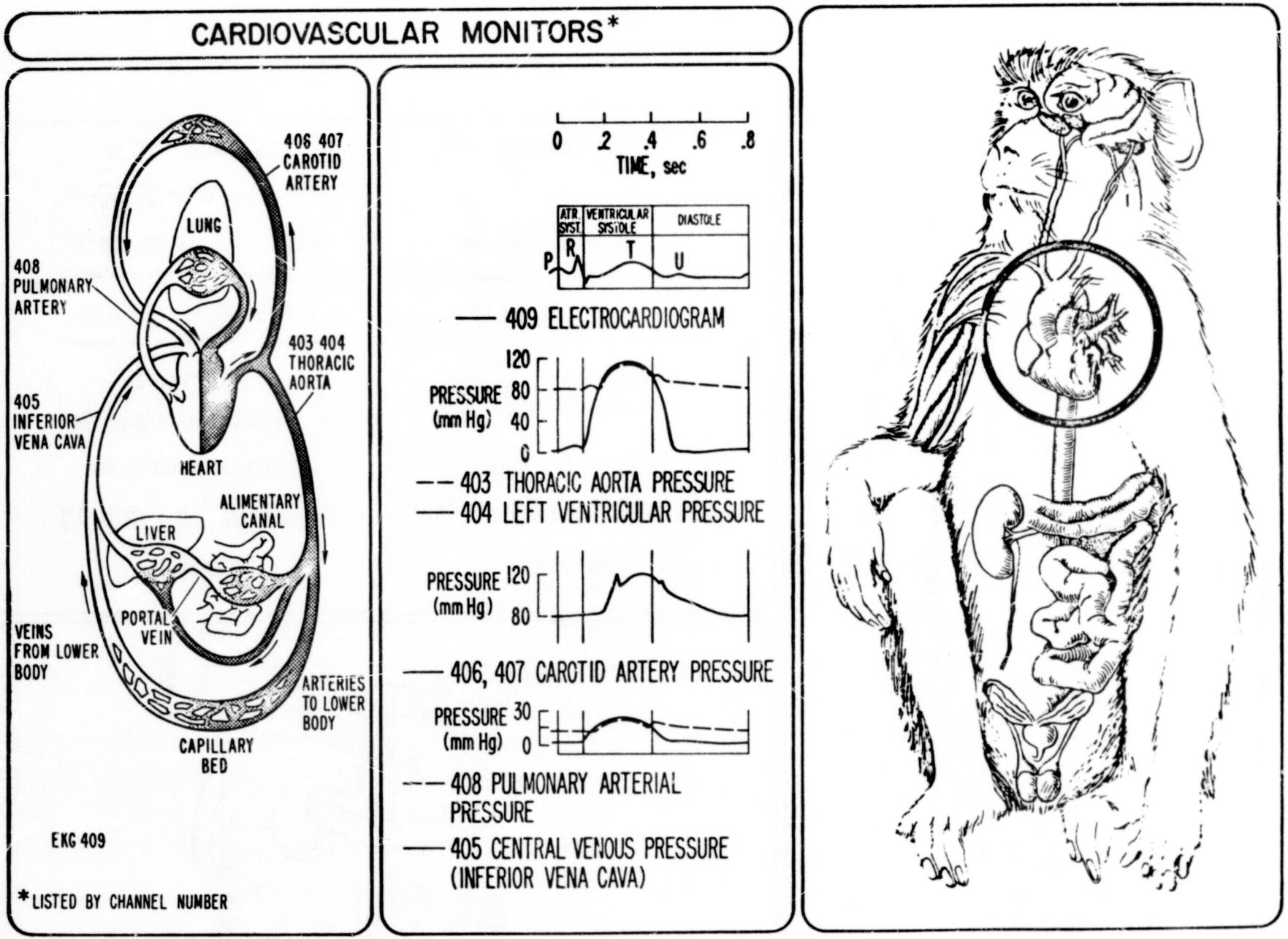

CARDIOVASCULAR MONITORS*
406 407 CAROTID ARTERY
LUNG
408 PULMONARY ARTERY
403 404 THORACIC AORTA
405 INFERIOR VENA CAVA
HEART
ALIMENTARY CANAL
LIVER
PORTAL VEIN
VEINS FROM LOWER BODY
ARTERIES TO LOWER BODY
CAPILLARY BED
EKG 409
*LISTED BY CHANNEL NUMBER
0 .2 .4 .6 .8
TIME, sec
ATR. SYST.
VENTRICULAR SYSTOLE
DIASTOLE
P
R
T
U
— 409 ELECTROCARDIOGRAM
PRESSURE (mm Hg)
120
80
40
0
--- 403 THORACIC AORTA PRESSURE
— 404 LEFT VENTRICULAR PRESSURE
PRESSURE (mm Hg)
120
80
— 406, 407 CAROTID ARTERY PRESSURE
PRESSURE (mm Hg)
30
0
--- 408 PULMONARY ARTERIAL PRESSURE
— 405 CENTRAL VENOUS PRESSURE (INFERIOR VENA CAVA)

Figure 11

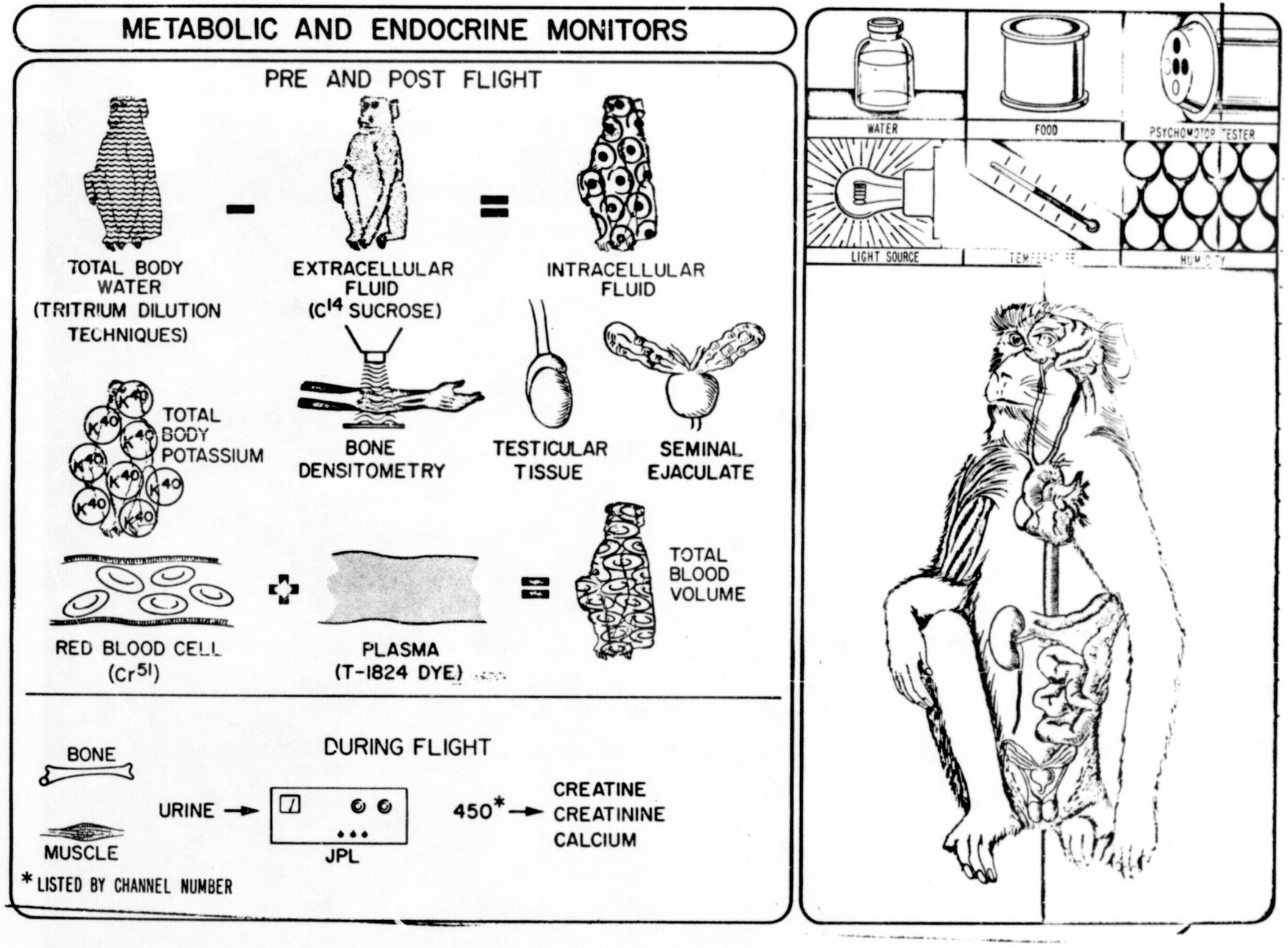

METABOLIC AND ENDOCRINE MONITORS
PRE AND POST FLIGHT
TOTAL BODY WATER (TRITRIUM DILUTION TECHNIQUES)
EXTRACELLULAR FLUID (C^{14} SUCROSE)
INTRACELLULAR FLUID
TOTAL BODY POTASSIUM
BONE DENSITOMETRY
TESTICULAR TISSUE
SEMINAL EJACULATE
RED BLOOD CELL (Cr^{51})
PLASMA (T-1824 DYE)
TOTAL BLOOD VOLUME
DURING FLIGHT
BONE
MUSCLE
URINE
JPL
450*
CREATINE
CREATININE
CALCIUM
* LISTED BY CHANNEL NUMBER
WATER
FOOD
PSYCHOMOTOR TESTER
LIGHT SOURCE

Figure 12

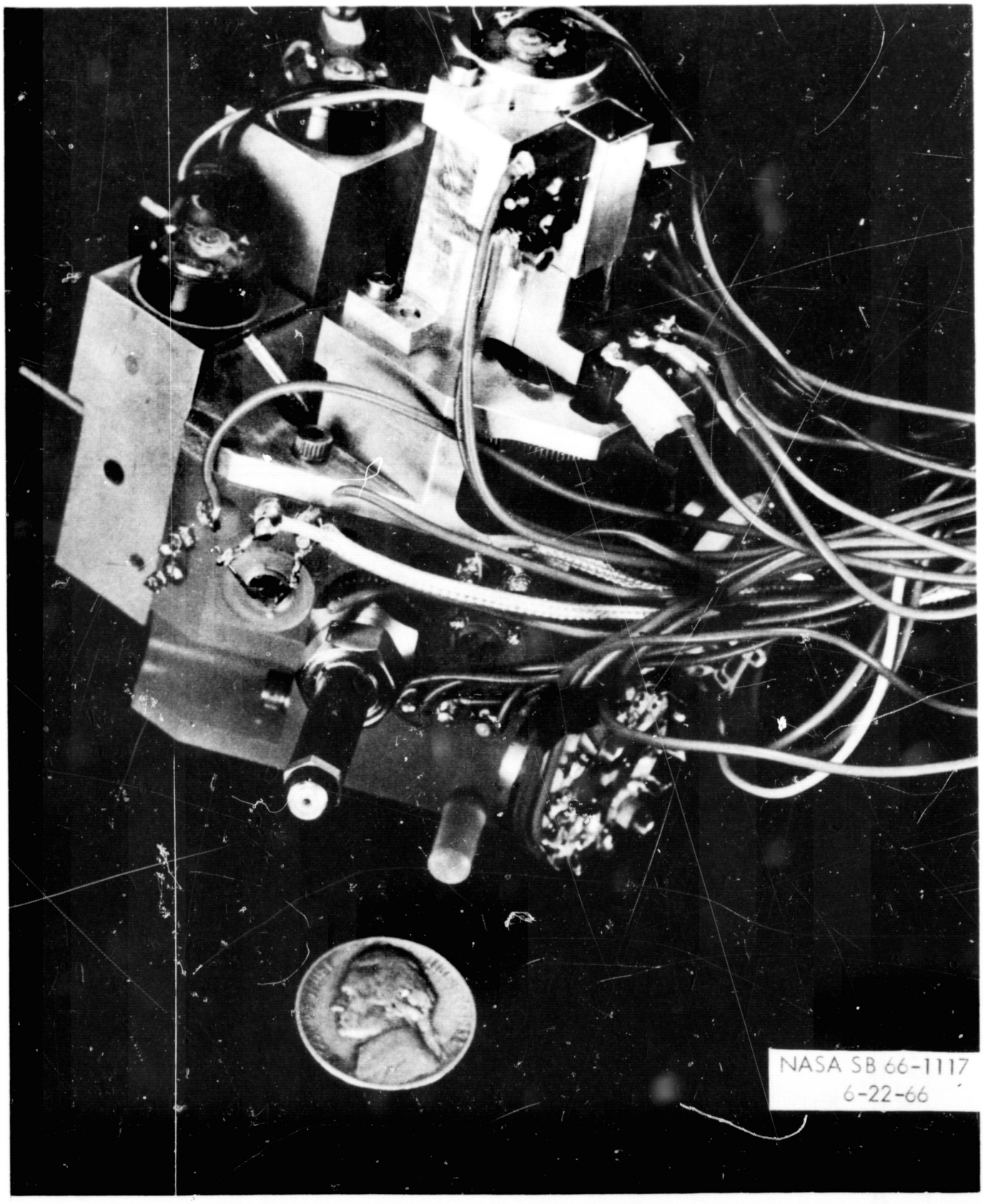


Figure 13. Biosatellite In-Flight Urinalysis System

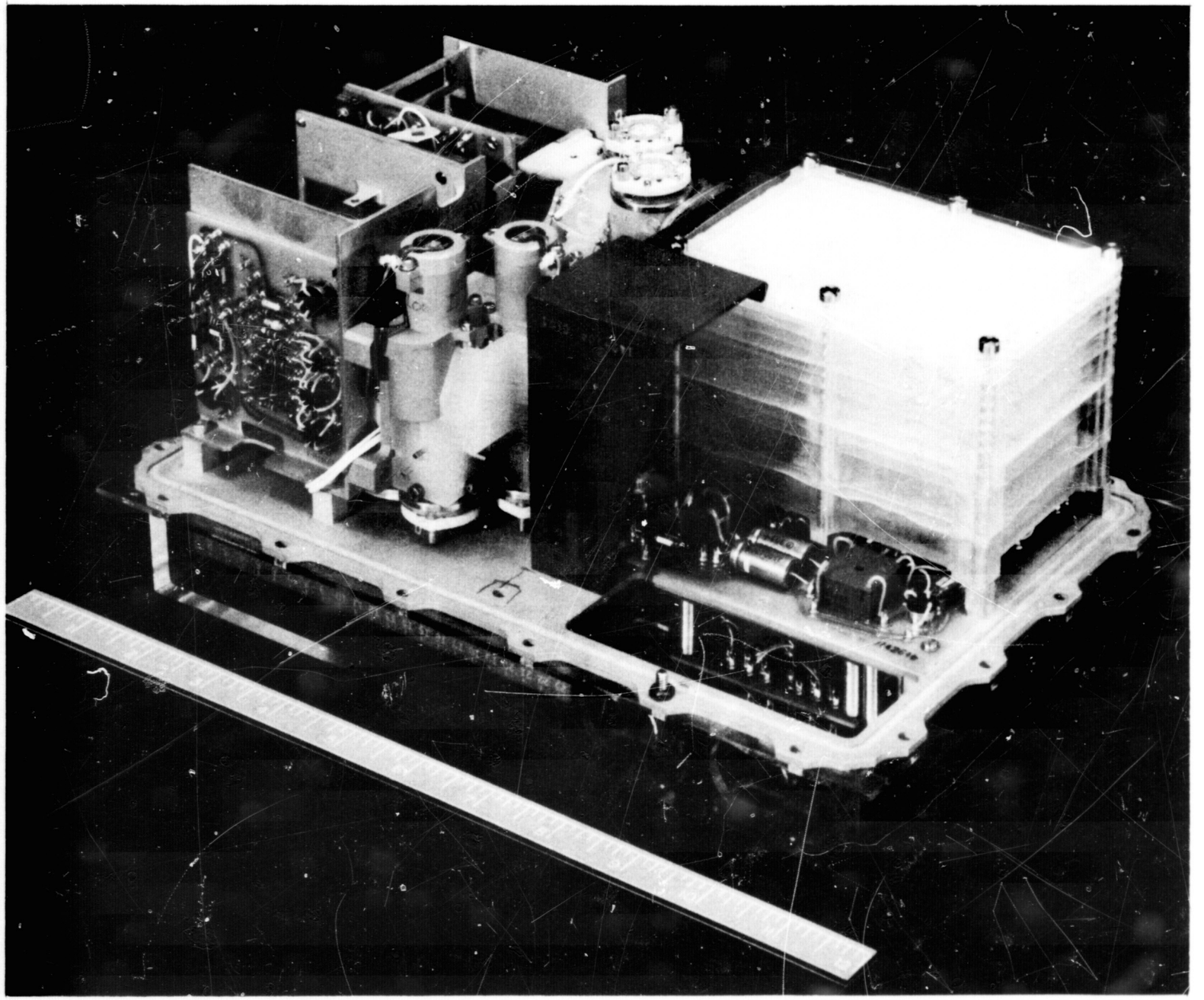


Figure 14

N70-21528

UNIT SEPARATION PROCESSES IN SPACE

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PHILADELPHIA, PENNSYLVANIA

ABSTRACT

Some unit separation processes used for purifying chemicals and biologicals (vaccines) are clearly affected by the earth's gravity and therefore might be improved by operation in space. Centrifugation and electrophoresis are the prime examples of such processes. Meanwhile other processes such as freeze drying and ultraviolet sterilization are desirable adjuncts in a spectrum of processes that could permit the complete preparation of vaccine or other materials in space. The freeze drying operation would take advantage of the low temperatures and vacuum of space.

These processes are being considered (by a team of General Electric and Wyeth Laboratories personnel, under contract NAS 8-24683) as a spectrum of interrelated processes that could lead to the complete preparation of vaccine or to the preparation of materials to be used in other processes and products.

INTRODUCTION

In generating, collecting, and assessing ideas for the space processing of materials, it appears that for both economic and technical reasons an integrated sequence of processes may be both desirable and necessary. From the economic viewpoint, it appears that the pre and post flight processing may well outweigh the contributed value of the operations performed in space. Unless the space operation such as zero g melting and solidification, does provide such unique set of properties, as we all hope it does, in the material that the value of this new product is greatly enhanced, the economics will be difficult to justify. From the technical standpoint, there may well be products of great economic and humanitarian value that must be completely processed through all stages in a relatively short time because of chemical or biological instability problems at various steps during the processing.

In the latter category, it appears for example, that vaccine preparation in a free rotor centrifuge or in the electrophoresis process using fluid suspensions may be improved by performing the separation in space under the nearly zero g conditions which provide nearly zero convection. However, the storage of such products on a space station before and after performing either of these operations in space would be undesirable if not impossible. It would therefore appear necessary to also perform the entire spectrum of processes to provide a finished product in space. In the case of vaccine, this might include: (1) the preparation of a virus culture, (2) the separation or purification process such as centrifugation or electrophoresis, (3) freeze-drying and (4) ultraviolet sterilization. Almost the entire space environment of radiation, low temperature, vacuum, ultraviolet, and low gravitational forces would be utilized. Although we can achieve comparable vacuum, low temperatures, and radiation (e.g. ultraviolet) here on the earth, we may well want to use the zero g for the separation processes and will then need to use the other aspects of the space environment for completing the vaccine preparation in an expeditious manner in order to obtain a more stable end product than would be the case if we only did the separation process in space.

In addition to the proposed study of the preparation of vaccine in space, there are potentially other products which can benefit from space processing and which require one or another of these unit processes. These include isotopes, chemicals, and food or food supplements.

Studies of each of the unit processes mentioned has recently been undertaken and a progress report on the work is presented here. It appears even at this early point in the study, however, that both electrophoresis and freeze-drying are attractive candidates for early space processing experiments.

They appear to be easy to design, build, and operate as space experiments and would be timely to perform as necessary steps in the development of an integrated space processing sequence for vaccines. The free rotor centrifuge is still under study but is not as ready for a definite recommendation as are the other two processes. However, there are clear cut cases of detrimental effects of gravity on the operation of conventional centrifuges so that a space experiment should be considered and planned even with a conventional centrifuge which could then be modified to permit the operation of a free rotor centrifuge at a later time.

"In the present course of vaccine development, a major consideration is the possible oncogenicity (tumor production) by viruses. Some viruses which are now used to produce experimental (and important) vaccines have the capacity to produce cancer in certain animals. Extensive studies have been underway in our laboratory to define conditions which would not only make such vaccines safe, but would also make possible the production of a cancer-virus where such becomes feasible using the present tumor viruses as prototype systems. There is already evidence that at least one form of cancer in man is produced by a virus and no suitable vaccine type is available or can be made with present knowledge.

Our approach has been to develop absolute separation methods with the intention of physically or chemically separating the antigenic (immunologically potent) proteins of the viruses from their genetic material. With such an approach one could be assured that such a possible cancer vaccine would not itself have the potential of producing tumors in the vaccinated subjects.

Attempts have been made to separate the protein structures by various forms of chromatography and electrophoresis. Similar separations have also been attempted by means of high speed gradient ultracentrafugation. In none of the earth laboratories has it been possible to obtain absolute separations by such physical means.

The space laboratories offer the possibility of greatly improving the precision with which physical separations can be done since the electrical or centrifugal forces employed can be isolated from the gravity forces that tend to diffuse the components. Although these diffusions may be only a very small percentage of the total movement of the components, the current problems require much more absolute separations. It could, therefore, be of great value to achieve such separations in zero gravity laboratories."*

CENTRIFUGES

The ultracentrifuge has historically been an important analytical tool for researchers in the chemical and biological fields. Until recently it was not widely used commercially, however, due principally to its small throughput. Recent developments at Oak Ridge National Laboratories and commercialization of these designs by several organizations indicates a large and increasing interest in the centrifuge for preparing high quality biologicals and pharmaceuticals. These have obviously great and well accepted economic and humanitarian value.

In parallel with this development, several organizations have been considering the possibilities for improving materials and processes in space. One of the ideas that we have been studying is that a simple rotating machine, such as a centrifuge rotor would not need bearings to operate in space. Further, it would not then have the mechanical connections through which vibrations and heat could be conducted and it should therefore perhaps yield better separations

*private communication by Dr. B. A. Rubin

by this minimizing of vibrations and convection. A review of literature on the use of centrifuges indeed indicates that these are two of the three most prominent problems with centrifuges. The third problem is often thought to be the only or the principal problem. It is related to the strength of materials and therefore the size or maximum peripheral speed of a centrifuge. Operating a centrifuge in space will not markedly improve this situation, although the new advanced composite materials may well do so. A second order problem in certain research uses of centrifugation is incidentally due to the presence of gravity which causes sedimentation during long (several days) runs. In spite of the large g forces acting normal to the (vertical) axis of a centrifuge the one-g force of the earth causes undesirable sedimentation.

These several aspects of centrifugation appear therefore to be prime reasons for further considering the development and operation of centrifuges in early space experiments.

The initial consideration in our study of centrifuges is on the vibration problem and this is presented here. Convection is also of direct interest in the operation of a centrifuge as well as in electrophoresis. However, for convenience it is discussed in the next section under 'Electrophoresis'.

Basically a centrifuge is an elastic cylindrical body with a liquid cavity. It is well known from the dynamics of elastic containers with liquid cavities that a partially filled cavity behaves very differently from the fully filled cavity and the empty cavity. It is observed in the operation of centrifuges that a "partially filled centrifuge can undergo dangerous oscillations, the amplitudes of which exceed considerably the amplitudes of oscillation of the empty or fully filled centrifuge." (Ref. 1) As a first cut model we chose a fully filled centrifuge so that a simple model for analysis could be studied to yield preliminary comparisons. The equations of an elastic container with a fully filled fluid cavity are completely analogous in form to those of solid elastic body with internal friction, the contribution of the fluid appearing in the internal friction terms. Thus the first cut model reduces to a cylindrical rotor with internal friction and if the cylinder is long compared to its diameter the basic first cut problem is a rotating shaft with internal friction.

The boundary conditions and energy requirements necessary to maintain a constant angular velocity differ in the operation of the centrifuge in a normal or in a weightless environment. On the Earth it is necessary to support the centrifuge and the boundary conditions are at best self-aligning bearings. In a weightless operation the centrifuge can be freely floating and bearing-free operation is possible. On the Earth energy must be supplied to maintain a constant angular velocity whereas in space no drive is required to maintain the free rotor after it attains the desired rotation rate. These are very important differences. The presence of support bearings means the presence of external friction and oscillations due to motions at the bearings. The necessity for supplying energy to maintain the rotation rate is an even more severe problem. The basic principle of building up vibrations in a flexible shaft is: "If the drive maintains a constant angular velocity irrespectively of the behavior of the shaft, then under certain conditions part of the energy supplied by the drive is absorbed in lateral oscillations; internal friction and similar factors then act simply as transmitters of energy." (Ref. 1) For a free rotor where it is not necessary to supply energy to maintain the rotation, there is no energy source to sustain lateral vibrations. Thus from energy arguments, a bearing-free rotor not operating at its critical velocity should not develop undesirable lateral vibrations if not disturbed.

Let us consider the centrifuge as a cylindrical elastic solid rotating about its cylindrical axis at angular velocity, "ω". If the cylinder is long compared to its diameter we can consider it as an unloaded rotating shaft. The following is observed when the rotation speed of an unloaded shaft is increased: It is found that a certain speed, called the critical speed, is reached at which instability will occur, the shaft deflecting into a single bow and whirling around like a skipping rope. If this speed is maintained the deflection will become so large that the shaft will be fractured; but if this speed is quickly run through, the shaft will become straight again and run true until at another higher speed the same phenomenon will occur, the deflection now, however, being in a double bow, and so on to the next critical speed. These are the critical resonances which are encountered in running up or slowing down a centrifuge to a desired rotation rate and these oscillations at the critical speeds will cause remixing of components and, if the centrifuge has not been designed properly, fracture of the rotor. It is further found when

considering the presence of internal and external friction that these critical speeds become critical regions through which lateral vibrations are sustained. Further, there may be a tendency to self-induced transverse vibrations at speeds other than the critical. In running up a centrifuge to a rotation above a critical speed, energy much be supplied; and thus, whether fixed or free, the critical resonance and the tendency to self-induced oscillations will be encountered during this phase and also during slowing down. It is in the operation at constant rotation rate that the free and supported centrifuges differ as has been stated above.

In practice, of course, no shaft or centrifuge rotor can be made perfectly straight or uniform in mass distribution. Thus practically we should begin with an initial bent configuration and a mass eccentricity distribution. Initially the problem we chose had no internal or external friction terms. The reason for this is that at this time we want to make a rough comparison of the critical speeds of a bearing-free centrifuge and a centrifuge constrained at each end by self-aligning bearings. Further analysis should be performed that will include both external and internal friction, mass eccentricity distribution, etc.

Sketches of the fundamental shapes associated with various resonant frequencies for both a free rotating shaft and a rotating shaft with self-aligning bearings are shown in Figures 1 and 2 respectively. Mathematical solutions for both cases were obtained (by G. Wouch) and are reported in the first quarterly progress report under this contract. The conclusions are summarized in Table I as the ratio of critical frequencies of free and restrained rotors.

TABLE I

Ratio of Critical Frequencies of Free and Bearing-Restrained Rotors

Mode	2	3	4	5	6
Free / Self Aligning	2.2	1.5	1.3	1.2	1.2

The ratio of critical frequencies is 2 for ω_2 and the free shaft's critical frequency is twice that of the shaft with self-aligning bearings.

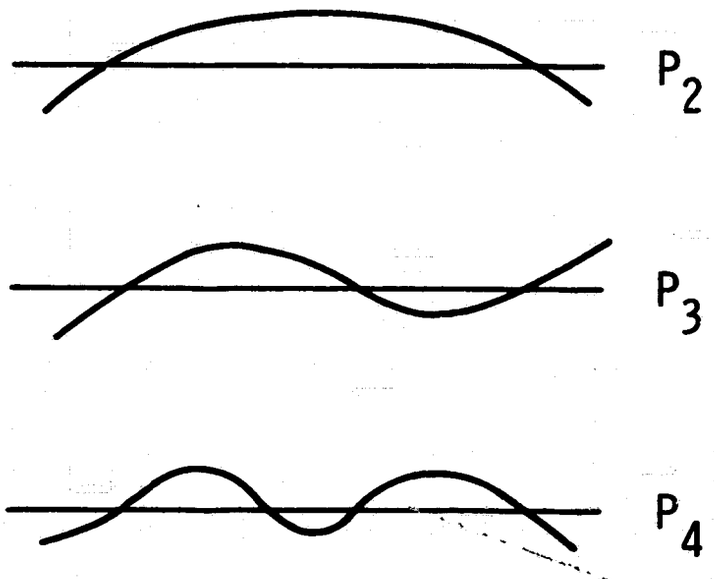


Figure 1. Fundamental Shapes Assumed by a Free Rotating Shaft

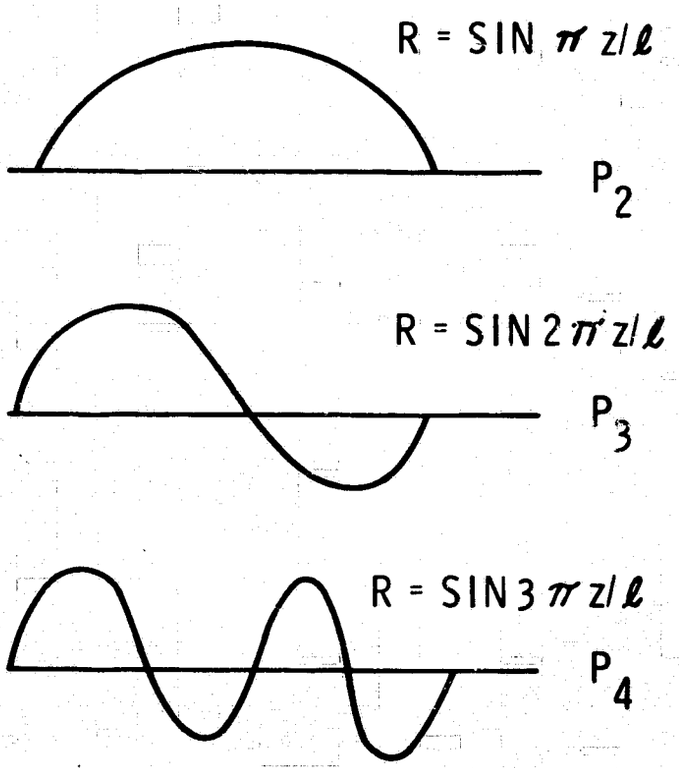


Figure 2. Fundamental Shapes Assumed by a Rotating Shaft with Self Aligning Bearings

We have considered here basically a bearing-free centrifuge and a centrifuge constrained at each end by self-aligning bearings, neglecting the external friction and internal friction terms. There are two basic conclusions that can be drawn from this simple comparison:

1. The first critical frequency of the free centrifuge is about twice that of the constrained centrifuge so that it could be operated at about twice the rotation rate of the constrained centrifuge before the first resonance is encountered;

2. The shapes assumed by the free centrifuge are different from the constrained centrifuge and there is a smaller deviation from the unbent configuration for the free centrifuge than for the so constrained centrifuge.

Dimentberg (Ref. 2) has succinctly and concisely summarized the steady state behavior of a rotating shaft: "The following picture can be built up for steady state movement of an unbalanced shaft at a constant speed of rotation. Under the action of unbalance forces and inertial forces, the shaft is subjected to static bending; its spatial elastic line is the superimposition of the harmonics of successive orders $(1, 2, 3, \ldots)$ each of which lies in a certain plane, the planes of the harmonics generally being different, since the coefficients are complex. The combination of the planes with the harmonics lying in them forms a 'rigid' configuration, rotating with the shaft with an angular velocity ω. The relationship between the moduli of the harmonics and also between their phases are disturbed when there is a change in the angular velocity ω." The effects of external and internal friction have not been considered.

Explicit in the development of the basic equations of the rotating shaft, neglecting friction terms, are the presence of external torques and forces. Driven centrifuges on the earth will indeed have unbalance forces and torques exerted on them even at constant angular velocity and so are treated either as rotating shafts with a disk attached or as rotating shafts. A bearing-free centrifuge rotating at constant angular velocity does not have this source of energy, and the dynamics of a free centrifuge rotating at constant angular velocity are very different from those of centrifuges on the Earth.

ELECTROPHORESIS

Electrophoresis refers to the movement of colloidal particles and macromolecular ions under the influence of an electric field. It is often the only method available for the quantitative analysis and fractionation of biological materials. While early work with the process was based on fluid suspensions, the difficulties imposed by convection and sedimentation have caused most of the recent work to be performed on a solid support such as paper or in gel-filled apparatus. There are cases, however, where successful purifications have been accomplished only in fluid sols. But while minute amounts of material can be fractionated for analysis by zone electrophoresis in the fluid state, the use of this technique on a preparative scale is severely limited by convection and sedimentation. It therefore appears to be desirable to operate a fluid state electrophoresis apparatus in space where convection and sedimentation would not be problems. It appears that a relatively simple apparatus could be designed for such an experiment. The primary requirements are that the apparatus remain filled with liquid regardless of addition or removal of material and that the apparatus be capable of being filled or emptied without being opened. We believe that both these requirements can be met.

The basic concept behind electrophoretic separations is the difference in rate and direction of migration of the components of the sol in the presence of an electric field. A sol containing many components will tend to separate into bands of a single species and if all the components have the same sign of charge the bands or zones will drift with velocities characterized by their respective electrophoretic mobilities toward either the cathode or the anode and could ideally be collected as they approached the electrode one at a time. This would be the ideal case of zone electrophoresis. Unfortunately there are many practical factors which make this ideal separation process more difficult, especially for scaled-up production.

While it is by no means the only consideration, the elimination of convection has been a major driving force in the development of paper electrophoresis, electrochromatography in slabs of porous material, continuous flow electrophoresis, and column electrophoresis in granular media, gels, and density gradient solutions. These methods have met varying degrees of success, but all

introduce some new problem such as loss of electrophoretic mobility, electroosmosis, precipitation of colloids, contamination of product with gel or density gradient material, minute sample size, and poor resolution.

The simplest effective electrophoretic apparatus is that of Tiselius (Figure 3). "The U-tube portion is in three parts, 1, 2, 3, which can slide horizontally with respect to one another. The lower parts 1 and 2 are filled with a buffer solution of known pH in which the proteins are dispersed. The part 3 which has been pushed aside, is then filled with the buffer solution alone and slid over to complete the U tube and establish a sharp boundary in each limb. Each of the large vessels 4 contains a silver chloride electrode 5. In the immediate vicinity of the electrode material is a concentrated solution of alkali-chloride, but the remainder of each of the vessels is filled with the same buffer solution as in the U tube, so this is continuous through the apparatus. A source of E.M.F. is then applied to the electrodes and electrophoresis commences; separate boundaries are formed due to the different speeds of the different protein molecules at the pH of the medium. By keeping the temperature at about $3^{\circ}C$, the point of maximum density of the buffer solution, convection effects at the boundaries due to heating by the current are minimized." Schlieren optical techniques are used to observe the positions of the boundaries. The sharp change at a boundary becomes apparent as a peak in the Schlieren pattern, and each boundary produces such a peak. A typical pattern is shown in Figure 4. For substances of low molecular weight, high voltages are generally employed because during a long running time the zones will tend to spread due to diffusion and good separations may not be obtained. For substances of high molecular weight, longer running periods can be employed because diffusion is relatively slow. This is advantageous in biochemical work because relatively low voltages and long running times may be employed to effect a separation.

Zero-gravity electrophoresis might be carried out in a straight glass tube with electrodes at either end and a means of collecting the fractions. It may be necessary to immerse the electrodes in potassium chloride solution and to isolate them from the sample with glass frits. Low voltages and long running times are contemplated. Initially non-hazardous biological materials should probably be separated. The initial experiment might involve a

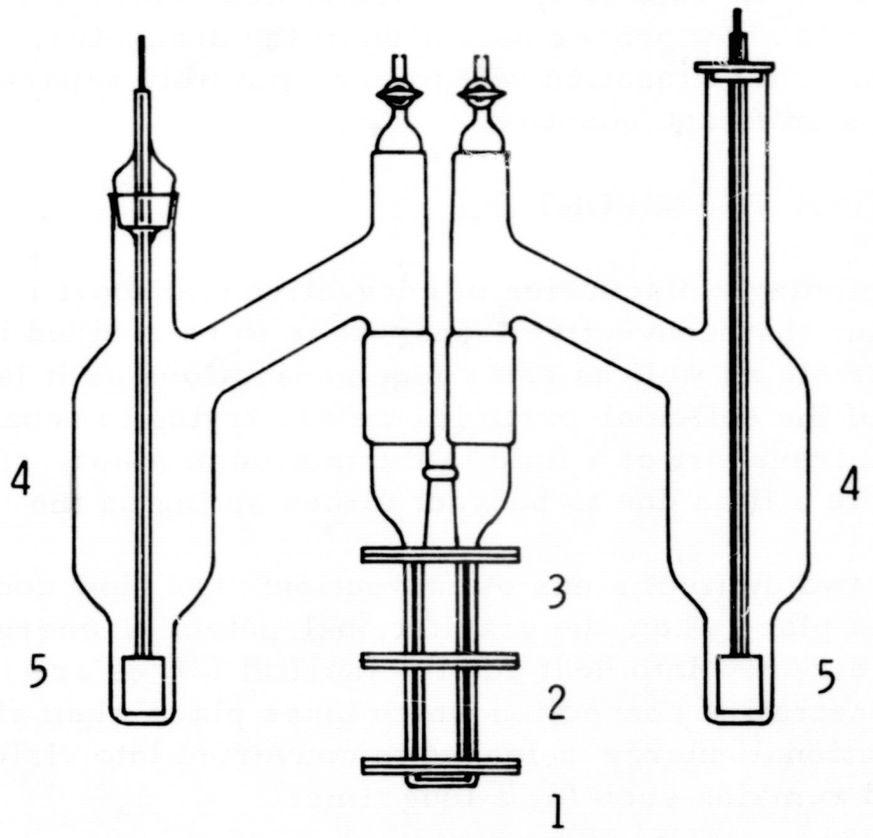


Figure 3. Tiselius Apparatus

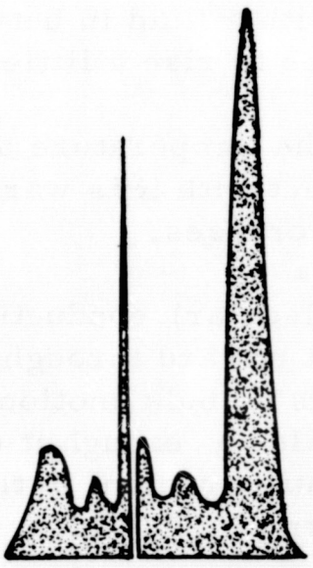


Figure 4. Typical Schlieren Pattern for Separation of Proteins

simple scaled-up replication of some typical blood serum separations to show proper operation of the apparatus. Then a more valuable fractionation will follow, possibly separation of a vaccine in significant quantity.

CONVECTIVE TRANSPORT

Before beginning a discussion of convective transport it is well to keep in mind that convective transport is to be avoided in electrophoretic as well as centrifuge separations as it leads to remixing of the colloidal particles we are trying to separate. Convective transport of a fluid is the motion of a body of fluid immersed in a fluid due to buoyant forces acting on the fluid body.

There are two distinct kinds of convection: (1) slow convection which takes place when the gravitational potential energy is converted directly into heat and the inertial forces are negligible; and (2) penetrative convection which takes place when almost all the gravitational energy released is converted into visible bulk motion and remains such for a long time.

SLOW CONVECTION

Slow convection can be set up in the following way:

- Consider two metal plates placed horizontally one above the other with a fluid in between and let the upper plate be free to rise a little

- Gradually raise the temperature of the lower plate. The fluid in contact with it is warmed, it expands and its density decreases.

- The thermal (molecular) conductivity of the fluid will transfer heat upward through the layer of fluid even when there is no bulk motion. If the lower plate is warmed slowly enough it can be ensured that the temperature gradient in the layer is practically uniform.

The criterion for warming up the bottom plate without setting the fluid in motion is that the thermal conductivity must transfer heat upward to the cold plate more quickly than if there were some motion.

If motion does take place it must be upward in some places and downward in others. See Figure 5. Warm fluid at A will be placed side by side with cool fluid at B_1 and B_2 and the thermal conductivity will begin to conduct heat horizontally, which will take heat from the fluid going upward and give it to the fluid going downward. This is a tendency to oppose the conduction of heat upward. These adjacent layers can not be far apart because the fluid would have to travel a large horizontal distance on reaching the other plate in order to return (a great deal of gravitational potential energy would have to be expended against viscosity in this horizontal motion and also a particle travelling to A would acquire enough heat to rise long before it reached A). They can not be too close because in addition to the wasteful horizontal conduction there would also be viscous forces resisting the relative motion of the closely placed up and down currents.

There is one optimum configuration (Figure 6) which can occur if the temperature gradient exceeds a certain minimum value related to viscosity and thermal conductivity. The shape of the cells is independent of the actual values of the physical quantities and is the same in all fluids (hexagonal or square). Experimentally it has been established that the direction of motion in the center of the cell is toward the region of smaller viscosity and for gases μ is proportional to T (downward at the cell center), for liquids μ is proportional to T^{-1} (upward at the cell center).

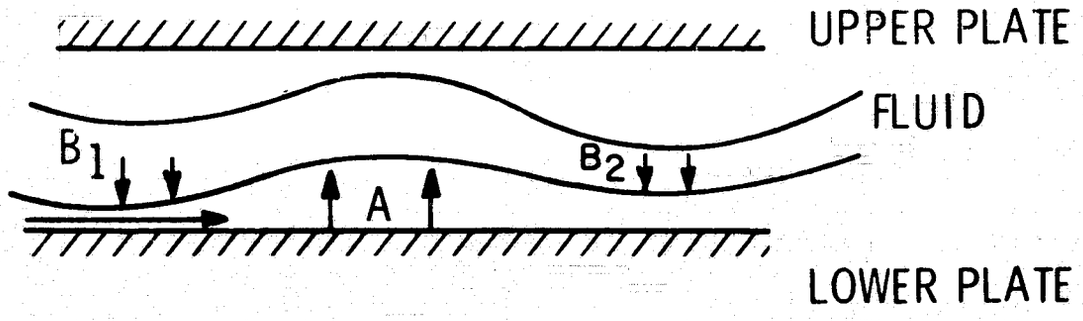


Figure 5
Incipient Slow Convection

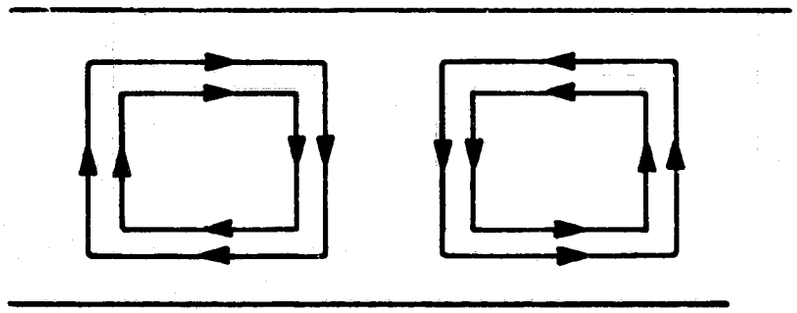


Figure 6
Representation of Slow Convection

The conditions under which slow convection is initiated are calculable from properties of the fluid. The density gradient required to start motion is:

$$\frac{g(\rho_b - \rho_t)}{L\rho_b} = K\left[\frac{\kappa}{\rho_b C_p}\right]\left[\frac{\mu}{\rho_b}\right]\left[\frac{1}{L^4}\right] ,$$

where:

g	=	gravitational acceleration	η	=	thermal conductivity of fluid
ρ	=	density			
L	=	height of layer	μ	=	viscosity of fluid
K	=	reciprocal of the Rayleigh number	C_p	=	specific heat capacity

subscripts "b" and "t" refer to "bottom" and "top"

Rayleigh found that

$$K = \frac{27}{4}\pi^4 \approx 670$$

though other values as high as > 1700 have also been reported.

Expressing density differences in terms of thermal expansion coefficient and temperature differences, and rearranging terms gives the equation in the form

$$\frac{g \rho^2 \beta C_p L^3 \quad Tb - Tt}{\kappa \mu} = K$$

It is found that, K, the reciprocal of the Rayleigh number depends upon:

(a) the motion is slow: the inertia forces are negligible (Reynolds Number small)

(b) the temperature and density differences are small, being only small fractions of their absolute values

(c) β, κ, C_p, μ are independent of temperature over the range

(d) the conditions at the boundary are the same for temperature and velocity,

(d) all the heat that goes in at the bottom comes out at the top.

PENETRATIVE CONVECTION

Putting in heat too rapidly means that requirement (a) above is violated, the motion is not slow and the inertia forces are not negligible so gravitational potential energy is converted into bulk motion as well as heat. The warm fluid rises in lumps, hits the other surface and spreads out forcing fluid down. The cells appear to grow from nothing to a very large size, and as they get bigger cells form within them giving rise to a quite chaotic and undesirable mixing motion as shown in Figure 7. A free upper surface becomes noticeably unlevel and may bulge upward if the bulk motion is large enough.

If (a) and (c) are violated then motion described above occurs. The lumps are called thermals. The thermals mix with the surroundings as they advanced and grow bigger. Between the core and the surrounding fluid where the density gradients are greatest the fluid is made to rotate. It is carried around into the rear of the thermal.

When it reaches the central region the vorticity begins to be slightly reduced because the fluid surrounding it is now more buoyant. The core is forced to advanced within the thermal because it is the most buoyant part of it. The points of zero motion relative to the thermal advance outward along the line bounding the region of mixing.

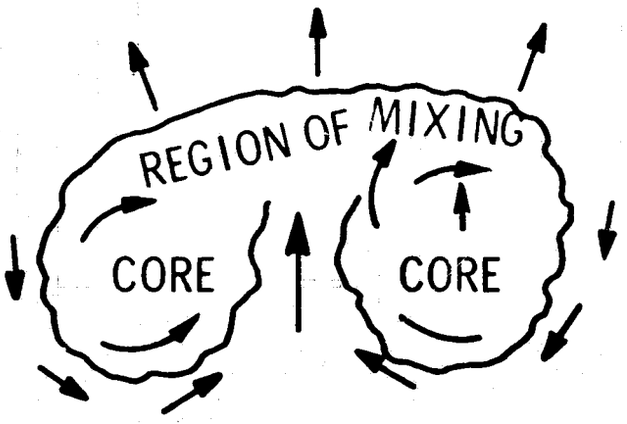


Figure 7. Penetrative Convection

FREEZE-DRYING

Lyophilization or freeze-drying is the removal of water from biological materials while in the frozen state. This process has long been used for the preservation of certain biological and biochemical properties. More recently, it has gained wider application in the preservation of organs and blood supplies.

Lyophilization may be a necessary adjunct to other processes carried out with biochemicals in space. For instance, if a separation process such as centrifugation or electrophoresis is used to purify a vaccine, lyophilization will be desirable or perhaps necessary to maintain the potency and safety of the product until the next shuttle can return it to earth.

Of further interest is the use of special lyophilization conditions for the production of unique biological products. In this category we may consider the preparation of vaccines for rabies or the arbor viruses. In both of these cases, the ability to produce suitable

vaccines has been limited by the difficulty of inactivating the viruses in a manner that suitably preserves the antigenicity (immunizing capacity) of such vaccines. We have preliminary evidence from our own experiments that high vacuum conditions may hold an answer to these problems.

A great deal of related work on the lyophilization and preservation of biological materials is available in the literature. We have conducted extensive experiments on the characteristics of lyophilized virus and virus antigens. Although some such preparations have indeed been very successful, a number of problems still remain which are difficult to resolve with existing equipment. When lyophilizing extremely minute volumes of viruses, we have been able to demonstrate that the bound water of the virus particle can be removed in a manner which inactivates the virus. Presumably, since the protein antigens may not depend on their water content, one can expect that the antigenicity will be preserved while it may be possible to destroy the dangerous viability. The investigation of this phenomenon is a space laboratory may be warranted as an adjunct to other processes.

Additional work has been done on the problem of the passage of water vapor through semi-permeable membranes of various polymer or rubber compositions. It appears feasible to permit lyophiliz ation through such membranes in space. Such an enclosed lyophilization procedure would have a number of advantages. It would, for instance, permit the lyophilization of important but very dangerous agents in a manner which would not create hazards. This technique may be essential for space lyophilization since the product could not easily be contained without gravity. Even in ordinary lyophil apparatus the fluffy, dried powders tend to escape." *

A space experiment on the freeze drying of virus is recommended. As currently visualized it would consist of a small (perhaps 6" x 6" x 6") chamber connected by a several inch diameter (valved) pipe to the exterior vacuum in the wake of the spacecraft where reportedly a very low pressure (10^{-10} to 10^{-12} torr) may be available. A heat pipe or similar heat transfer device would permit the initial freezing of the product and would be used in conjunction with heaters to control the product at the desired temperature.

*Private communication by Dr. B. A. Rubin

The initial experiment could be performed with or without the use of a condenser to collect the effluent water; however, it is envisioned that any eventual scale-up of this type of process would involve recovery and reuse of the water for economy reasons.

Artist's sketches of equipment for space experiments with Free Rotor Centrifuges, Zero-G Electrophoresis, and Freeze-Drying are shown in Figures 8, 9 and 10 respectively. In Figure 8 a free rotor centrifuge (lower right) is shown with a torquer (lower left) which would be used on two rotors to spin them in opposite directions. The centrifuge has a chamber containing tanks to hold the various solutions and suspensions used in the preparation and purification of biologicals. Figure 9 shows a fluid filled electrophoresis cell for use in space experiments. Figure 10 is a freeze drying chamber for vaccines or other chemicals. A heat pipe, the small tube in the lower left, is a potential means of providing cooling to the sample holder plate. The valved vacuum pipe is shown as extending through the rear bulkhead of a space vehicle to permit use of the reportedly very low pressures achievable in the wake of the vehicle.

ACKNOWLEDGEMENT

The ideas and work behind this presentation are by no means entirely that of the authors, although they accept the responsibility for the presentation. Many of the ideas and analysis came from others and in particular, Dr. R. T. Frost and Gerry Wouch, of General Electric Space Sciences Laboratory and Dr. B. A. Rubin of Wyeth Laboratories, deserve great credit for their contributions to this work.

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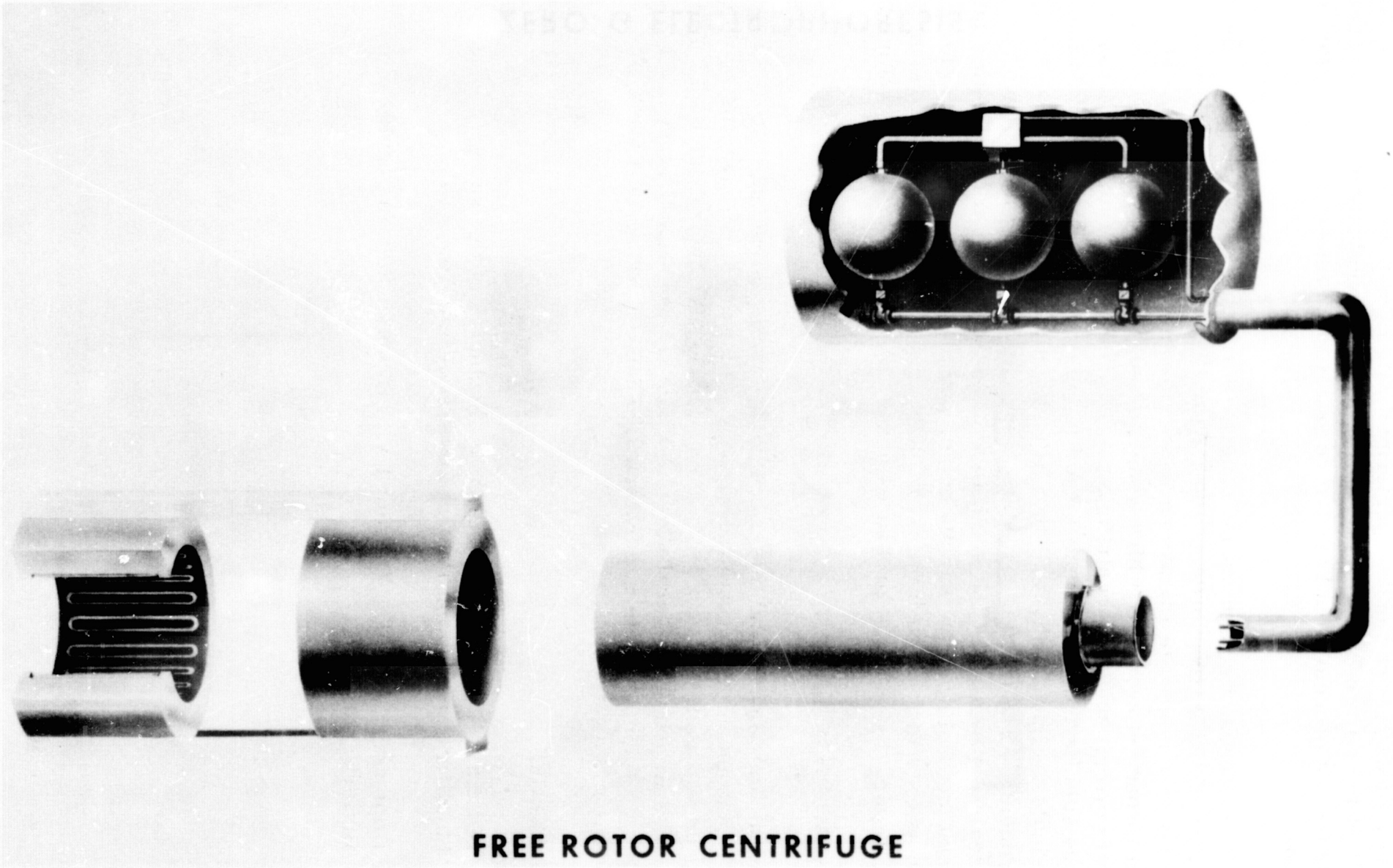
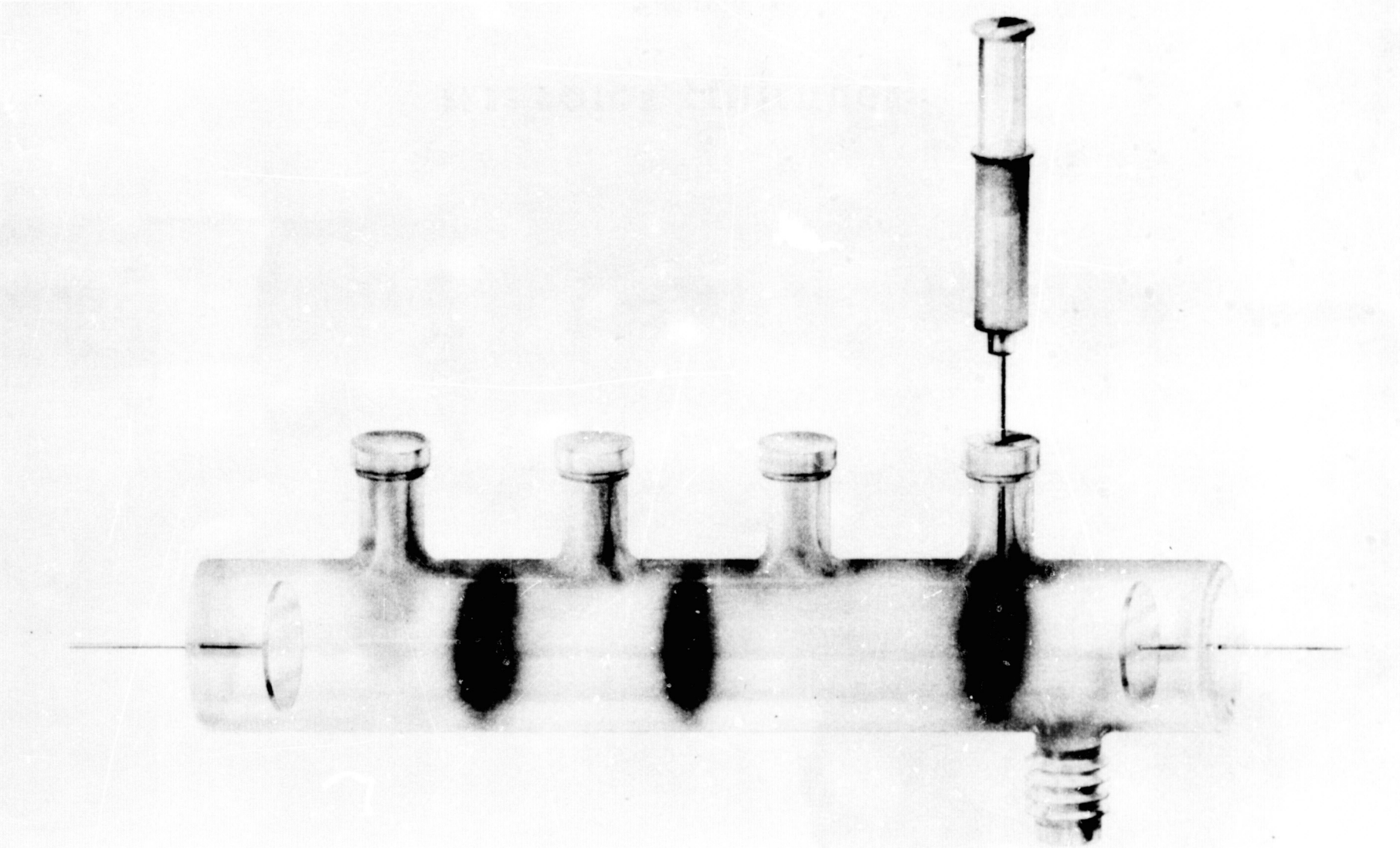


Figure 8



ZERO-G ELECTROPHORESIS

Figure 9

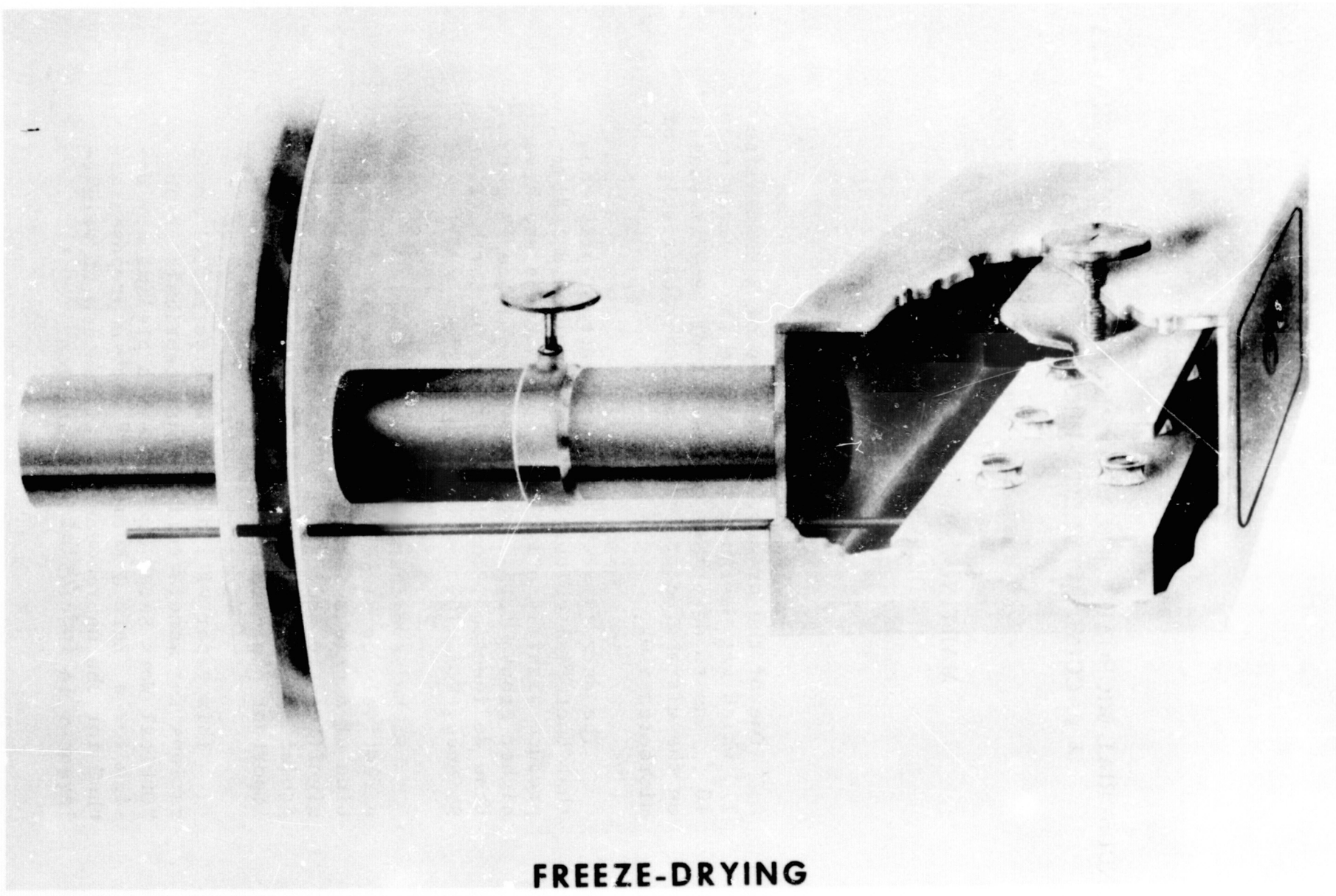


Figure 10

N70-20529

INDUSTRIAL MICROBIOLOGICAL APPLICATIONS IN ZERO GRAVITY A VACCINE SATELLITE PROGRAM (VACSAT)

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ABSTRACT

One of the primary objectives of Biosatellite II, which was designed to minimize the g force to 10^{-5}, was to determine the effect of weightlessness on the ultrastructure and growth characteristics of microorganisms.

The data from these experiments clearly show that bacterial cultures grown in a liquid medium produce significantly larger populations and have higher growth rates, as a result of space flight, than do identical control cultures on Earth (BioScience, Vol. 18, No. 6, June 1968).

We believe that zero g and dialysis can be effectively combined for the design and fabrication of a unique fermentation apparatus which will significantly increase product yields and shorten production times of a large number of medically important pharmaceuticals.

This paper will discuss some potential applications for manufacturing pharmaceuticals in an "Orbital Work Shop" and present a preliminary design for a "Zero G Fermenter" with a proposed method for the unprecedented utilization of weightlessness in industrial fermentation.

SUMMARY

1. A method is proposed for fermentation dialysis in zero g. The concepts, theories, designs and applications described for microorganisms, also apply to mammalian cells.

2. Biosatellite II experiments clearly show that bacterial cultures grown in a liquid medium produce significantly larger populations, and have higher growth rates during space flight, than do identical cultures on Earth.

3. Increased microbial populations and higher growth rates in zero g are believed due to (a) random cell distribution with increased efficiency of nutrient transfer into the cell and waste transport from the cell, (b) multidimensional growth in zero g compared to two dimensional growth on Earth, plus various physical chemical and environmental factors such as improved oxygen diffusion, absence of bacterial sedimentation and better foam control during aeration and laminar flow mixing.

4. Dialysis has been shown to prolong active multiplication of microorganisms and produce higher maximum populations.

5. It is believed that dialysis can be effectively combined with the design and fabrication of a unique zero g fermentation apparatus to significantly increase product yields and shorten production times of a large number of medically important pharmaceuticals.

INTRODUCTION

The effective utilization of outer space for the benefit of all mankind presents one of the most challenging opportunities of our time. New technologies and capabilities developed for the exploration of space now provide tools never before available for exploitation. We believe that the important factor of weightlessness in space, coupled with readily available energy sources can be used to advantage for enhanced growth of microbial cells and increased production of their valuable metabolic end products by fermentation.

The purpose of this paper is to propose a method for fermentation dialysis of microorganisms in zero g. The concepts, theories, designs and applications to be discussed apply also to mammalian cells. Since zero g cannot be reproduced, and at best poorly simulated on Earth, arguments presented for manufacturing in hypogravity are based on extrapolations of the theory and practice of land-based fermenters.

Although industrial fermentation techniques have been known and practiced for centuries, the departure in our approach will combine the unique factor of zero g and dialysis with conventional fermentation procedures. We believe that zero g and dialysis can be effectively combined with current fermentation techniques to significantly increase product yields and shorten production times of a large number of medically important pharmaceuticals.

Since industrial fermentation is a complex series of integrated procedures, an in depth comparison of land-based fermentation techniques with proposed zero g applications would be beyond the scope of this paper. Instead, we have selected what are generally agreed to be the most critical controlling factors for a successful fermentation process on Earth, i.e.,

1. Microbial growth (growth rate and density),

2. Aeration (oxygen supply to medium),

3. Gas diffusion (oxygen saturation and carbon dioxide removal), and

4. Agitation (turbulent mixing)

as our comparative basis for justifying their use in a weightless environment. The above controlling factors of fermentation can be interrelated and optimized in zero g to provide new approaches to fermentation not possible on Earth.

BIOSATELLITE II DATA

One of the primary objectives of Biosatellite II was to determine the effect of zero g, or weightlessness, on bacterial growth and

ultrastructural changes that might be influenced by the space flight environment. The data from these experiments clearly show that bacterial cultures grown in a liquid medium produce significantly larger populations than do identical cultures on Earth.

In a personal communication, Dr. R. H. T. Mattoni, Principal Investigator for space-flight effects and gamma radiation interaction on growth and induction of lysogenic bacteria in the Biosatellite II experiments reconfirmed the results of his published report which appeared in Bio-Science (1).

In summary Dr. Mattoni stated:

> "The particular space-flight factor of interest was weightlessness. Biosatellite II was designed to minimize the g force to approximately 10^{-5}. The vehicle also contained an on-board radiation source to permit estimates of the biological effects of γ radiation interacting with space-flight factors".
>
> "The biologically important parameters to be estimated included: (1) bacterial growth - viable cell density by plate count and total cell density by electronic particle (Coulter principle) count; (2) free bacteriophage density; (3) bacteriophage produced by induced cells; and (4) ultrastructure description by electron microscopy".
>
> "The summed data for both strains of bacteria used clearly show that cultures grown in liquid media produce significantly denser populations as a result of space-flight than identical cultures on Earth".
>
> "We believe that the greater bacterial densities were a function of random cell distribution in the liquid medium under reduced gravity conditions. Such distribution would increase the efficiency of nutrient transfer into, and waste transport from, the cell".

ADVANTAGES OF ZERO G

Although the exact mechanism which could account for both higher growth rate and density of microorganisms during space flight is unknown, several physical chemical and environmental factors such as oxygen supply and demand, sedimentation of bacteria, aeration and agitation and foam control might be playing an important role.

OXYGEN SUPPLY AND DEMAND

Oxygen is a relatively insoluble gas, at 20°C and in an atmosphere of air, water will hold only approximately 9 parts per million (ppm)

of oxygen. As the temperature is raised, oxygen like any other gas becomes less soluble. At 37°C for example, water in perfect contact with air contains less than 7 ppm of oxygen. The solubility of oxygen is substantially independent of the total pressure and the presence of other gases. It is however, directly proportional to the partial pressure of oxygen in the gas phase.

Since respiratory enzymes are embedded within aqueous protoplasm, microorganisms can utilize only dissolved oxygen, even if grown at an air-water interface. Furthermore, oxygen is so insoluble that there exists at any time only a small reservoir of it in solution. Upon this reservoir the microorganisms are continuously drawing, and into the reservoir there must flow a fresh supply of oxygen to balance the demand. Because the reservoir has such a low capacity and because the oxygen demand of microbial tissue is so high, the rate of supply must at least equal the rate of demand in every portion of the culture fluid. Otherwise, there will be local or temporary depletion which damages the respiring cells. Such damage was dramatically shown by Hromatka, Ebner and Csoklich (2) who found that interruption of the airflow to Acetobacter for 15 seconds disrupted metabolism and caused death. This and other aspects of oxygen uptake by cells and tissues are fully treated in reviews by Goddard (3), Tang (4,5), and Kempner (6).

The only known way on Earth to achieve a high dissolved oxygen concentration is by bubbling air or oxygen into the intensely turbulent region at the periphery of a high speed impeller, submerged in the culture medium. The resultant upward buoyant rise is turbulent, causing a vast number of bubble collisions and coalescence (7). This loss in bubble surface areas means that the oxygen dissolution rate is inadequate for many fermentation processes.

In zero g it appe[illegible]le that swarms of minute bubbles can be formed from a sparger [illegible] laminar flow, so that micron-sized bubbles could be dispersed uniformly through the culture medium yielding the required high rate of oxygen supply.

MICROBIAL SEDIMENTATION

Because of gravity growth of living systems on Earth may be considered essentially two dimensional and oriented in a vertical configuration. For example, microorganisms grown in a standing liquid culture medium sediment at some average velocity due to gravity. Upon sedimentation, nutrients and waste gradients occur that give rise to microniches which inhibit growth and spread of the microorganisms. Pockets of central necrosis throughout the microbial population ensue due to toxic waste concentration and nutritional depletion resulting in accelerated death of all microorganisms. The absence of microbial sedimentation in "submerged cultures" grown in zero g minimizes or eliminates

nutrient and waste gradients which give rise to microniches of central necrosis. This undoubtedly contributes to the greater growth rate and density of microorganisms in a weightless environment.

One of the most important factors contributing to the death of aerobic bacterial cultures on Earth is the lack of oxygen available to the sedimented microorganisms. No other aspect of the fermentation process has received more attention from chemical engineers than the aeration and agitation of the culture medium. Aeration and agitation, in a sense, is an artificial mechanical method used on Earth to obtain the optimum "submerged culture" conditions which occur naturally in zero g. The supply of oxygen to cultures is so critical that if interrupted even briefly there may be damage to the respiring cells of highly aerobic organisms (2).

It is impossible to aerate all portions of a culture fluid without some degree of stirring. Agitation - aeration therefore comprises one of the most important elements of the fermentation process. In this discussion we are concerned with the physical rather than the biochemical aspects of oxygen uptake. Our aim is to suggest that aeration of mass cultures in zero g can be accomplished without the deleterious effects of turbulent mixing required for adequate oxygen supply in land-based fermenters. It is believed that effective aeration due to laminar flow in zero g, without the need for turbulent mixing to meet oxygen demand of growing cultures, will significantly shorten fermentation cycles, increase product yields and widen the spectrum of product synthesis.

DELETERIOUS EFFECTS OF OVER-AGITATION - MIXING

Several reports have appeared in the literature indicating that too much agitation (8, 9, 10, 11) has interferred with the yield of a particular fermentation product. It is believed that under high-speed stirring fermentation may proceed so rapidly that pH changes or degradative reactions are accelerated. Another type of artifact associated with vigorous agitation is the loss of volatile intermediates such as acetaldehyde (12) or the loss of CO_2 (13). An interesting example in which the cause of adverse results was traced, is reported by Pfeiffer and his associates. In an early study (8) it was believed that poor results in the riboflavin fermentation were caused by over-agitation and over-aeration. Later work (14), which was done on a different fermentation process, demonstrated that excessive amounts of antifoam agent could account for the low yields.

There are of course, some serious harmful effects from over-agitation. Outright rupture of the cells is appreciable, especially when there are abrasive particles present (15) or when there is cavitation (16). As fermentation reactions proceed, older cells become so fragile that high-speed agitation may well influence their lysis. Ackerman (17)

has attempted to define the limits of shear, both for breakdown of cell clumps and for cell rupture, during fermentation by providing quantitative comparisons of cell fragilities during high-speed agitation.

Relatively little work has been done on the biological effects of agitation, although Dion et al (18) observed altered morphology in Penicillium chrysogenum. Short, branched hyphae were formed when the agitation was vigorous in contrast to thin filamentous hyphae formed when the agitation was mild. Still more intense stirring of the culture caused autolysis and decreased yield of penicillin. Further breakdown of mold clumps and damage caused by shear have been reported by Finn (19). Cell damage is related to tip speed of the impeller, Midler and Finn (20).

Differences, often observed between the performance of shake flasks and stirred tanks may be as much due to the changed agitation as to any difference in aeration. This point was illustrated in studies of kojic production by Aspergillus flavus (21).

FOAM CONTROL

As a result of the passage of air most fermentation media, especially those based on complex protein materials will foam. In one g, limitation of foaming by restricting the air-flow rate or agitation intensity may result in marked loss of productivity. Baffled vessels, steam jets, ultrasonic vibrations and mechanical devices of various kinds have been used to suppress foam.. In one g fermenters, however, the use of antifoam chemicals is essential. These include silicones, higher alcohols and solutions of detergents in animal, vegetable and mineral oils. Unfortunately, the additions of antifoams are known to diminish oxygen transfer, reduce product yield by decreasing the effective operating volume of the vessel, interfere with fermentation processes in general and make more difficult the recovery of fermentation products. Due to the lack of buoyancy effects in zero g, the deleterious consequences of foaming on air-flow, loss of productivity and the use of antifoams can be largely eliminated or greatly minimized in fermentation processes.

During the past 20 years, products of oxybiotic synthesis, antibiotics and the like, have largely displaced in importance such classical anaerobic products as ethanol and butanol. The trend continues, making even more valuable our knowledge of cell respiration and aerobic tissue culture. The new era in fermentation was heralded by the introduction in 1933 of a shake-flask technique by Kluyver and Perquin (22). Developed initially for culturing molds in the laboratory, the "Schuttelkultur" method was soon adapted to a factory scale by using horizontal rotating drums (23) or vertical deep-tank fermenters with spargers and

mechanical stirrers to disperse the air. The latter type is now standard apparatus for the submerged production of vitamins and antibiotics from a variety of bacteria, molds and actinomycetes. Its historical development has been reviewed by Hromatka and Ebner (24).

Recent evidence from a number of sources has begun to demonstrate specific relationships between environment, bacterial growth rate, and the size and chemical composition of the cells. Some of this recent work and its implications for fermentation have been summarized by Blakebrough (25). The subject has been covered in depth by Nerdhardt and Magasanik (26) and Kjeldgaard (27). Critical reviews have been made by Maaløe (28), Herbert (29) and Magasanik et al (30).

The advantages of accelerated growth rates of microorganisms with increased microbial densities can best be demonstrated by specific examples taken from industrial fermentation applications and vaccine production on Earth. One of the most important benefits which might be derived from accelerated growth rates of biological systems in zero g is increased production of critically needed vaccines in a shorter period of time.

The periodic introduction of foreign strains of flu virus which resulted in serious epidemics among susceptible populations in the United States presents a recurring threat to the health and welfare of a large segment of our population. The 1967 flu epidemic emphasized the need for exploring new approaches to vaccine production. The shortage of life-saving vaccines, due to lengthy culture and testing procedures, resulted in needless suffering and loss of life. The manufacture of urgently needed vaccines in a space environment where weightlessness could play a significant role in reducing the vaccine-production process appears to be a compelling argument for instituting a program to manufacture in zero gravity.

ECONOMIC ADVANTAGES OF ZERO G MANUFACTURING

Manufacturing in space might also provide very important economic advantages. The most important factor responsible for the marked increase in the efficiency of penicillin fermentation in the past twenty-five years has been the selection of high yielding strains of the Penicillium notatum-chrysogenum group. Backus and Stauffer (31) have described the development from P. chrysogenum, mutant strains capable of producing 3000 units of penicillin per ml. A tenfold increase in titers was obtained over a ten-year period. In 1941 a unit of penicillin cost over one hundred ($100.00) dollars to make. Today penicillin costs less than one cent per unit. The dramatic reduction in costs of manufacturing penicillin is primarily due to the proper selection of penicillin producing microorganisms which can be cultured under conditions which provide accelerated growth rates with increased

microbial densities. The Biosatellite II experiments clearly show that zero g during forty-four (44) hours of space-flight significantly increased both the growth rate and population densities of microorganisms (1). The United States Tariff Commission, Washington, D.C., reported that in 1958, 200,000 pounds of tetracycline antibiotics were sold in the United States at a value of 105 million dollars. At that time, tetracyclines, had the greatest sales value of any American fermentation product. Today the demand for antibiotics of the tetracycline class has more than tripled, but the cost of manufacture has remained essentially the same. Antibiotics would therefore appear to be potential candidates for manufacture in space in order to increase production rates of antibiotics utilizing the important factor of weightlessness.

Additionally, in 1957 the United States Tariff Commission reported that 1,000 pounds of cobamide (Vitamin B_{12}) were sold for 44 million dollars ($\$44 \times 10^6$). A comprehensive survey of the literature on the microbial synthesis of natural and "unnatural" cobamides has been prepared by Perlman (32). This review, and related information compiled from other sources, indicate that manufacturing in space utilizing the important factors of weightlessness, hard vacuum and readily available energy sources could provide a natural environment for a rapid, economical and effective manufacturing space station.

FERMENTATION DIALYSIS

The design proposed for a zero g fermenter (Fig. 1) will combine the culture microorganisms with nutrient and metabolic reservoirs coupled to an effective dialysis system. In our proposed fermenter the culture vessel and the nutrient reservoir both can be of conventional fermenter design with modifications for operational use specifically adapted to zero g performance. Remote from the various reservoir vessels but connected with them by tubing and pumps is a dializer through which the culture medium is continuously circulated. An important attribute of this system is that it allows the use of membranes in sheet or tubular form, which are commercially available in a wide range of materials and types. This "dializer-dialysis system" is inherently capable of independent control of the component operations; for example, the culture can be agitated and aerated as much as necessary while the reservoir is held quiescent to help guard against contamination. Furthermore, the system can apparently be adapted to any size simply by scaling up each part in proportion. The key to effective operation of the proposed dializer-dialysis culture system is a suitably designed dialyzer coupled to appropriate aeration-agitation components for oxygen supply, carbon dioxide removal and metabolic colloid and crystalloid separation. (Fig. 2)

The main result of dialysis conditions is a prolongation of active multiplication to reach a higher maximum population, which in most

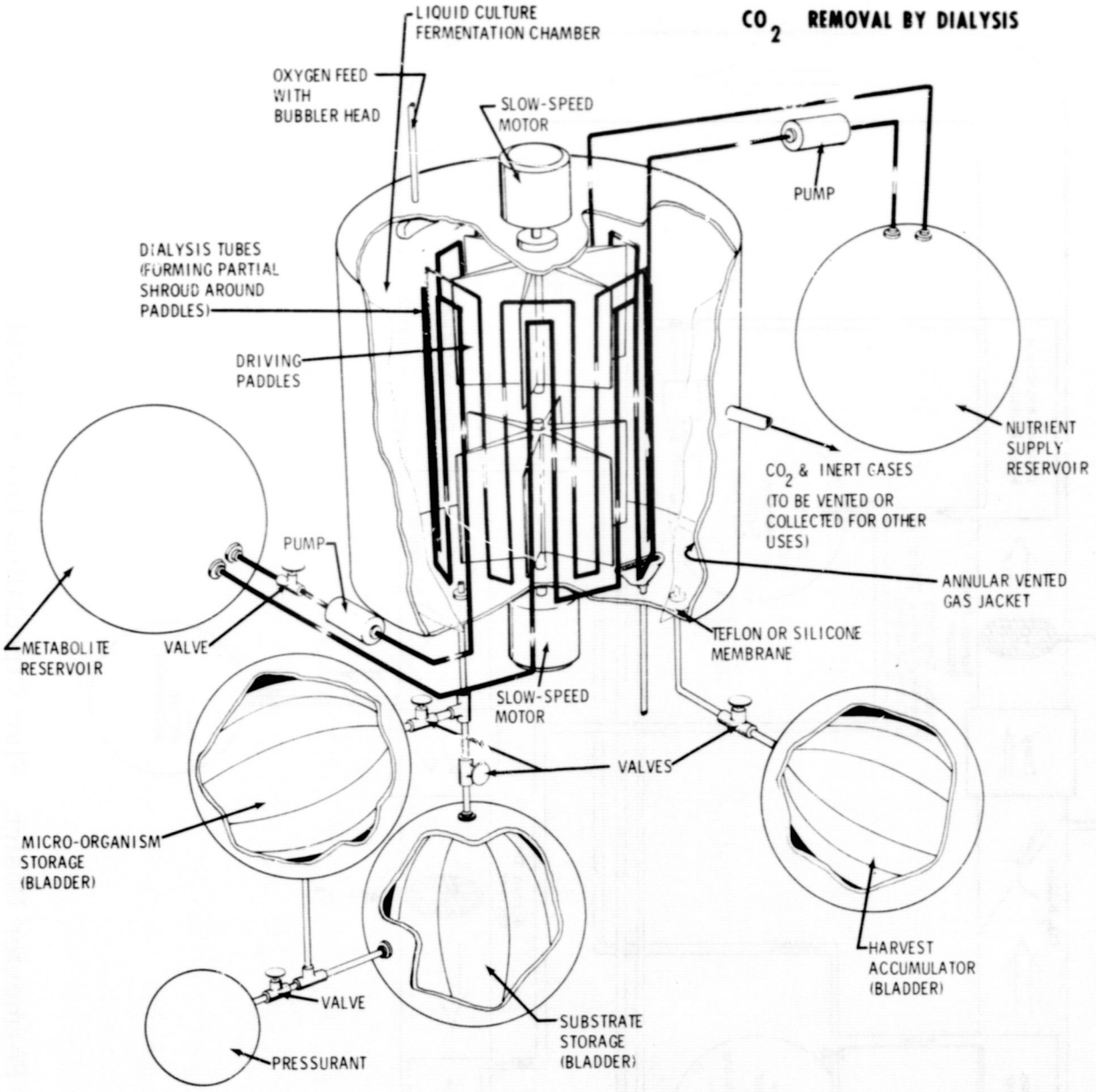


Figure 1. Zero-G Fermenter Design, Tank Type

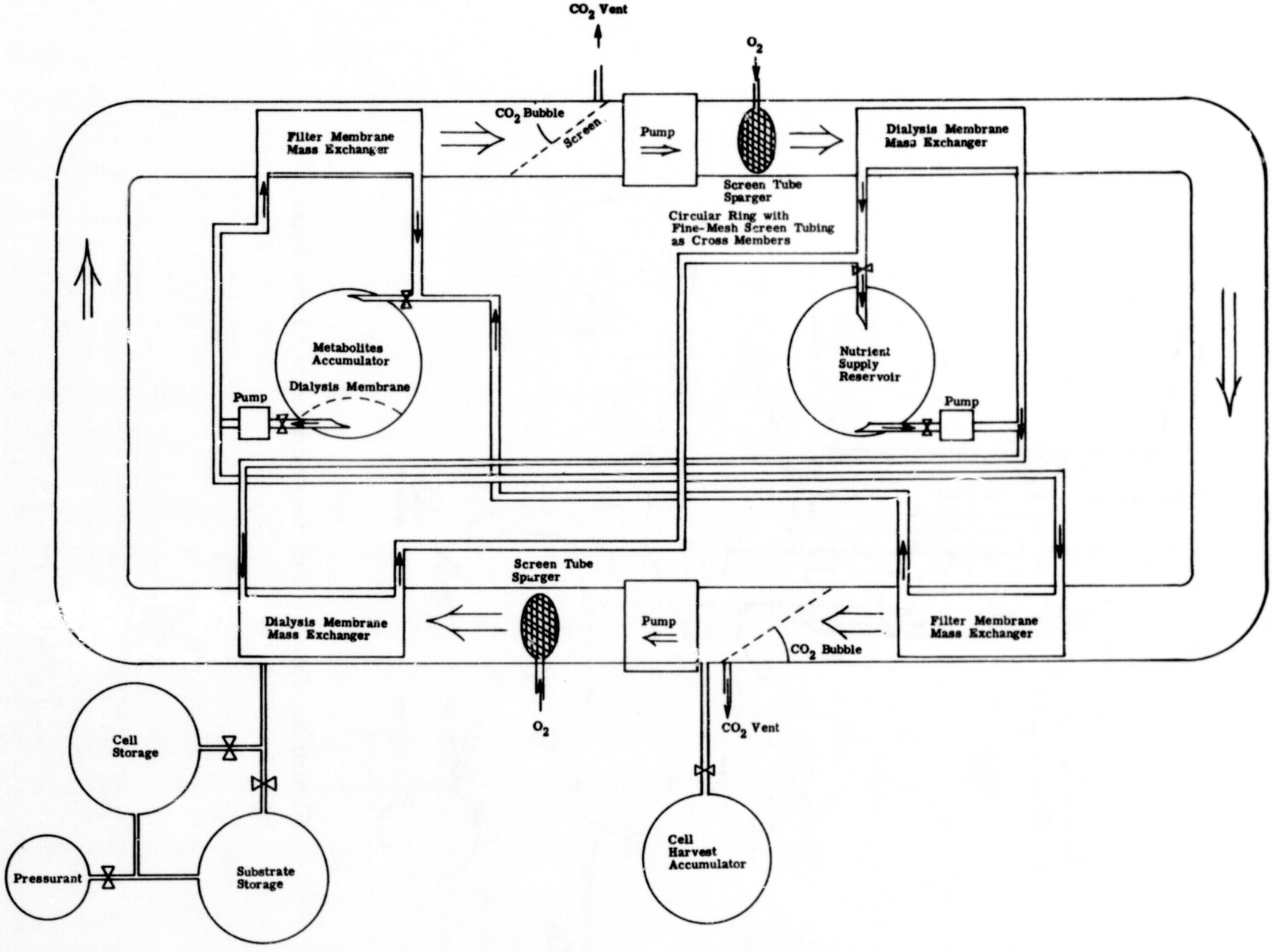


Figure 2. Zero-G Fermenter Design, Flow Circulation Loop Concept

instances is extraordinarily dense (33). This conclusion is supported by viable-cell counts during the growth cycle which have been compared with total cell counts, dry weight deoxyribonucleic acid analysis, and turbidity measurements (33, 34). Viability approximated 100% of the total cell counts throughout the growth and plateau phases of dialysis cultures, but the percentage of living cells decreased rapidly after growth ceased in nondialysis cultures.

A second main consequence of growing cells in dialysis culture is a stabilization of the maximum stationary phase and the terminal phases of the growth cycle: viability is sustained both in the culture and after cells are washed and stored (35).

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FACILITY FOR SPACE EXPERIMENTS M512 AND M479

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ABSTRACT

The capability for conducting Space Manufacturing Engineering Experiments during an Earth-orbital mission are contained within a completely integrated system.

This versatile system provides the facility for conducting six (6) experimental tasks and consists of a vacuum work chamber, a control panel and a 2 kilowatt electron beam welding and heating system. This experimental facility is shock mounted on a vibration dampening panel and attached to the M. D. A. longerons in a vertical position. The work chamber is vented through the outer wall of the M. D A. to provide a vacuum of 2×10^{-4} torr required for the experiments.

Six (6) experiments, E. B Welding, Exotherm Brazing, Gallium Arsenide Single Crystal Growth, Exotherm Composite Material Melting, E. B Metal Melting and a series of Flammability Experiments will be conducted in the facility chamber.

INTRODUCTION

The series of Material Processing in Space Experiments, as with all space exploration efforts, will be worked from the ground up. The Saturn work shop in which these experiments are to be conducted is

a cluster configuration designed to orbit beyond the earths atmosphere and in zero gravity.

Figure 1 "Apollo Application Program Cluster"

This AAP-1Cluster is made up of a S-IVB upper stage fuel tank which has been modified to provide a work shop and crew living quarters as shown in the cutaway section. Electrical power is provided by the Solar Array Wings mounted about center of the work shop. The next section of the cluster is the Multiple Docking Adaptor MDA it is connected to the work shop by an air lock. This section of the cluster houses the facility in which the Space Approved Experiments M512 and M479 will be conducted. Attached to the side of the MDA is the Apollo Telescope Mount, ATM which will be used to perform solar observation studies above the earth atmosphere The Solar Array Panels will provide electrical power for the ATM. Forward or to the left of the MDA is the Command and Service Module.

Figure 2. "The Multiple Docking Adapter"

The MDA assembly, cut away to show the M512-479 experiments facility in place, is a cylinder 10 ft. in diameter by 17 ft. in length The facility is mounted on the cylinder longerons in a vertical position with the long axes parallel to the direction of maximum acceleration. The in-line design, with the vacuum vent line connecting through the upper dome, is designed to provide maximum structural advantage during launch loading.

Figure 3 "The Space Experiment Facility"

The experimental facility, shown in the horizontal position is a (6) section, completely packaged assembly 92-inches in length mounted on a honeycomb shock absorbing, vibration dampening panel, approximately 42 x 79-inches. Especially designed containers for each experiment module will be mounted in a readily accessable position on the face of the panel

The 4-inch diameter by 42-inch long vacuum vent line assembly consists of the MDA connecting flange, the flex bellows, the valve and the work chamber connection port flange.

The experiment work chamber is a 16-inch diameter 0.060-inch thick stainless steel sphere designed to accomodate each experiment module. This chamber too is shown in detail in Figure 5.

The Control Section, which is mounted on the E B. system contains all operating controls for the E. B. system and each experiment.

The E. B. section which will also be shown in greater detail later in Figure 4, and the battery container is shown on the right end of the E. B. system.

The integrated design of the experiments facility provides for simple mechanical installation in the MDA and ease of operation during flight and in the laboratory prior to flight This complete facility is a compact package weighing about 258-pounds.

Figure 4 "Cameras, Controls and the E B. System"

The Electron Beam Welding Device is 30-inches long, 12-inches in diameter and weighs, without controls about 105-pounds. It is battery powered the battery case provides 2 KW power at 20 KV for approximately 10 minutes continuous operation. Contained within the case is the inverter power supply, power conditioning circuits, electron gun and lens. As far as is known it is the smallest 2 KW E. B. device in the World.

The control panel used for all experiment controls is positioned adjacent to the experiment work chamber door for ease of astronaut control during experiment operation The control panel is 12 x 14 inches in dimension and weighs 7-pounds.

Figure 5 "Work Chamber - Experiment in Place"

The 16-inch diameter 0.060-inch thick stainless chamber is shown with access door in the open position and the data recording Maurer camera attached at the camera view port.

Visible inside the chamber is the protruding end of the electron beam gun at the extreme right, in the center is the mounting facility common to each experiment module. The sphere shell is capable of withstanding severe pressures never attained during experimentation

and is more than adequate to protect the operator from hi-voltage radiation exposure. The view ports are made of heavy leaded glass,

Figure 6 "Controls"

The control center, a 12 by 14-inch package, is modular in design with each module engineered for a specific experiment. For example, the E. B control section contains all controls and meters required for the welding and melting experiments. The astronaut will have direct control of beam current; he can also control lens current to optimize beam focus for welding or melting. Modules for the control of the other experiments, Single Crystal Growth, Exotherm Tube Brazing and Composite Material Melting and the series of Flammability Tests are contained in the control center. These experiments which are scheduled for the Saturn Workshop I flight in early 1972, their one gravity development, the ultimate objectives and the manner in which they will be carried out will be discussed by the experimentors following this presentation

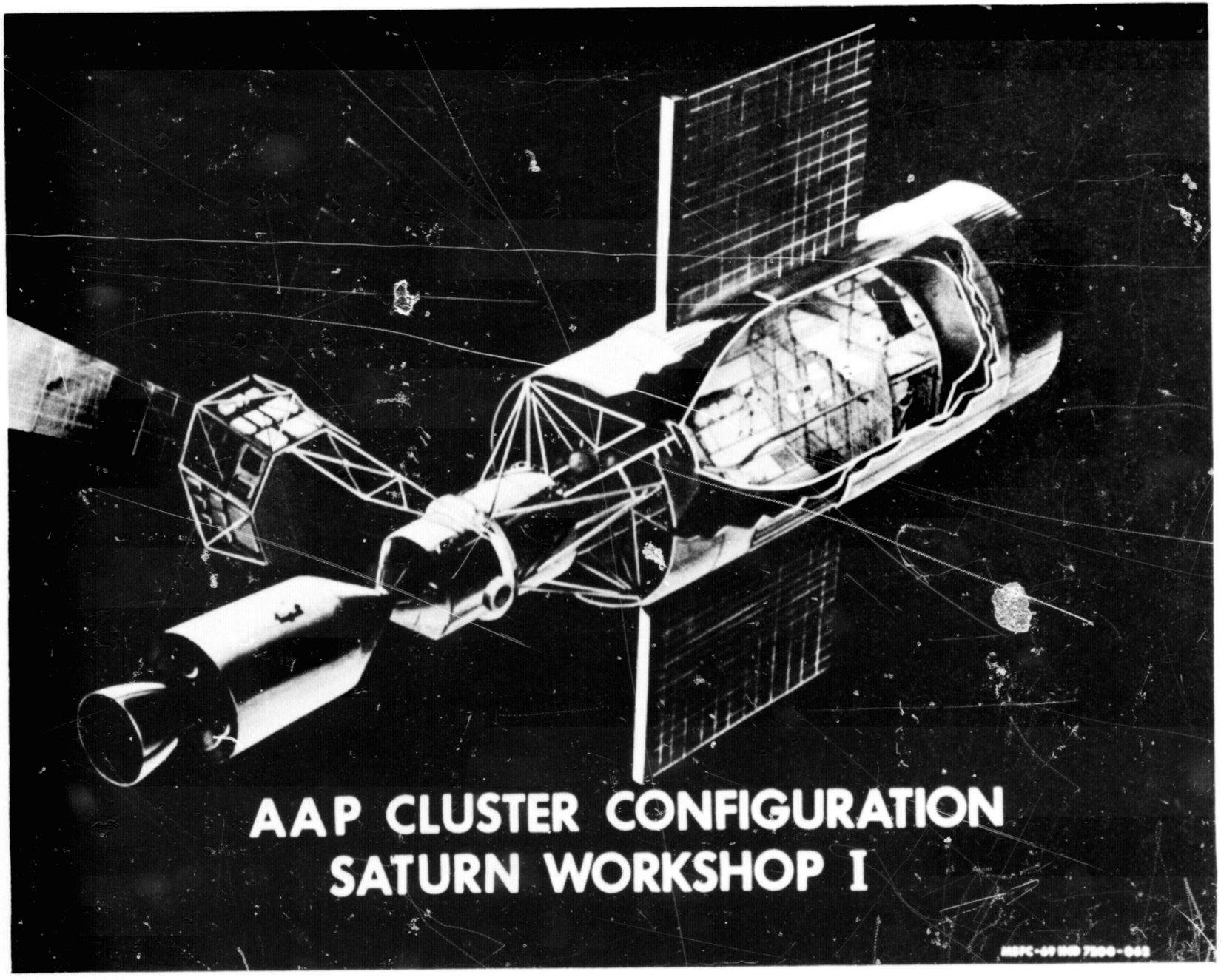


FIGURE 1

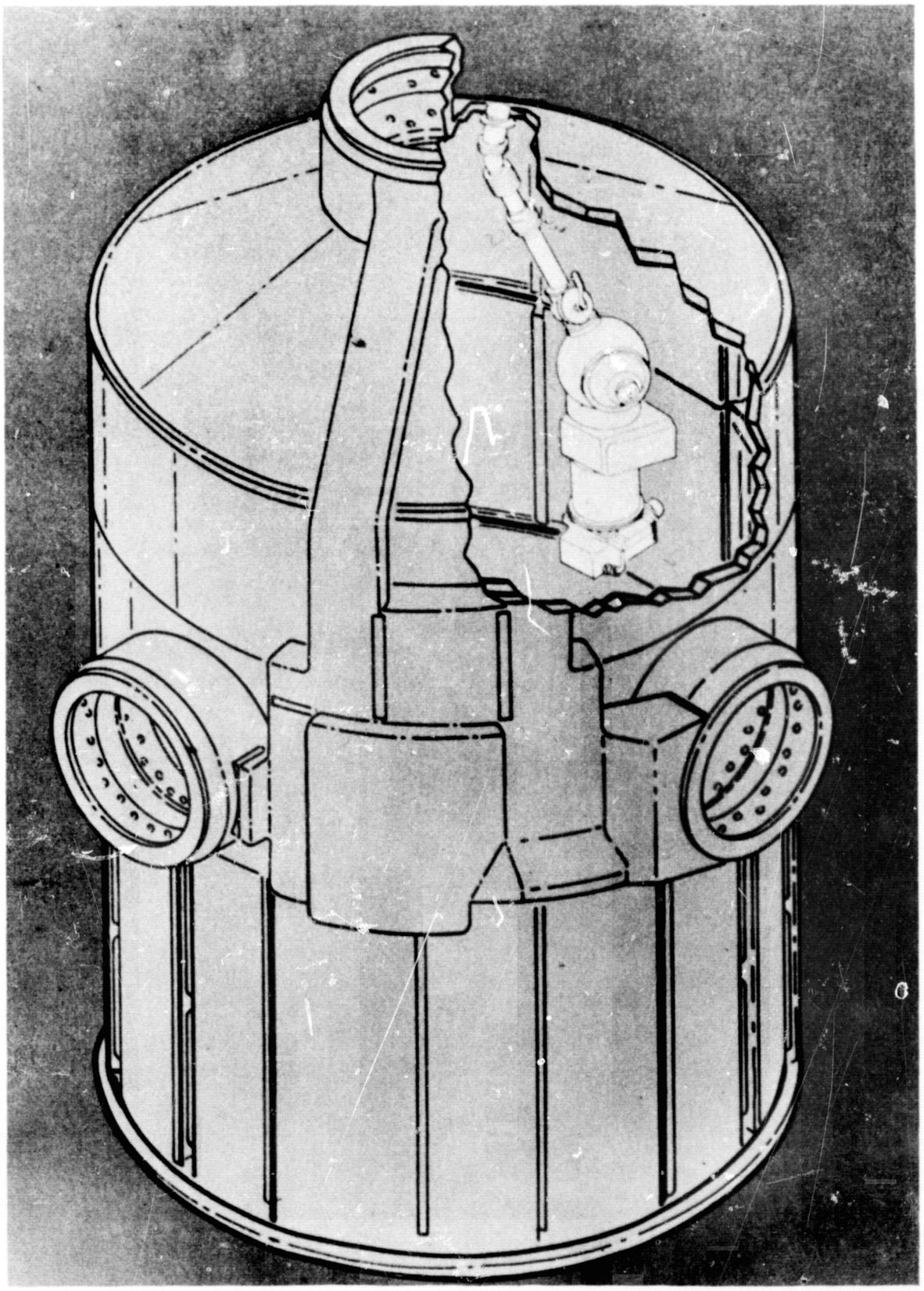


FIGURE 2. M512 AND M479 (MDA)

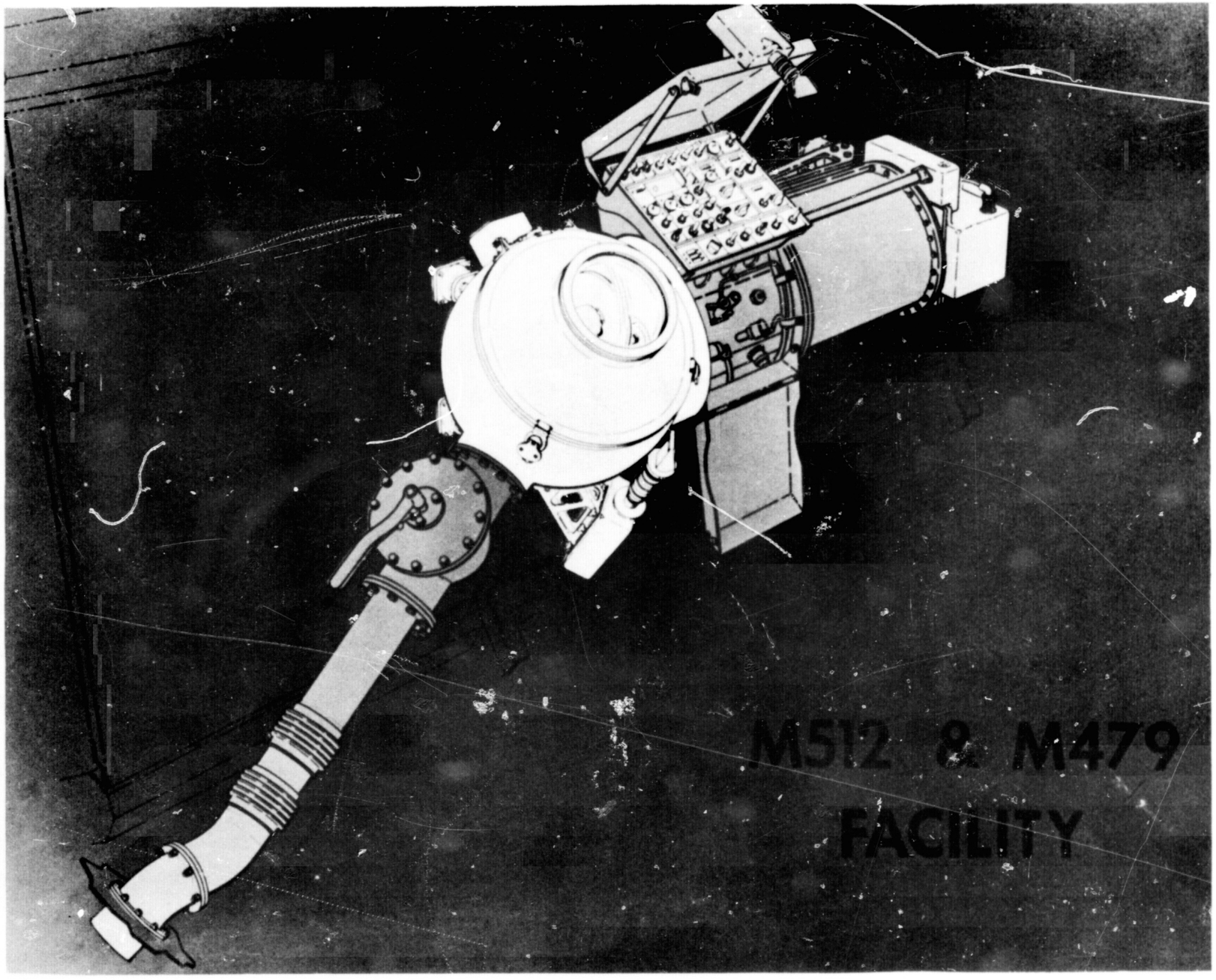


FIGURE 3

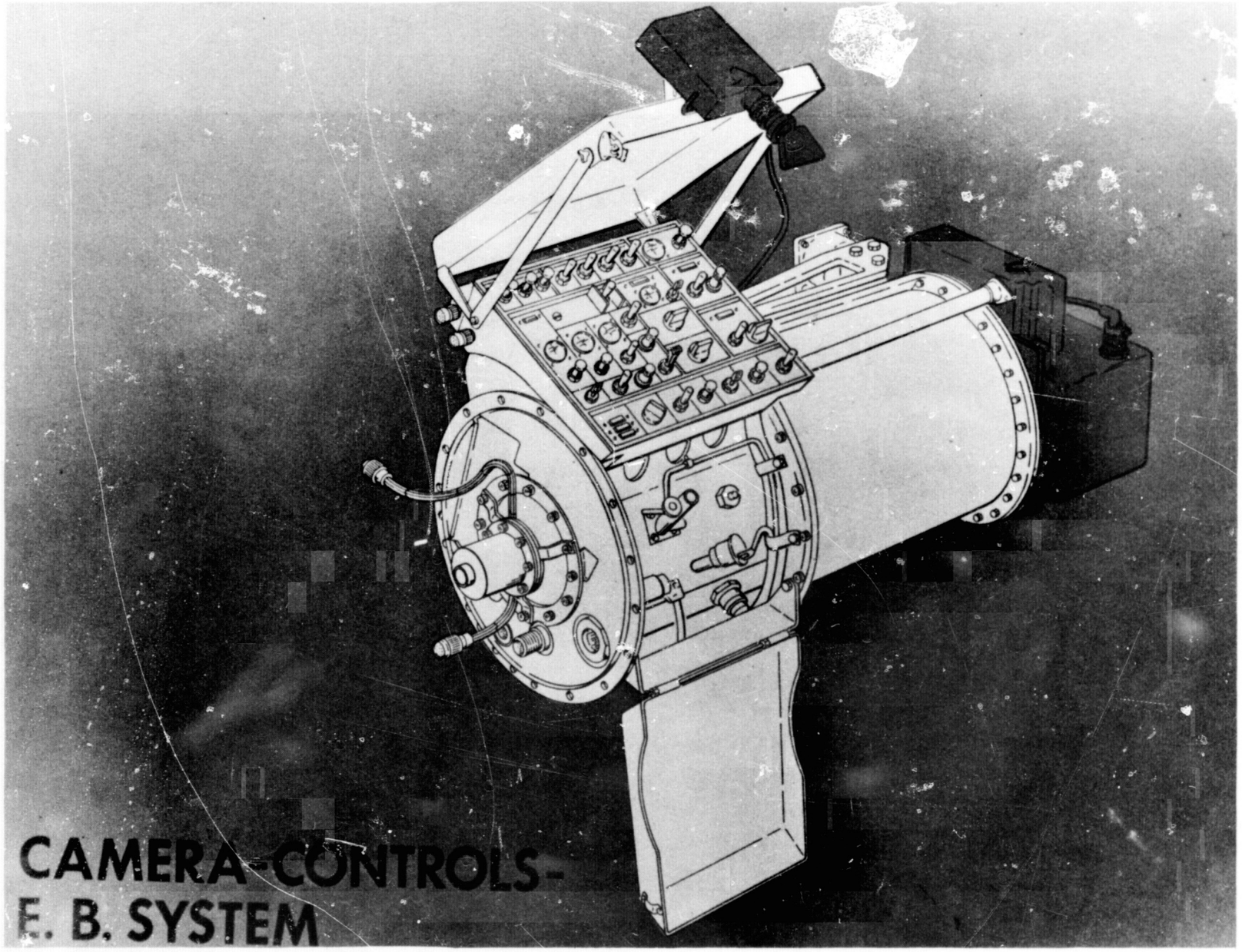


FIGURE 4

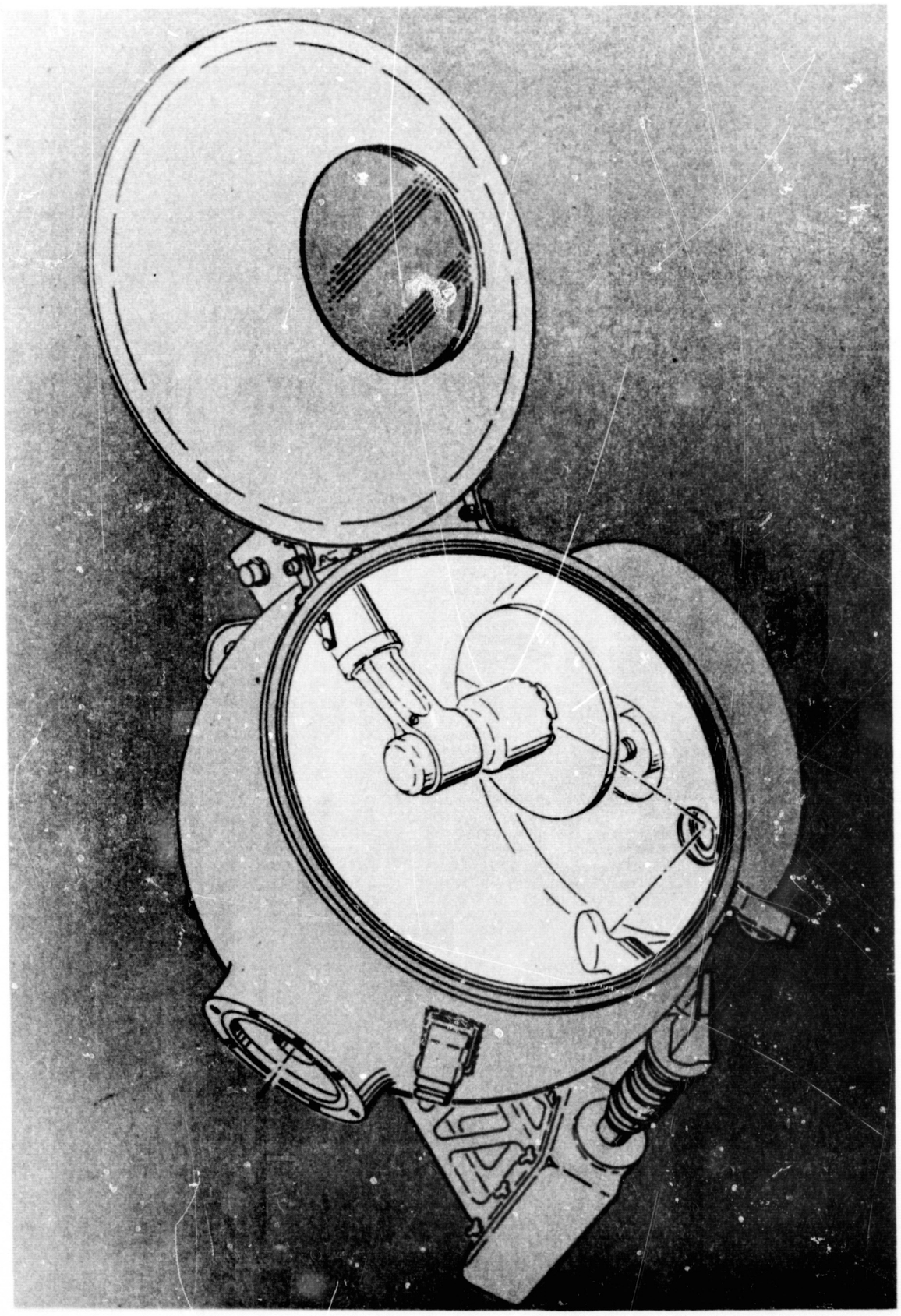


FIGURE 5. WORK CHAMBER — EXPERIMENT IN PLACE

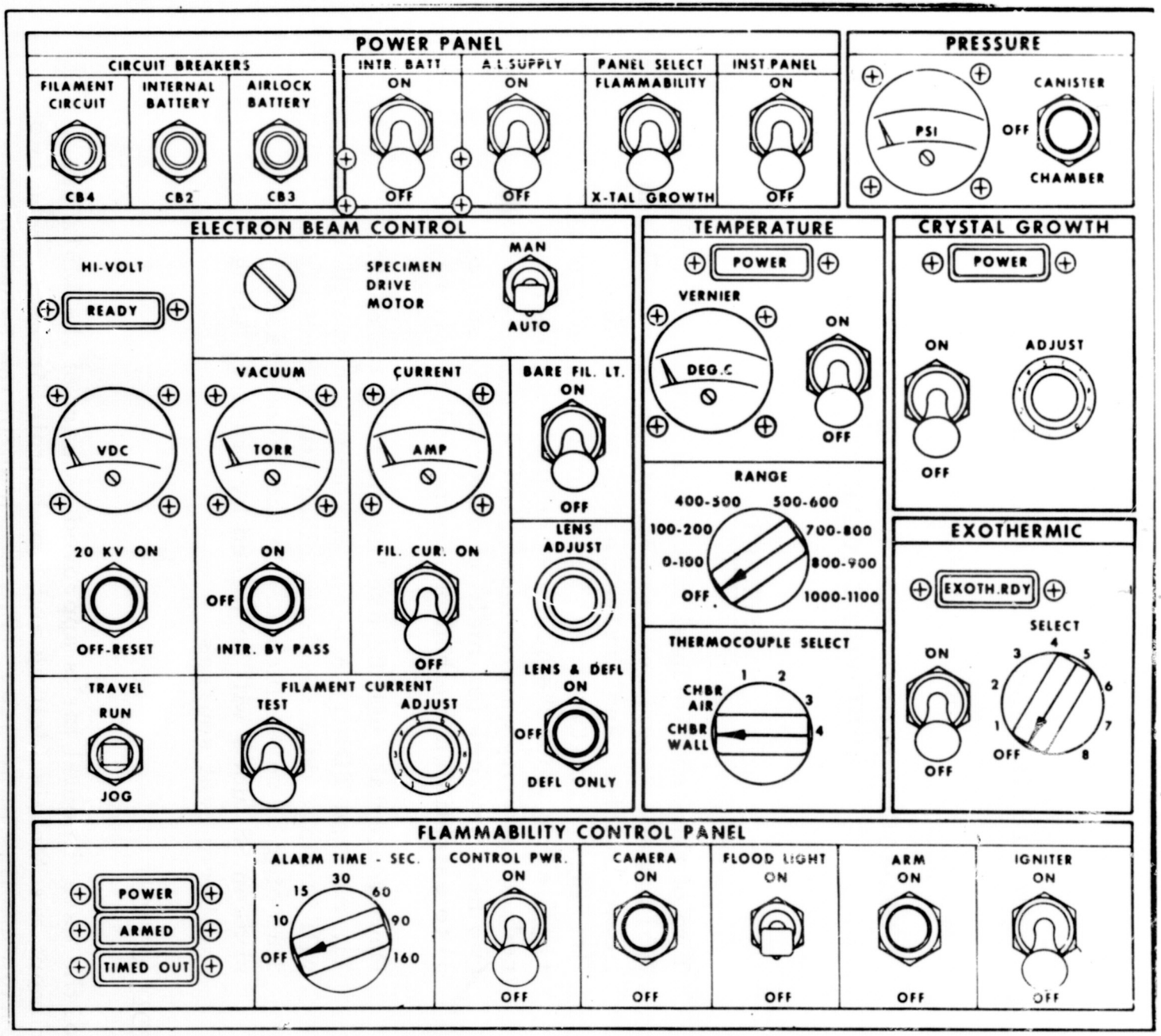


FIGURE 6. CONTROLS

N70-20531

METALS MELTING AND EXOTHERMAL HEATING

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ABSTRACT

Two of the experimental tasks approved as part of M512 space experiment are Metals Melting (Electron Beam Welding) and Exothermal Heating (Tube Brazing). The two tasks have similar objectives: 1) to learn about the behavior of molten metal in a reduced gravity environment, and 2) to demonstrate two heat sources for melting materials in space, 3) to establish a method of joining and repairing.

Four materials will be used in the first task - SS, Ti, Al, and TDNi. A beam of constant power density will impinge on a revolving plate with a melt circle diameter of seven inches. In the second task, sixteen SS tubes will be joined by brazing, using exotherm heat sources.

INTRODUCTION

Two of the experimental tasks approved as part of the M512 space experiment are Metals Melting and Exothermic Brazing. The two tasks have similar objectives: 1) to learn about the behavior of molten metal in a reduced gravity, 2) to demonstrate two heat sources for melting materials in space, and 3) to establish means of joining that will lead to manufacturing in space, either for space products or products for earth.

The characteristics of molten metal in a space environment will not be conclusively defined until experiments have been conducted in space. Any space experiment that involves molten metal provides an opportunity to measure constituent distribution, solidification shape, surface finish, capillary flow, etc.

The electron beam melting system is compatible with a space vacuum environment (the master chamber, so to speak). An exotherm system is also well suited for space. The chemical reaction is contained within the system and can be initiated with a low energy source.

The exotherm joining system is simple and reliable but limited to a temperature of 2500°F. The electron beam system, although more complex, has a high energy density that can be used for joining many types of materials. The absence of earth gravity on molten metal would permit greater tolerance between the parts to be joined. For example, when an electron beam is used to weld two pieces together on earth there should be no gaps between the abutting surfaces. In space, however, where the cohesive force of a metal is dominant, the tolerances for mechanical fixturing could be substantially relaxed. Fabrication and assembly of space components could thereby be considered as a feasible process, not requiring the same sophisticated tooling as on earth.

Four materials will be used in the metals melting - SS, Ti, Al, and TDNi. The specimens will be mounted on a drum and rotated under the electron beam. Figure 1. The specimens are tapered in thickness from 1/4" to 1/16". With a beam of constant power density and a constant speed of rotation, the molten metal zone will vary in width from 1/32" to 3/8". A portion of the specimen is .030" thick, at which place the beam "cuts" or separates the material. The partial spheres will be measured for contour, location, and frequency. Figure 2. Other samples for melting and cutting will have gaps machined into them to compare the effects of melting in zero-g when gaps other than ideal are present between the abutting surfaces.

After the astronauts return the specimens to earth, a comparative analysis of materials melted under one gravity and reduced gravity will be made. The analysis will be based on measurements of tensile strength, hardness, distortion, melt geometry, and microstructure. For example, attempts on earth to weld particle dispersed composites

such as TDNi, have led to agglomeration and massive segregation of particles. Figure 3. Agglomeration is probably the result of thermal convection, and massive segregation of particles is almost certainly due to gravity. Melt forming or casting of particle dispersed composites should be more successful in zero-g.

An exotherm material will be used in the second experimental task to braze 1/4" and 3/4" diameter stainless steel tubes. Each assembly consists of tubes, silver copper lithum braze alloy, a sleeve, exotherm material, insulation, a housing, and igniters. Figure 4. Eight such assemblies will be placed into the vacuum chamber and ignited in sequence from the EB battery.

Comparative analysis will be based on the uniformity and extent of alloy flow. Figure 5 shows the effect of one-gravity on liquid braze alloy. When the rings of braze alloy are melted, the excess alloy settles at the "bottom" of the tube interior. A typical x-ray of a brazed tube assembly is shown in Figure 6. In space, where "bottom" is meaningless, the alloy should be uniformly distributed around the tube. Capillary flow will be measured in two different size gaps between tubes and sleeves. Capillary flow and surface wetting in space should be uniform and unlimited, as long as an adequate temperature is maintained.

In summary, the metals melting and exothermic brazing tasks will be a first step toward joining of components in space and will yield data of behavior of molten metal in a space environment.

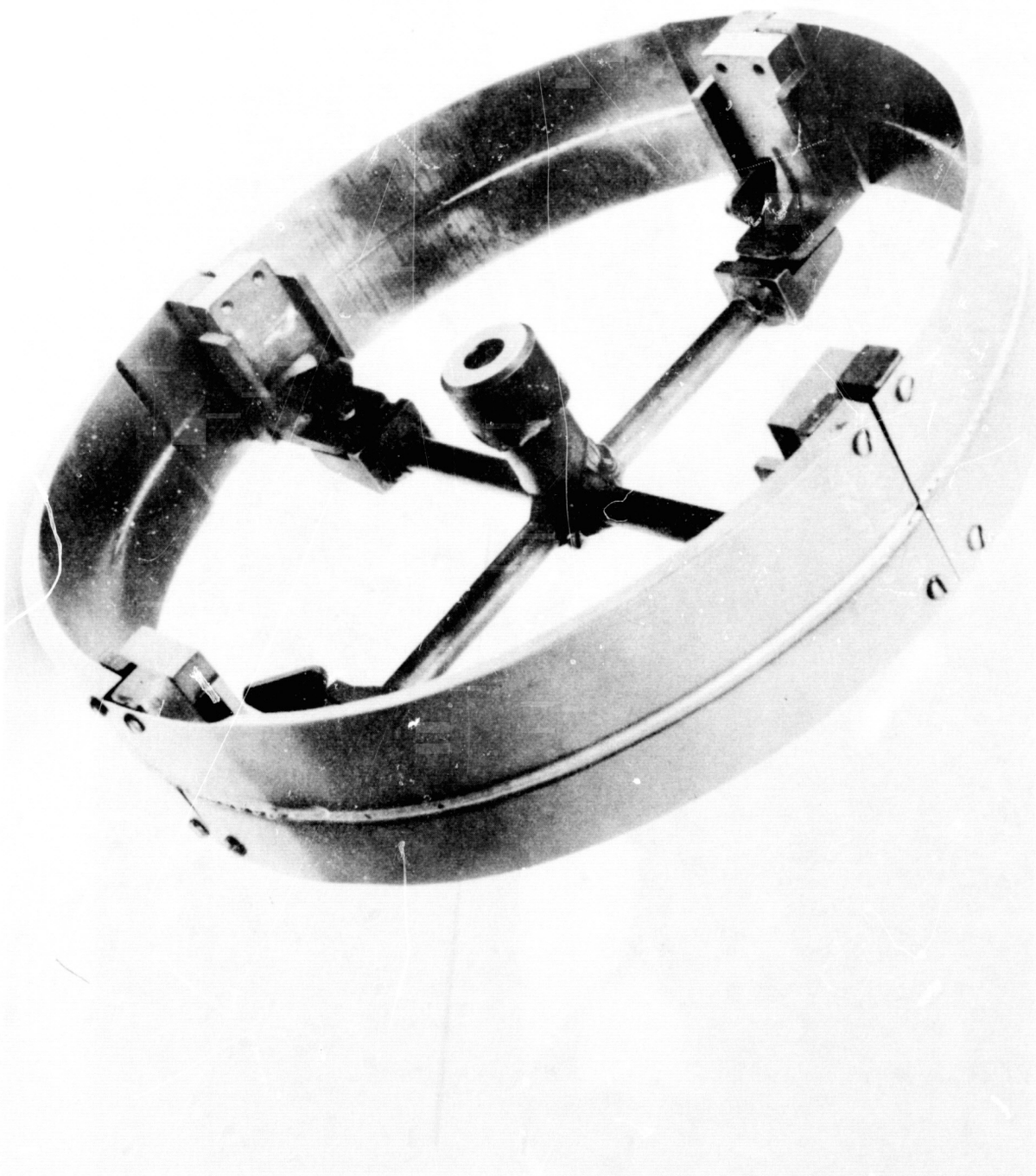


Figure 1

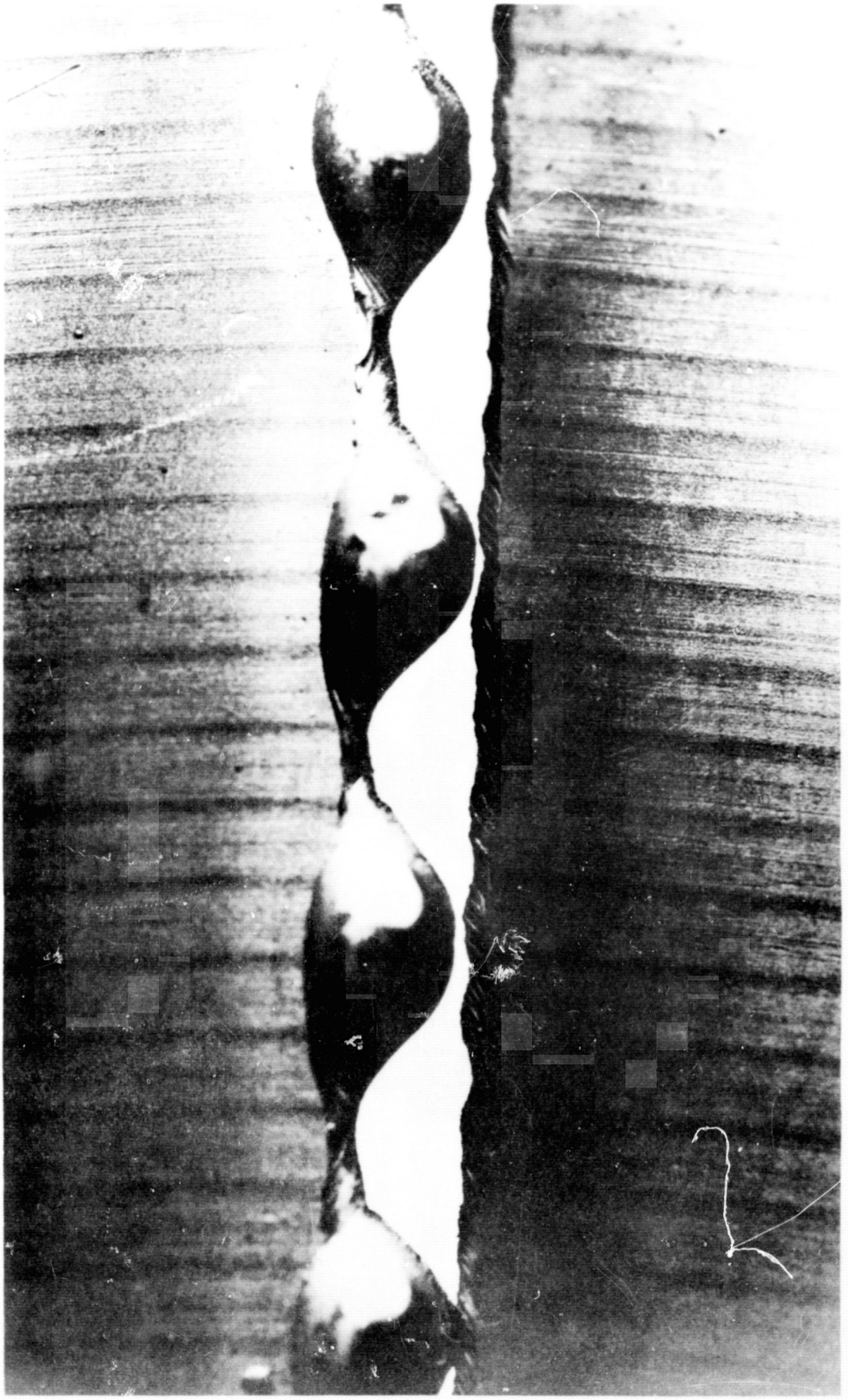


Figure 2



Figure 3


insulation
tubing
sleeve
braze alloy
casing
exothermic material
igniter
exothermic braze unit
8 thermal braze units comprise 1 package
3 packages will be brazed in space
same container used for brazing and welding
brazed tubing
cutaway brazed section
EXOTHERMIC BRAZING
A method of joining metals utilizing chemical reaction as the heat source. The braze unit is light-weight and self-contained

Figure 4

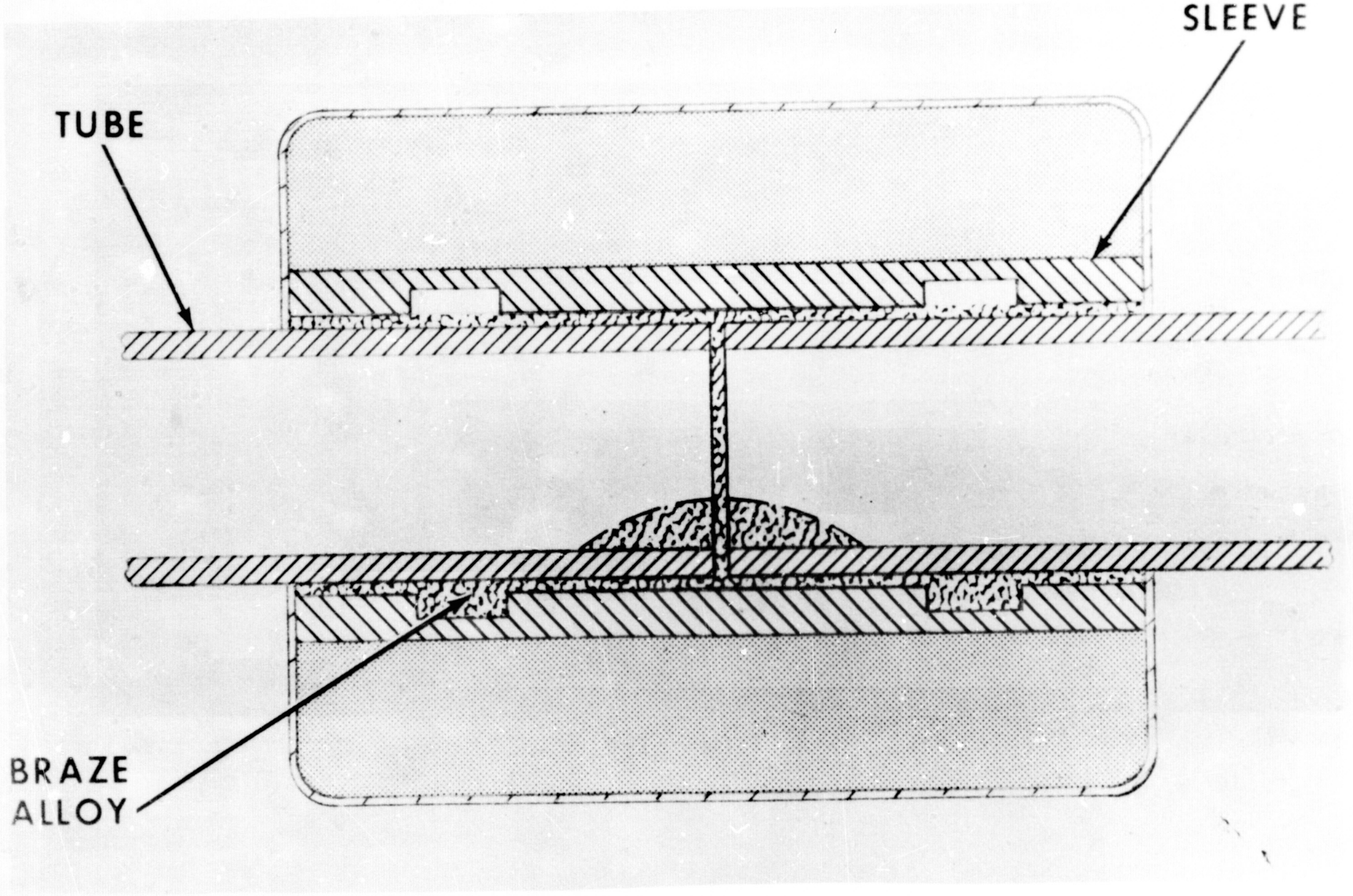


Figure 5

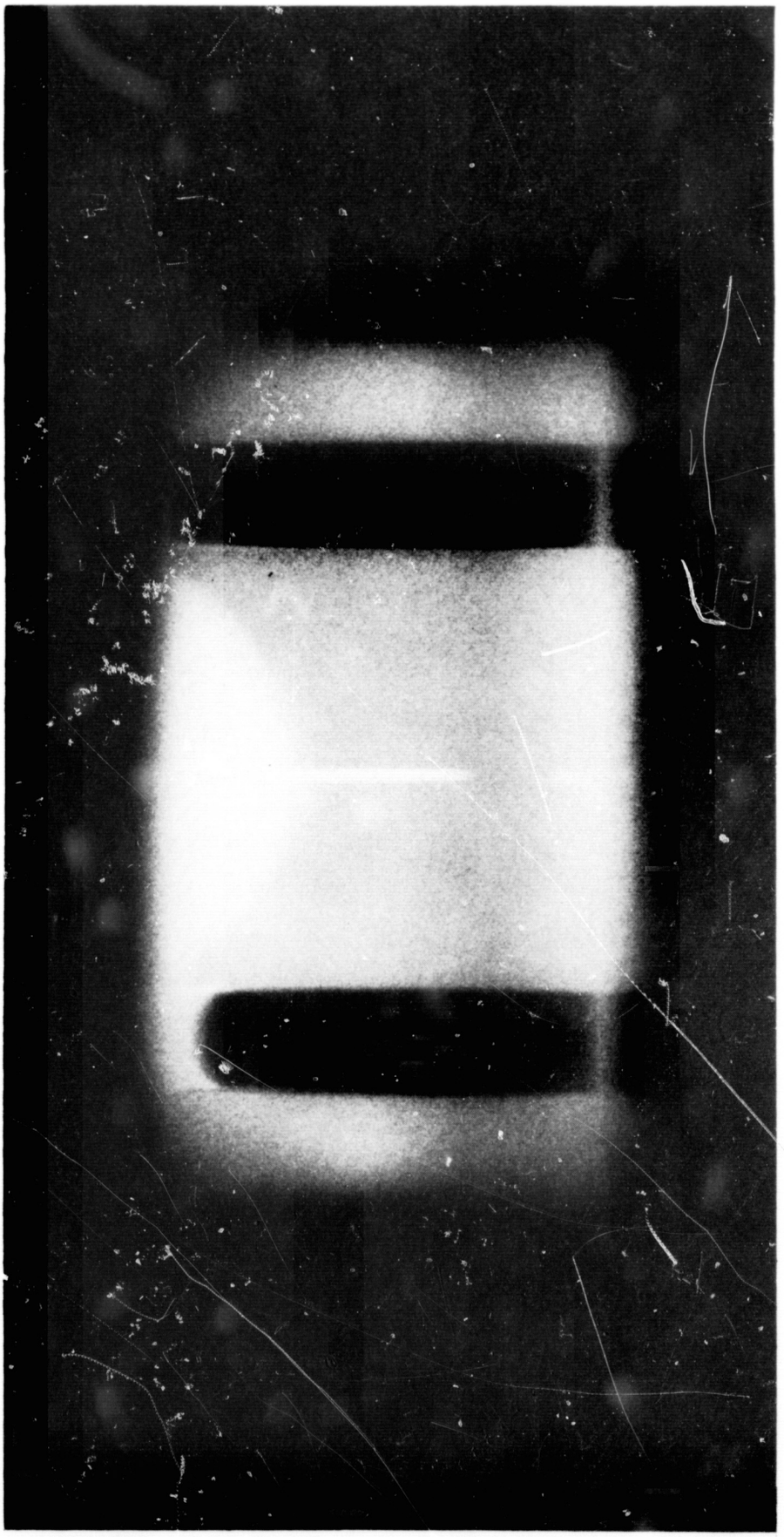


Figure 6

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SPHERICAL FORMING AND COMPOSITE CASTING IN ZERO-G

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ABSTRACT

The formation of spheres in the zero-g environment of an orbitting spacecraft has the potential for enhancing the surface finish, hardness, sphericity and microstructural properties. Casting of composites has the potential for better fiber alignment and a more homogeneous structure which could lead to improved strength or unique physical properties. This paper describes a program conducted to assist the Manufacturing Engineering Laboratory of NASA/MSFC in the identification and selection of materials and methods for the spherical forming and composite casting experiments of the AAP Workshop.

INTRODUCTION

The Manufacturing Engineering Laboratory of NASA/MSFC has proposed several experiments to demonstrate the feasibility, practicability, and the scientific, technical and economic justification of forming spheres and casting composites in space. Formation of spheres in the zero-g environment has the potential for enhancing the surface finish, sphericity, and microstructural properties. Casting of controlled eutectic composites has the potential for superior micromorphology, while the production of controlled monotectics becomes a meaningful concept. In addition, many of the very severe problems encountered in producing whisker reinforced composites may be overcome under zero-g

since direct melting of the matrix is possible.

The basic concepts of the composite casting and spherical forming experiments and experiment guidelines have been formulated by the Manufacturing Engineering Laboratory. However, the materials, heating, melting and forming methods, and the parameters to be studied in these experiments must be carefully identified and selected to insure that meaningful manufacturing technology experiments acceptable to the science and engineering community can be conducted successfully in the planned materials processing facility.

This paper describes the status of the work conducted by Arthur D. Little, Inc., in behalf of the Manufacturing Engineering Laboratory, NASA/MSFC, in the design definition of the spherical forming and composite casting experiments of the AAP Workshop Program. First, we will summarize the experiment description and guidelines which provided the criteria for selecting materials and methods to be used in the experiment. Then we will discuss the identification, laboratory evaluation and selection of materials and methods for spherical forming and composite casting. Finally, we will present some preliminary hardware considerations and a projection for future experiments.

EXPERIMENT DESCRIPTION AND GUIDELINES

Facilities and Equipment

The composite casting and spherical forming experiments will be performed in the Space Facility described in earlier papers in this symposium. Each experiment has a modular design; i.e., an experiment package containing a set of about six samples mounted in a framework will be placed in the facility and positioned by the astronaut. The packages must be compatible with the chamber, rotation mechanism, heating system, i.e., electron beam gun or exothermal heaters and storage areas. The samples must not interfere with the rotation mechanism or vacuum system seals. Materials which are evolved during the experiments must not coat the interior of the viewing window or otherwise restrict photography. A moderate speed sequence camera is available to record necessary information during the experiment.

Energy Sources

The guidelines established by the Manufacturing Engineering Laboratory are to use the electron beam power source for the spherical forming experiments and exothermal heaters for the composite casting experiments. The capabilities of these systems have already been discussed in previous papers.

Astronaut Activities

The essential contributions of the astronauts in performing experiments in the Mercury, Gemini, and Apollo programs are well known. One of the

objectives of the materials processing experiments is the effective use of man in space. Sample positioning, heating, photographic control, and experiment coordination and judgment will be the principal astronaut functions. However, because of the many demands placed on astronaut time and function in the Workshop Program, the experiments should not require complex manual manipulation, excessive time commitment or low priority peripheral measurements or control functions. The safety of the astronaut must be considered in all aspects of the experiment. Potentially toxic, extremely reactive, and flammable materials must be avoided.

Residual Accelerations

Although it would be desirable to conduct materials experiments in as close to zero-gravity as possible, e.g., a free floating condition, this will not be possible. A residual gravity field in the workshop arises from the radial gradient of the earth's gravity. Astronaut movement and rotation of the Workshop may result in accelerations of about 10^{-4} g to 10^{-5} g in the Materials Melting Facility. These accelerations limit the time available to complete an experiment in which the sample is free floating, thereby placing constraints on the sample size, type, cooling rate and other experiment parameters. Astronaut movement must be restricted during critical experiments in which free floating conditions are required. We have postulated that either samples will be attached to the experiment package during both melting or forming or will be attached during melting but not during solidification. For the first Workshop, we have not considered sample position control by rf levitation or astronaut manipulation because of the electrical power required, the complexity of the system, and the additional astronaut requirements.

Chamber Pressure

The Space Facility will be connected to space with a four-inch pipe and valve. At orbital altitudes of 150 and 300 kilometers, the mean atmospheric pressure is about 4×10^{-6} and 1.5×10^{-7} torr, respectively. Because of the conductance of the four-inch line and the natural leakage rate of the spacecraft, the minimum pressure in the chamber may be as high as 10^{-5} torr. The electron beam system does not operate effectively at chamber pressures greater than 10^{-4} torr. Therefore, the amount of sample outgassing during melting and casting operations must be minimized.

Materials Considerations

The objective of the spherical forming experiment is to demonstrate the ability to prepare materials in spherical shapes which cannot be produced on earth to the desired accuracy, uniformity, or sphericity. Ideally, the spheres should meet the following requirements: Rockwell C hardness

of 60; 1 microinch roughness; 5 microinch diameter tolerance; homogeneous structure; mechanical properties similar to ball bearings. In the low gravity of a spacecraft, it is anticipated that solidification under controlled conditions will result in almost perfect solid spheres and could possibly result in hollow spheres with uniform wall thickness. However, because of the many constraints in the first experiment, it is doubtful that all of the desired properties can be met. We consider that the experiment would be successful if a single advancement over terrestrial technology is confirmed, e.g., producing spheres of lower mass, greater surface hardness, better surface finish, new or more uniform microstructure, or finer grain structure. We gave only limited consideration to forming hollow spheres, even though such an experiment could show great advantages over terrestrial fabrication techniques but evaluated a broad range of materials, not only those presently used in ball bearing manufacture.

The objective of the composite casting experiment is to demonstrate the ability to process in earth-orbit a composite which has more uniform composition, better density control or whisker alignment or other improvements over similar products prepared on earth. We have broadened our examination of composite materials to consider not only whisker or fiber composites, but also particle dispersions, and composites formed from monotectic and eutectic solidifications because these materials may also result in unusual and advantageous structural, magnetic, electrical or strength properties. We selected materials for the matrix and filaments (or dispersion) with significantly different densities which exhibit difficulties in preparation on earth because of buoyancy effects. We considered materials which may exhibit unusual properties when prepared in zero-g because of lack of convection during solidification.

Heat Transfer Considerations

We performed heat transfer calculations to determine the melting and solidification rates of various candidate materials using the electron beam or exothermal heaters. The results showed that samples of 1 cm diameter or less of most practical materials could be melted with the electron beam or exothermal heaters within 20 seconds. The time required for solidification varies from 1 to 400 seconds, depending upon the melting point and thermal properties. High melting materials will solidify quicker because of the rapid rate of radiative heat transfer. Low melting materials may cause problems if they are not attached to stings because of the long time required for solidification. Stings will result in anisotropic cooling unless they have a small diameter and a low conductivity. Chemical compatibility of stings with the sample must be assured. Directional solidification of samples can be easily controlled by using radiation as the primary heat transfer mechanism.

FORMATION OF SPHERES

The zero-g environment will affect solidification for two basic reasons: (1) buoyancy forces due to density differences or thermal convection are non-existent; and (2) surface tension forces assume a more prominent role. Although in principle it should be possible to carry out containerless solidification of a perfectly spherical shape, it is unlikely that all of the desired properties of hardness, surface roughness, sphericity, and low mass can be met by a single material or a single sphere forming technique during the initial flight experiments. However, our objective was to meet as many as possible of these requirements with experiments designed to evaluate experimental procedure and provide insight into basic solidification phenomena. Several other implications of zero-g solidification are important. By solidification of "containerless" melts, a high degree of supercooling may be possible because of the absence of container walls to act as nucleation sites. Several materials have been undercooled on earth with substantial structural modification; undercooling and solidification in space may result in finer, less segregated structures than are possible on earth. The absence of convection in the zero-g environment may also have a large effect on the size and distribution of inclusions in alloys; and segregation due to constitutional density differences should not be possible. These factors could result in the formation of extremely fine dendritic structures in zero-g if uniform cooling were insured.

Methods for Sphere Forming

We considered several techniques suitable for forming spheres:

- Spheres on stings--use of a captive sting, a prenecked sting, non-wetting sting
- Spheres formed within a viscous melt
- Spheres formed within a wetting or non-wetting container
- Melting of wire or tubing to form spheres

The use of a sting provides the advantages of position control of the sphere yet maintains "containerless" conditions over the majority of the surface. The principal disadvantage is that true "zero-g" is achieved. If the sphere is held captive on the sting, cooling will not be uniform and the sting may act as a nucleation site. It may be possible, however, to melt a sphere on the end of a sting (an electrical conduction path is required when using electron beam heating) and then detach it. Methods for detachment include a non-wetting sting, vibrating or impacting the sting, or a pre-necked sting. The advantages of

detachment are the attainment of a "free float" condition with the associated uniform containerless cooling and solidification. It will, however, be difficult to remove the sphere with a controlled acceleration so that it does not rapidly impact the vacuum chamber. Furthermore, oscillations in the molten sphere induced on separation must be damped before solidification. Casting of a sphere around a low density core held on a sting was examined briefly but considered not practical within the restraints of the first experiment.

We examined solification of a sphere within a viscous glass melt as an alternate to achieving a "free float" condition. This approach would reduce contact of the sphere with a "container" and provide for uniform cooling. By using an appropriate glass, a smooth surface finish might result. The disadvantages of this method are that "containerless" or "free float" conditions are not really achieved, it may be difficult to prepare and melt a glass with desired temperature-viscosity characteristics, and compatibility of the sphere and glass restricts materials selection.

Solid or hollow spheres could be formed in a container by melting of a non-wetting or wetting sample. If the sample were completely non-wetting, surface tension forces should result in a sphere not in contact with the container. The materials choices for sphere and container are restricted, however, and the small accelerations in the experiment chamber would result in the sphere striking the container. Conversely, if a spherical container were used, and a wetting sample were melted internally, a hollow sphere could result. However, materials combinations are again restricted and there is no definite proof that a uniform wall thickness hollow sphere would be prepared.

By melting an electrically heated resistance wire, small solid spheres could result. Although this technique is simple and might be used to form hollow spheres if tubing were melted instead of a wire, we concluded that the size of the spheres prepared would be limited by available electric power and position control of the spheres would be impossible.

We selected three sphere forming methods for laboratory evaluation: spheres captive on stings, spheres removed from stings after melting, and formation of spheres in a viscous glass melt.

Preliminary Materials Selection

Five basic types of materials were considered for spherical forming: ferrous alloys, cobalt base alloys, and refractory materials for hard wear resistant spheres; pure metals to achieve sphericity and surface finish; and casting alloys to demonstrate the effects of zero-g on solidification.

Ferrous Alloys

52100 steel is used most extensively for bearings. It combines good strength, hardness, fatigue and hardenability properties, yet has a relatively low alloying content and is inexpensive. It has a quite high carbon content, however, and is not likely to possess sufficient toughness in the as-cast condition. D6AC and 300M have a somewhat higher alloying content, and are capable of achieving hardness better than Rc 60 despite a relatively lower carbon content. These are both relatively low alloy steels, so that undesirable solidification structures may be minimized. D6AC has the advantage that it is an air-hardening steel. 300M has been successfully cast experimentally although at a lower carbon content, thereby decreasing the attainable hardness. Both alloys are likely to have low hardness in the cast condition, but are more likely to possess a better combination of hardness and toughness properties than 52100.

The 18 Ni maraging grades of steel depend on a precipitation reaction of titanium and aluminum for their strength rather than on carbon. The maraging grade which has a tensile strength of 250,000 psi in wrought form is also available in a casting grade which provides a hardness of Rc 50. This material has very good ductility and toughness. Other grades may provide greater hardness.

440C stainless steel is another alloy used extensively in its wrought form for bearing components, capable of Rc 60 in its wrought form. Despite its high carbon content, it finds some use in investment castings, and may therefore be capable of yielding a cast sphere having a suitable combination of properties.

The age hardening stainless steels, e.g., 17-4 PH and AM-335, also depend on a precipitation reaction to achieve their properties. Many of these alloys are used for investment casting, but they cannot achieve much more than Rc 50 in hardness. Tool steels represent another class of alloys which have been developed for high strength, high hardness applications. However, we feel that other ferrous alloys are more attractive than the tool steels in the initial experiments.

Cast Cobalt-Base Alloys

Cobalt alloys have long been used in applications requiring hardness and wear resistance; many of them are used in the form of castings. Stellite Star J is a cobalt-chromium-tungsten alloy which has an as-cast hardness of Rc 55-62. Although it is somewhat sensitive to stress concentrations, it has promise for bearing components at elevated temperatures. This alloy is one of the most promising for fulfilling the objectives of the program.

Refractory Hard Materials

A number of oxides, carbides, nitrides, borides and intermetallics have promise as load bearing, wear resistant components. Because of the expected experimental difficulties in melting these materials by the electron beam and thermal shock problems, we have considered them inappropriate for the initial Workshop Program.

High Purity Materials

None of the materials mentioned above are ideal from the standpoint of producing a highly spherical, smooth sphere, because they are complex alloys and have only moderate thermal conductivity. A better material would be a very high purity metal, oxide-free or capable of dissolving its oxides when molten, having good thermal conductivity, and a proven capability for achieving large undercooling, e.g., the noble metals, silver, nickel, cobalt, and iron. Nickel appears to be the most attractive because it has been undercooled as much as 285°C in the laboratory. Solidification of a pure metal at undercoolings (not possible terrestrially) could result in homogeneous nucleation.

Casting Alloys

Most of the materials discussed above are complex alloys in which the unique effects of zero-g on solidification may be difficult to detect. A very useful alloy from this standpoint is an Al-4.5% Cu casting alloy. This alloy has a fairly wide freezing range and a significant density difference between the two phases. It has been studied extensively, and forms the basis of much of our understanding of alloy solidification in normal gravity. Much information on the structure resulting from a wide variety of solidification conditions is available. It is an ideal alloy for investigating those aspects of solidification which may be unique to a zero-g environment. Because of its low melting point and long solidification time, this alloy might not be compatible with the experimental techniques. Possible substitutes include Ni-14% Al, Ni-7.5% Al, or Ni-12% Sn.

Experimental Evaluation

From the materials described above, we selected the following for laboratory evaluation:

Al-4 1/2% Cu alloy	350 T maraging steel
Ni-12% Sn alloy	Co-Cr-Mo alloy "Star J Stellite"
Low alloy steel-"Astralloy"	440 stainless steel

We melted sample rods about 1/4" diameter using a pancake rf coil in an apparatus shown in Figure 1. The samples were suspended in a quartz "drop tower" about 3" diameter and 48" long; argon purge gas was used. The melted portions of the samples were allowed to drop onto quartz wool or into an oil bath or permitted to remain on the sting support.

The aluminum-copper alloy proved difficult to use because of the low melting point, high thermal conductivity and long projected solidification time. The nickel-tin alloy showed considerable improvement. Some shrinkage porosity was observed, but sphericity was quite good and surface smoothness was adequate (see Figure 2). The as-cast hardness was found to be Rc = 10.

Spheres of good surface finish and sphericity were obtained with Astralloy, although the hardness was not as high as desired and some shrinkage porosity was observed. We subsequently repeated tests after increasing the carbon content of the alloy; good results were obtained.

Tests with maraging steel resulted in samples of good surface finish and sphericity, no internal shrinkage porosity, but a hardness of Rc = 25. A suitable aging treatment could improve the hardness. Tests in which solidification occurred on the sting demonstrated the deleterious influence of cooling by the sting.

Star J Stellite seemed to be the best material in terms of overall performance. No internal shrinkage, surface wrinkling, or marked departures from sphericity were observed (see Figure 3). The as-cast hardness was Rc = 61.

440 stainless steel was melted with no difficulty, but both surface finish and sphericity were poor.

Several experiments were conducted to melt copper and nickel in a viscous boron oxide-barium oxide glass. The results were not satisfactory because of the difficulties in controlling the viscosity and temperature of the melt.

Materials Selection for Flight Experiments

As a result of the screening and experimental evaluation, we selected four materials for the flight experiments: Star J Stellite, 350T maraging steel, Ni-12% Sn and Astralloy. We plan to use both the captive sting method and the wetting or non-wetting sting technique. Several methods for removing the samples from stings are now under investigation as part of the hardware development efforts.

CASTING OF COMPOSITES

There are two general types of composites of current interest, dispersed particle composites and fiber reinforced composites; each imparts increased strength to structural alloys in a different manner. The dispersed particles are not load-bearing elements and do not contribute directly to the strength of alloys, but rather serve to inhibit grain boundary shear and migration and to pin dislocation tangles. To be effective, particles should be in the 500-100 Å size range with a spacing of about 1μ. In fiber reinforced composites, on the other hand, the fibers contribute directly to the strength of the composite. Both continuous filament reinforcement and discontinuous whisker reinforcement increase strength, provided that the fibers are aligned, well-bonded to the matrix, without being degraded by it, and that the volume fraction exceeds a minimum value of about 0.2. Composites have been produced by eutectic and monotectic solidification as well as by direct bonding between separately manufactured fiber and metallic matrices. Because eutectic and monotectic composites have many other applications in addition to strengthening, we have considered them important in our program.

Candidate Materials and Fabrication Methods

Particle Dispersed Composites

Particle dispersed composites are presently made by internal oxidation or carburization of alloys; by mixing, hot pressing, and extrusion of small particle size metals and oxides; and by coprecipitation and subsequent powder metallurgy (TD-Ni and TD-Nichrome). Attempts on earth to grow particle dispersed composites from the melt have led to agglomeration and massive segregation of particles to the top or bottom of the melt. Agglomeration is probably the result of thermal convection, and the massive segregation is almost certainly due to gravity; therefore, melt forming or casting of particle dispersed composites should be far more successful in zero-g. Experimental methods for forming a particle dispersed composite such as TD-Ni or TD-Ni-Cr include melting on a sting, as in the spherical casting experiment, melting by an exothermal heater, or using the materials in a welding experiment.

Fiber-Reinforced Composites

The major problems in the production of fiber-reinforced composites have been alignment, bonding to the matrix, and chemical reaction between the fibers and the matrix. These problems are equally as critical in zero-g as on earth, and any fiber-matrix system selected for space fabrication must previously have been shown to be physically and chemically compatible on earth. The composite forming processes should be improved in the absence of gravity, particularly when a molten metal is

involved in the process. It should be possible to vacuum infiltrate a much longer filament bundle with molten metal in space, where only capillary and surface tension forces are operative, than on earth, where run-down and spill-down of the molten metal is a problem. With whisker reinforcements, alignment is very much more difficult than with continuous fibers, and gravity separation during infiltration with molten metals is a well-recognized problem.

We believe that the materials used in the initial Workshop experiment should be confined to metal-matrix composites. Resin-matrix composites are in such an advanced state of development that even if important improvements in properties were demonstrated in zero-g fabrication, it would be difficult to gain widespread acceptance in the industry. Ceramic-matrix composites, on the other hand, are in such a primitive state of development that there is still controversy over whether they are at all functional. Metal-matrix composites are exciting a considerable interest, although only Al-B is in commercial use. Most of the work to date on metal-matrix composites has been done with model systems and has been aimed at demonstrating that the principles of fiber reinforcement are sound. It is unlikely that a product brought back from space will be commercialized immediately; however, we hope to design experiments with a maximum probability of demonstrating successfully the kinds of improvement in properties that can be expected in zero-g. Then, once the imagination of earth-bound manufacturers is stirred, important commercial applications can be expected to follow.

We considered the composite systems shown in Table I.

Table I

COMPOSITES FORMED BY LIQUID INFILTRATION

Matrix	Fiber	Matrix	Fiber
Cu	W	Cu	WC
Cu-alloy	W	Haynes 36	Al_2O_3 or SiC
Al	SiO_2		
Ag, Al, Ni	Al_2O_3 Whiskers	Ni, Al	Al_2O_3 Whiskers
Ag	Steel or Mo	Ag	W or Steel
Al	B_4C	Cu	Ta
		Al-alloy	SiC Whiskers

Discussions with workers in the field, suggested that the systems with the greatest potential for zero-g fabrication are: SiC whiskers in Mg-35% Al (MAG) and Al_2O_3 (sapphire) whiskers in Al.

Two types of zero-g experiments were considered. First, melting a pre-aligned, cold pressed composite in space with an exothermal heater to demonstrate feasibility without fiber segregation or agglomeration. A more satisfying experiment, and more complicated, would involve magnetic alignment in space of the nickel-coated SiC fibers contained within a tube, followed by partial immersion of the end of tube in an Mg-35% Al melt to bring about vacuum infiltration. The complexity of this experiment, however, is too great for the initial Workshop Program.

Monotectic Composites

A monotectic point is an invariant of a binary system where two liquids (usually of different density) and a solid are in equilibrium. Considering binary metal systems alone, over a hundred exhibit monotectic behavior. One of the most intensively studied monotectic systems is Cu-Pb. During solidification on earth, gravity causes the Pb-rich liquid to sink to the bottom of the crucible (Figure 4). Solidification involves formation of solid copper and enrichment of the liquid between the dendrites with lead. As cooling proceeds, the lead melt rejects dendrites of copper until it freezes as pure lead at 327°C. Under zero-g conditions, massive segregation of the lead and copper-rich liquids cannot take place, and a very different structure must result on solidification.

Directional solidification of monotectics can give rise to rod composites. Although none of the monotectic systems we have considered appear to be of interest for strengthening applications, Cu-Pb, for example, may exhibit anisotropic superconducting behavior. Another monotectic system that might have considerable potential for superconducting applications is Nb_3Sn-Sn. It is possible that directional solidification from compositions in the two liquid region will result in long continuous rods of tin in a Nb_3Sn matrix. The material could be of interest as an anisotropic superconductor, or could possibly be treated to remove the tin, leaving long continuous filaments of Nb_3Sn. Aluminum-indium is another monotectic suitable for demonstration of the effects of zero-g.

The experimental methods most suitable for monotectic systems would be directional solidification of materials such as Nb_3Sn-Sn and Bi_2Se_3-Se. Cu-Pb could be prepared by simple casting in an ingot mold. Exothermal heaters would be used.

Directional Solidification of Eutectic Compositions

Directional solidification of eutectics gives rise to lamellar or rod-like composites. A lamellar structure generally results if the relative

volumes of the two phases are approximately equal; and rod, needle or whisker composites result if one phase is present in much greater volume fraction than the other. Table II shows a number of eutectic systems that have improved strength characteristics compared to the pure metal. Although many of these systems are covered by patents, none are under commercial development at present. Because the primary aim of the eutectic melting experiments of this program is to demonstrate that in the absence of thermal convection, more perfect composite structures will result, the most reasonable system to examine appeared to be $CuAl_2$-Al. The eutectic temperature is modest, the $CuAl_2$ lamellae do strengthen aluminum, and a great deal of background information is available. Termination faults obtained on earth may be eliminated in a zero-g fabrication procedure. Pb-Sn is an alternate for the copper-aluminum eutectic.

Table II

EUTECTIC STRUCTURES WITH HIGH STRENGTH

Al_3Ni-Ni	Cb_2C-Cb
$CuAl_2$-Al	BeNi-Ni
Ta_2C-Ta	MoNi-Ni

While fiber composites have been investigated primarily for high strength, eutectic composites have been explored for many other applications in optics, electronics, and magnetics. Some of the more interesting systems are summarized in Table III. The anisotropic properties of the thermoelectric eutectics can be advantageous in electronic applications. NiSb-InSb exhibits a very large magnetoresistive effect, and all of the eutectics based on InSb can be used as infrared polarizers. The use of controlled eutectics for nonstructural applications is still very much in its infancy. Hence, if real improvements in eutectic structure can be brought about in zero-g, the possibilities for space manufacture can be brought to the attention of the technical community before possibly more cumbersome methods of earthbound manufacture become firmly entrenched.

Directional solidification is the preferred experimental method using exothermal heaters. An interesting experiment would be to use Al_2O_3 whiskers incorporated into the $CuAl_2$-Al eutectic composition. The whiskers should segregate to the $CuAl_2$ lamellae. This would produce a "double composite" system which could have higher strength than either the eutectic system alone or sapphire whisker reinforced aluminum. Bi-Bi_2Se_3 is another alternative. This system can be directionally

solidified as Se rods within a single crystal Bi_2Se_3 matrix. Like the eutectic Bi_2Te_3-Te, the selenium system could be interesting for anisotropy of thermoelectric power and thermal and electrical conductivity, particularly if zero-g fabrication reduces the number of rod terminations.

Table III

EUTECTIC COMPOSITES FOR OPTICAL, ELECTRONIC AND MAGNETIC APPLICATIONS

Thermoelectric Eutectics		
InSb-Sb		
Bi_2Te_3-Te		
Magnetoresistive and Infrared Polarizing Eutectics		
NiSb-InSb		MnSb-InSb
CrSb-InSb		FeSb-InSb
Superconducting Eutectics		
Pb-4 atom %	Ag	Sn-15 Zn
Pb-74	Sn	Bi- ε(Pb-Bi)
Pb-17.5	Sb	Sb-Sb_2Tl_7
Pb-28	Cd	β-InSn-γInSn
Sn-43	Bi	In-$BiIn_2$
Sn-33.5	Cd	Pb-$AuPb_2$
Optical Eutectics		
NaF-LiF		CaF_2-NaF-LiF
NaF-CaF_2		LiF-NaCl
NaF-MgF_2		NaF-NaCl
NaF-PbF_2		NaF-NaBr
$PbMoO_4$-PbO		ZnO-$Zn_3Nb_2O_8$
Ferromagnetic Eutectics		
Fe-FeS		Co-CoSb $BaFe_{12}O_{19}$-$BaFe_2O_4$
Fe-Fe_xSb		Ni-Ni_3Sn
Co-Y_2Co_{17}		Ni-$Ni_{15}Gd_2$

Experimental Evaluation

Based upon our screening of the candidate materials, we selected the following systems for laboratory evaluation:

Al-Al_2Cu	$Co_{17}Y_2$-Co
Pb-Sn	Cu-Pb
Nb_3Sn-Sn	Al-In
InSb-Sb	SiC whiskers in aluminum alloy
TD-Ni	Al_2O_3 whiskers in aluminum alloy
TD-Ni-Cr	

Figure 5 shows the experimental apparatus used for directional solidification experiments. It consists of a wire wound furnace having an inner tube 6" long and 1" diameter, closed at one end. The temperature gradient in the specimen is produced by a 1/4" diameter tungsten rod held in contact with the upper surface of the melt and water-cooled at the other end. The gradient can be varied by control of the water flow rate. The furnace is continuously flushed with argon. The samples are contained in boron nitride crucibles with thermocouples used to measure the temperature gradient. Samples were melted, directionally solidified, and subsequently examined metallographically.

Eutectics and Monotectics

Experiments with Cu-Pb alloy resulted in very rapid freezing. The microstructure was quite homogeneous, although there was a gradation in size of the copper phase as a result of the density difference between the copper and lead. We feel that other materials would provide more interesting and practical information than the Cu-Pb system.

The Al-Al_2Cu alloy was melted and directionally solidified with no major difficulties. Temperature gradient of 23°C/cm was used together with a growth rate of 27 cm/hr. The fault density was found to be quite high (Figure 6) but this may decrease during zero-g preparation.

We experienced great difficulty in preparing $Co_{17}Y_2$-Co alloy because of the dissolved gas released on melting. Similarly, the Nb_3Sn-Sn system was not promising because of the high reactivity of the Nb. The micromorphology of the InSb-Sb system we investigated was lamellar but with some tendency toward degeneracy due to the difficulty in obtaining high temperature gradients in the static arrangement used experimentally.

We selected Al-In as an alternate monotectic system for study. Samples prepared under a temperature gradient of 23°C/cm showed that there was a tendency for the In phase to form a rod-like morphology (Figure 7). The formation of rods is marginal. However, in zero-g a rod-like structure may occur and suggests that Al-In is a good candidate for the flight experiment.

Experiments with Pb-Sn resulted in the growth of a lamellar eutectic at a temperature gradient of 5°C/cm. The low melting point of the material may, however, give some problems in the design of the exothermal heaters and achieving the desired gradient in the flight experiment.

Whisker Composites

We examined the chemical compatibility of SiC whiskers in an aluminum matrix, and α-Al_2O_3 whiskers in an Al-Cu matrix. Ni plated SiC whiskers, and chromium and molybdenum Al_2O_3 whiskers were used. The experimental SiC whiskers were found to react after 1 minute exposure with the molten aluminum, and degrade completely after about 2 minutes. The Cr and Mo-coated αAl_2O_3 whiskers were wetted readily by the Al-Cu matrix maintained at the melting point. The whiskers showed some tendency towards segregation to the Al_2Cu lamellae. There are no chemical compatibility problems with this system.

Dispersed Composites

We also prepared spheres from T.C. nickel and T.D. nickel chromium by melting rods in the rf furnace described earlier. The selection of these materials was predicated on the fact that in zero-g, particle agglomeration and separation due to differences in density would be eliminated during melting. However, our experiments showed that gross agglomeration occurred as a result of "sweeping" the thorium oxide ahead of the advancing solid front during freezing. Because we feel that this sweeping would also occur in zero-g, we do not recommend experiments with these materials.

Materials Selection for Flight Experiments

We conclude that a monotectic, eutectic and a fiber or whisker composite should be used in the first orbital experiments. We selected the Al-Cu system because of its more practical application than the Pb-Sn eutectic. We chose Al-In as a demonstration monotectic system for the initial experiments because it is representative and may show significant effects of zero-g formulation. Coated Al_2O_3 whiskers, using an Al-Cu matrix, was selected as the fiber reinforced composite. Selection of these materials reduces experimental complexity because the exothermal heating devices and directional solidification gradients are identical for all samples.

HARDWARE DESIGN CONSIDERATIONS

Our present efforts are directed toward preliminary hardware design, based upon the materials and methods chosen for the flight experiments and described above.

Heat Sources

The sphere forming and composite casting experiments will use the electron beam and exothermic heat sources, respectively. To determine the operating parameters required for melting samples using the electron beam facility, a series of tests were conducted at NASA/MSFC using a prototype electron beam source. The following table summarizes the operating conditions used to melt 1/4" diameter samples of the materials selected for the flight experiment.

Material	KV	Amperes	Time to Melt (seconds)
Astralloy	15	.010	70
350T maraging steel	15	.012	30
Ni-12% Sn	14	.018	7
Star J Stellite	14	.016	14

Thus the planned 2 KW electron beam facility will be more than adequate for melting the samples in a reasonable time.

Based upon the results of our directional solification experiments, we have prepared specifications for the temperature profiles and rate of cooling to be provided by the exothermal heaters for the composite casting experiment. We plan to use a sample about 4" long and 1/4" diameter, to achieve a reasonably large temperature gradient and provide a significantly large sample region not affected by boundary conditions. The exothermal heater system is being developed by the Whittaker Corp., under separate contract to NASA/MSFC.

Experiment Package

Efforts are now underway at Arthur D. Little, Inc., and NASA/MSFC on the design of the experiment packages for the sphere forming and composite casting experiments. The components of the package for the sphere forming experiment include a sample holder assembly, rotation and positioning mechanism, the samples themselves, and a "sting release" mechanism. Important factors in the design of the package include volume and weight limitations, the need for accurate positioning in the electron beam, adequate electrical connection paths, sample viewing capability, heat transfer shielding to prevent stray radiation from reaching the vacuum chamber, and a means for removing the molten sphere from the sting with a controlled acceleration.

Several methods for removal of molten drops from stings have been proposed and require evaluation. It may be possible, by properly shaping the sting and sample, to develop a configuration which inherently results in a free molten sphere with little or no acceleration. The force of the electron beam itself will tend to provide some acceleration

to the molten sphere as it is released. The use of a non-wetting sting has been suggested. In this system, surface tension forces may result in the formation of a sphere which could move away from the sting because it does not wet it. This method may be limited by the chemical interaction between the sting and the sample (carbon or graphite would most likely be used as a sting) and the difficulties in completely melting the sample before dewetting occurs. A third method for removal of a molten sphere from a sting is to mechanically impact, vibrate or accelerate the sting. Energy will be transmitted to the sphere, resulting in detachment and motion. Detailed investigation is required to determine the most suitable method.

The experiment package for the composite casting experiment is less complex because movement and free float conditions will not be used. The basic components of the package will include a supporting framework, exothermal heater packages containing the samples and ignition sources, and heat sinks to assure the required temperature distribution for directional solidification. Design problems involve exotherm outgassing and temperature control among the samples to be heated.

FUTURE PROGRAMS

Because of the many limitations imposed on the experiments for the first orbital Workshop program, only a few materials and experimental methods can be studied. Clearly, there will be a need for follow-on work to examine other materials in which great advances in bearings, super and semi-conductors, whisker and dispersion reinforced composites, and optics could be made through processing in zero-g. Specific experiments must be designed to give true "zero-g" conditions with position control through rf levitation or other mechanisms. Sample size must be increased, along with power sources, to demonstrate the ability to prepare large quantities of materials and to provide means for studying those phenomena which occur only in a bulk substance. Preparation of hollow spheres by a variety of techniques and vacuum infiltration of long fiber bundles could then be attempted. More complex processing involving sample rotation, extension and forming, and increased astronaut control would increase the potential results of subsequent experiments.

We believe that the composite casting and spherical forming experiments are an essential step in the scientific, technological and practical demonstration of the unique features which can be imparted to materials processed in the orbital environment. The results of these experiments will provide an incentive to mobilize industrial and governmental interest and support in those space manufacturing processes which have potential economic benefit on earth.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the guidance and support of Mr. E. Hasemeyer, Mr. R. Hoppes and Mr. G. Parks of NASA-MSFC throughout the program. The expert advice of our consultants: Prof. M. Flemings, Prof. C. Smith and Prof. A. Sarofim of the Massachusetts Institute of Technology; and S. Bradstreet, the contribution of our many industrial and university colleagues; and the assistance of other ADL staff members, materially aided the identification and selection of materials and methods for these planned space experiments.

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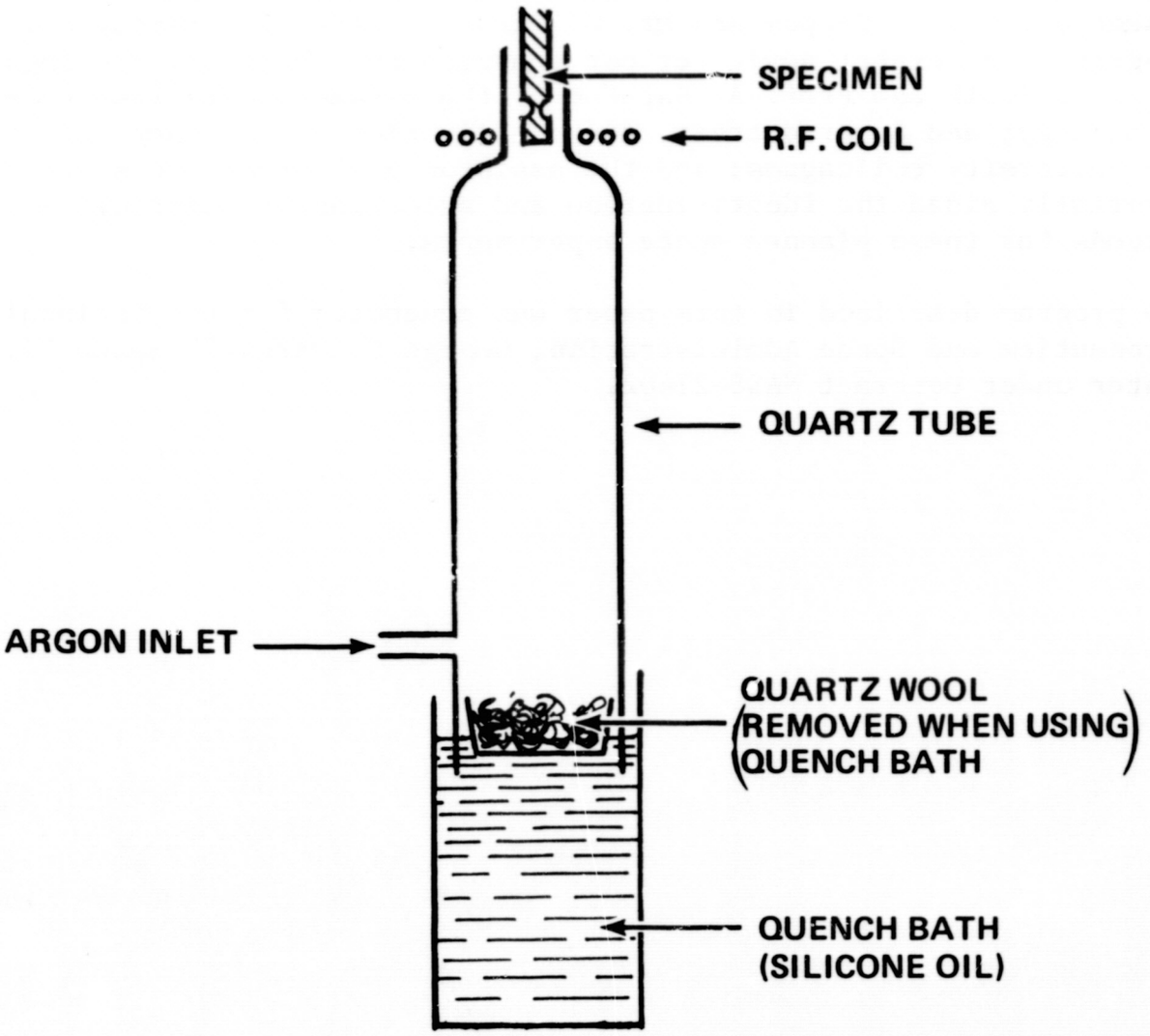
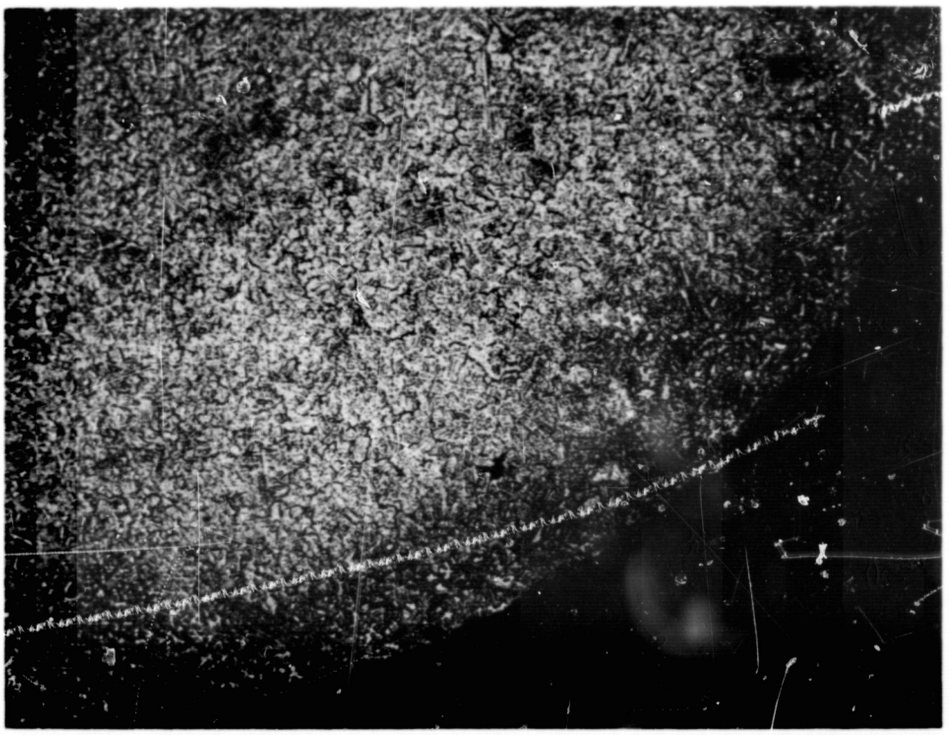
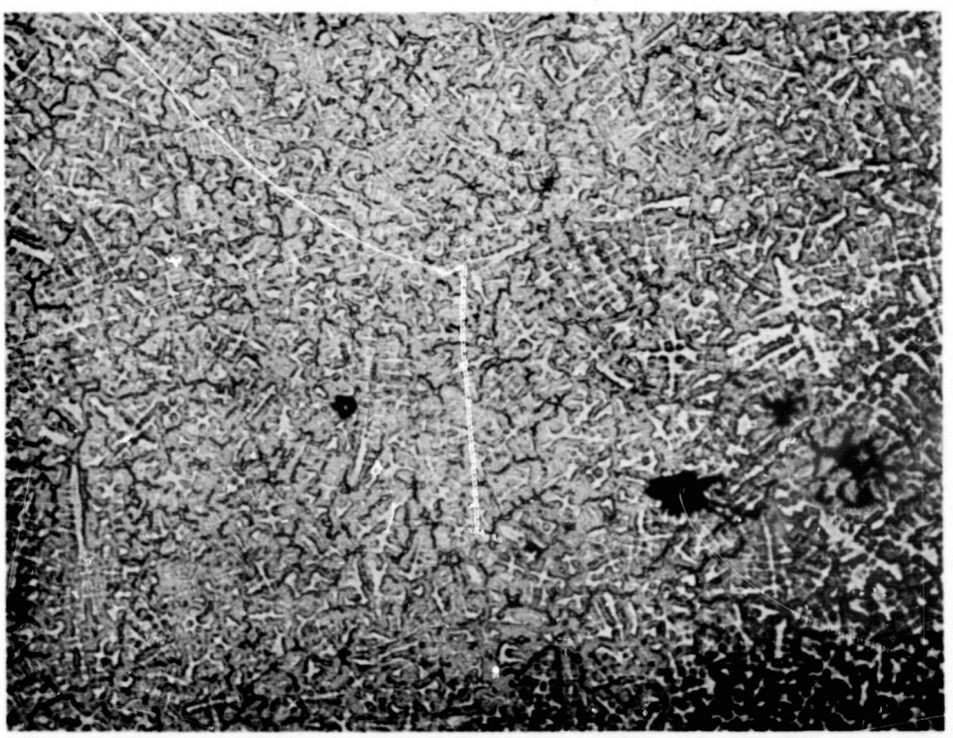


FIGURE 1. DROP CASTING APPARATUS



(a) Mag × 62



(b) Mag × 225

FIGURE 2. STRUCTURE OF A DROP CAST BALL OF Ni-12wt% Sn ALLOY



FIGURE 3. MOSAIC PHOTOMICROGRAPH SHOWING STRUCTURE OF A DROP CAST BALL OF STAR "J" STELLITE (Mag × 62)



FIGURE 4. MICROSTRUCTURE OF Cu-50% Pb ALLOY

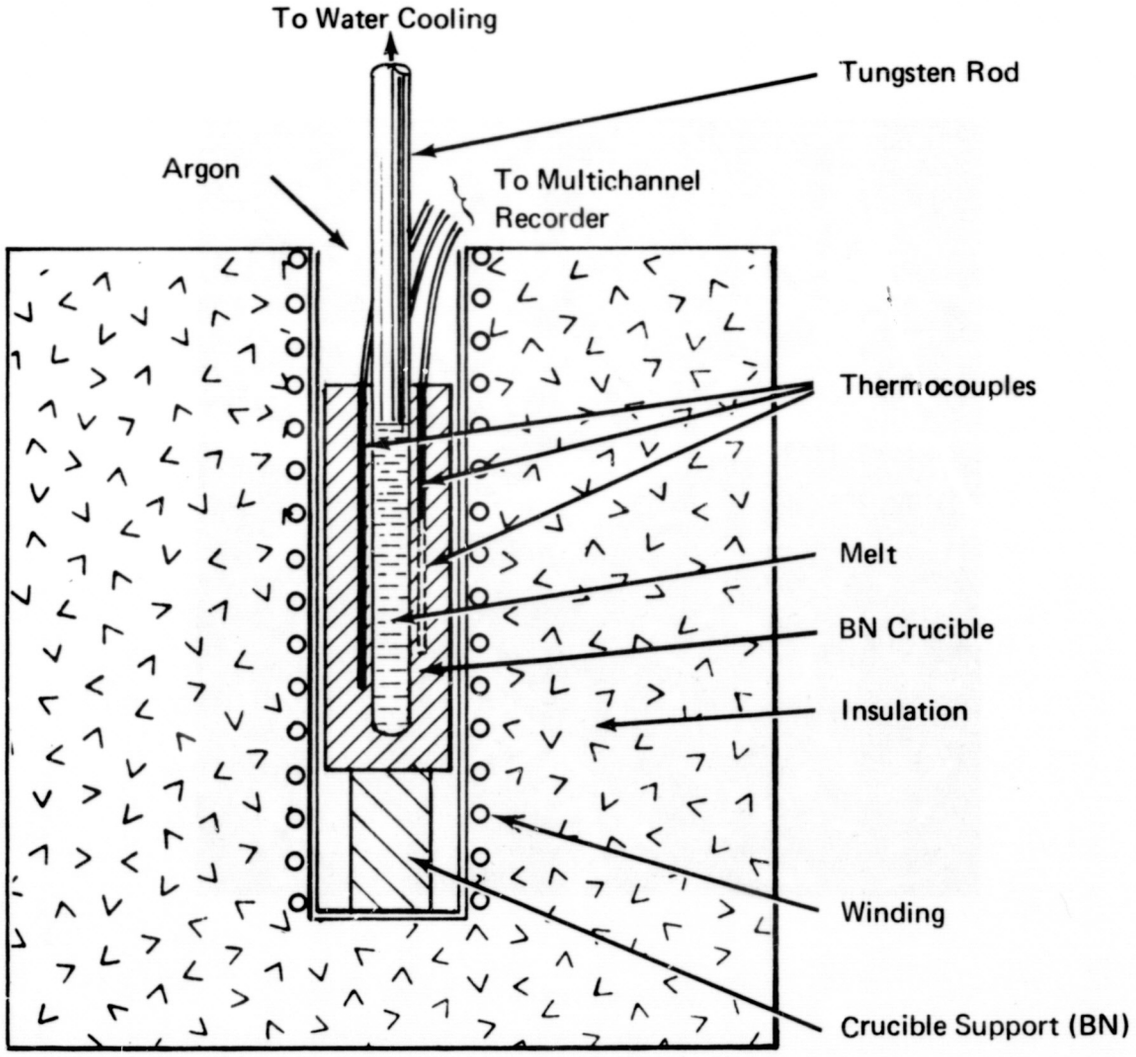


FIGURE 5. DIRECTIONAL FREEZING EQUIPMENT

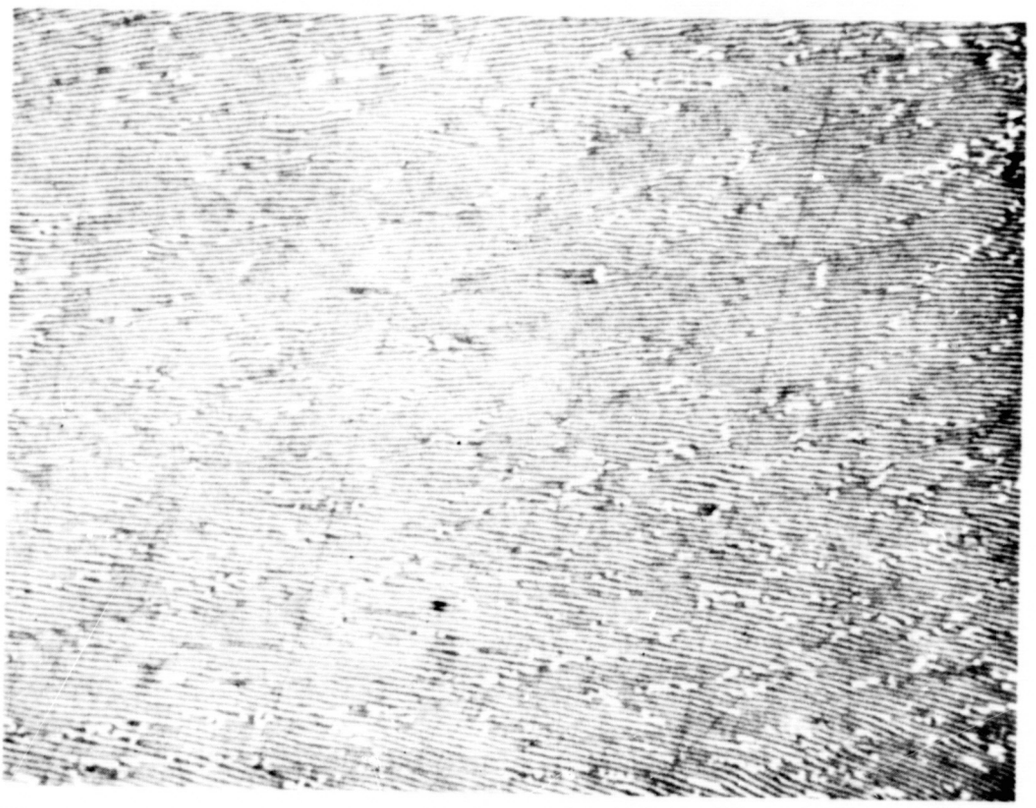
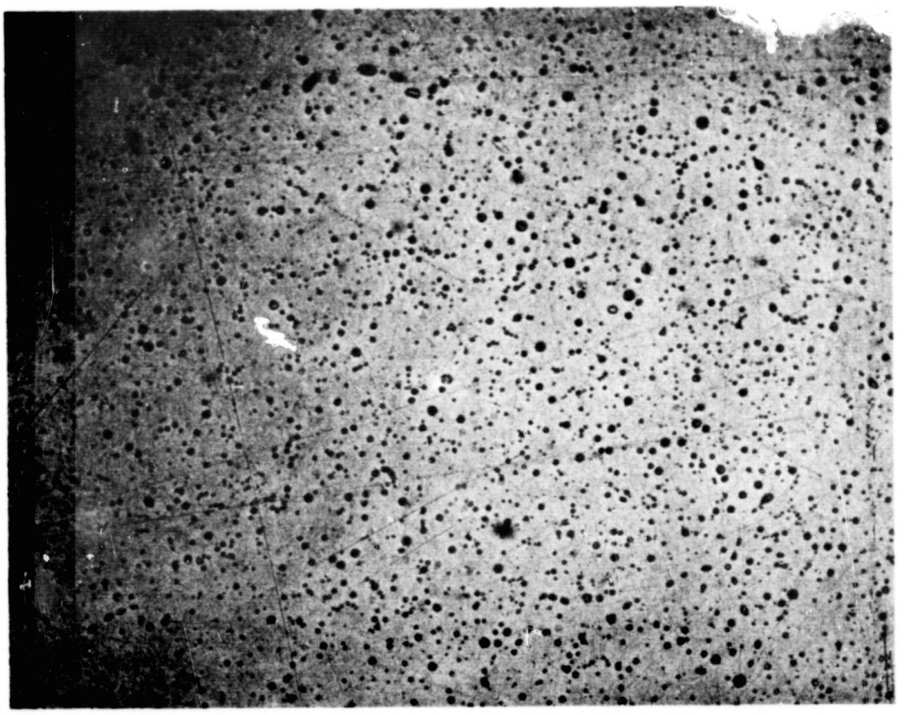
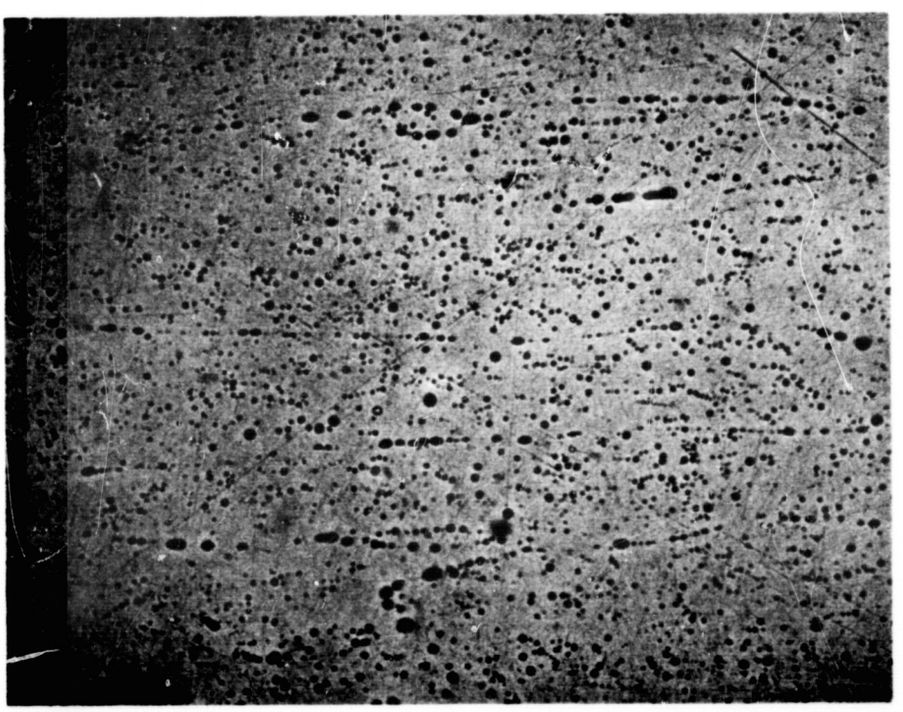


FIGURE 6. LONGITUDINAL SECTION OF Al-Al_2Cu CONTROLLED EUTECTIC (Mag × 625)



(a) TRANSVERSE SECTION Al-In CONTROLLED MONOTECTIC



(b) LONGITUDINAL SECTION

FIGURE 7. Mag × 125

N70-20533

ZERO GRAVITY CRYSTAL GROWTH

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ABSTRACT

This talk briefly reviews the principles of crystal growth and describes the different techniques that are regularly used. The advantages and problems of the various techniques are characterized. It is shown that for at least the preliminary attempts at crystal growth, solution growth has the advantage over other techniques in that it will require the minimum amount of operator time, lower temperature operation, and will not require unusual safety requirements. An outline of the projected experiment in solution growth at zero gravity is described.

The advance in the state of the art of crystal growth has resulted from and to a large extent, is responsible for advances in electronics technology. To take specific areas as an example, the requirements of crystals for the sophisticated areas of laser and semiconductor technology include stringent control of both purity and crystal perfection. These effects are, in fact, inter-related since impurity distribution (including doping impurities) can be strongly dependent on crystal perfection with impurity concentrations varying significantly at dislocations or grain boundaries. In addition to the effects of inhomogeneous impurity distribution the crystal perfection has a pronounced effect on physical properties such as the scattering of carriers or light at dislocations resulting in unacceptable device performance. In order to attain the intrinsic properties of materials it is necessary to strive for crystals of maximum perfection. To do this crystal growers have investigated and developed techniques and sophistication of techniques to control the parameters that affect

the perfection of grown crystals. In essence, these parameters reduce to controlling the development of the interface of the growing crystal; i.e., its shape, stability, and rate of advance.

The methods of growth that are used can be reduced to three general types:

1. Vapor Growth
2. Melt Growth
3. Solution Growth

The last two are similar in that both involve solidification from a liquid and control of the nucleation of the solid. The primary difference is that melt growth is characterized by solidification of the liquid when the liquid and solid are essentially the same composition, while in solution growth the solid is nucleated from a liquid of considerably different composition. Some crystals lend themselves specifically to one kind of growth method. With others all types of growth techniques can be successfully used. I would like to briefly describe and explore different methods and some variations of the methods and give a general concept of their applicability and advantages.

Vapor Growth

The process of vapor growth is in essence the formation of a vapor of a given material, the transport of the vapor to a nucleation site, and the nucleation process itself which will release the heat of condensation that then must be removed. When a material is not volatile, it is necessary to form a volatile compound which must then undergo a chemical reaction at the nucleation site resulting in by-products that must be removed. Although this technique is applicable to the growth of large bulk crystals, its major utility to date has been in the formation of thin hetero- or isoepitaxial growth.

Cadmium sulfide is usually grown from the vapor phase to form crystalline thin film for such applications as transducers. The usual apparatus is a vacuum jar in which there are positions for the source material and the substrate, the temperature at each position being controlled independently. The source can be either purified polycrystalline CdS or two separate sources containing cadmium or sulfur. The temperature of the source is controlled such that a desired vapor pressure of CdS or cadmium and sulfur vapor is maintained. The substrate, frequently located above the source material is maintained at an experimentally determined temperature that will give optimum nucleation. The vapor fills the vacuum chamber until supersaturation occurs. With the proper design of the vacuum chamber and a judicious

choice of temperatures, nucleation and growth occurs on the substrate.

Growth from the vapor can also occur via a chemical reaction. Many materials are grown by this technique the best known being the III-V compounds such as gallium arsenide. This material melts at a relatively high temperature, 1237°C, and at the melting point has a high dissociation pressure. As a result the direct heating of GaAs will result in the distillation of arsenic with only negligible amounts of GaAs being evaporated. Gallium itself is a liquid over a wide temperature and has a very low vapor pressure. In order to get gallium to vaporize it is necessary to use a volatile compound of gallium. One of several such compounds is $GaCl_3$. The usual technique used for growing GaAs is a flow system. In essence, a gallium source is held at one temperature, the arsenic at a second temperature, and the substrate at a third. The volatile components and a carrier gas is introduced into the reactor. For example, gallium will react with the chloride in HCl gas to form the trichloride. The arsenic will vaporize both as arsenic vapor and compound arsenic. Both species will be transported by the carrier gas to the substrate where a temperature proper for the formation of GaAs is maintained. The gas phase reaction is complex and involves several steps. However, one can describe the overall reaction by the equation

$$GaCl_3 + AsH_3 \rightarrow GaAs + 3HCl$$

Using this and related techniques good quality GaAs films having an excellent quality surface can be routinely made.

In vapor growth as in all other techniques of crystal growth it is important to control the development of the interface of the growing crystal. That is, although the vapor should be slightly supersaturated, a large excess of components at the interface can result in nucleation of multiple crystals and result in polycrystalline films. Since temperature and convection are important parameters in controlling this concentration, both must be carefully controlled.

Melt Growth

This is the most generally applied technique for crystal growth. It has many advantages such as fast growth rates, no contamination from solvent or gas phases, and, with carefully controlled growth parameters, the opportunity to prepare large crystals of high perfection. Some of the disadvantages include the requirement for a container in some applications of the technique, the high temperature required for growth of some materials, the possibility of severe thermal gradients during growth, and the need for the material to be congruently melting.

(The composition of the liquid and the solid frozen from the liquid is the same.) The requirement for working at the melting point of a material can in some cases result in difficulties in growth. In the case of high melting materials the control of thermal gradients in the melt and grown crystal, convection in the liquid, and temperature at the solid-liquid interface require a high level of sophistication in equipment and technique. This difficulty is compounded by the possibility that the compound or one of its constituents have a high vapor pressure. In spite of these difficulties much success has been had in obtaining highly perfect crystals of germanium, silicon, aluminum oxide, and yttrium aluminum garnet to name a few.

In the ideal case growth from the melt is not a function of the composition of the melt. As a result, growth is controlled by the rate at which the material will crystallize, the rate at which the heat of fusion can be removed from the growing interface, and the control of temperature and convection such that the growing interface will remain stable and nearly flat. Therefore, it is necessary to maintain a delicate balance between the heat going into the system to maintain the liquid, the heat lost by radiation and conduction, and the heat supplied by the heat of fusion on solidification. Most usually it is also necessary to accommodate the presence of impurities normally added as doping in dilute concentrations. These impurities are often more soluble in the liquid than in the solid resulting in impurity build up at the interface of the growing crystal. These impurities must be removed from the interface by diffusion and stirring or the impurity concentration will build up to the point where interface breakdown will occur.

There are many variations of melt growth and I will describe only a few here. The earliest high temperature melt technique is the Verneuill technique. In essence the technique consists of melting small controlled amounts of powder in the hot portion of a torch flame. Usually, a hydrogen-oxygen torch is used and controlled quantities of powder are vibrated from a source into the flame. The heat melts the powder into droplets which are directed onto a seed whereupon they solidify. As the crystal builds up the seed and solidified crystal is withdrawn from the cone of the flame and additional solidification and growth occurs. Ruby over a foot in length has been grown by this process. The advantages of this technique are that no container is needed and high temperatures are readily available. However, unless stringent precautions are observed, the fact that the temperature of the flame can't be controlled results in high thermal gradients in the crystal which cause strain. In addition, the liquid is subjected to temperatures much above the melting point which in some cases can cause dissociation of the compound as well as creating stresses due to the high thermal gradient. If the stresses get large enough to exceed the elastic limit of the crystal, the

crystal will deform and large numbers of dislocations can be produced. In some crystals which have low thermal conductivities the gradients and stresses can become particularly large and cause fracture.

Another commonly used technique is called the Bridgman method. In this technique a mass of polycrystalline material is placed on a non-wetting non-contaminating container and placed in a furnace above the melting point of the substance. The container is usually shaped to provide the opportunity for the propagation of a single grain. A controlled thermal gradient is imposed on the system such that one end of the charge is slowly solidified. The gradient or crucible is moved so that solidification occurs directionally at a rate commensurate with that required for crystal growth. The rate of cooling and the temperature is arranged such that the heat of fusion is dissipated in the system, the interface shape is controlled, and the growth rate does not proceed at a fast enough rate for spontaneous nucleations to occur. A wide variety of semiconductors and alkali halides have been grown using this method. The major problem has been in finding crucible materials. If the crucible is wetted by the material being grown, stresses caused by differential thermal expansion can crack the crystal. If the crucible is attacked, impurities can adversely affect the perfection and purity of the crystal.

One of the most generally used methods of melt growth is pulling from the melt or Czochralski growth. In this technique the molten reservoir of liquid is kept in a non-contaminating container. A seed is placed in the liquid and the temperature of the liquid controlled until the liquid will just begin to solidify on the seed. Most frequently the seed is rotated to help maintain temperature homogeneity and assist the diffusion of impurities away from the interface. The seed is then withdrawn at a controlled rate in a smooth fashion and the crystal is propagated along the direction of pull. Many crystals have been grown by using this technique including ruby, silicon, germanium, and gallium arsenide.

Solution Growth

Solution growth is perhaps the oldest method of crystal growth and is the method most simple in concept and most general in applicability. One is not limited to growth at melting temperatures where vapor pressures may be high, the solid is not stable, and temperature control is unreliable. Furthermore, the use of lower temperatures for solution growth and the choice of more than one solvent tends to relieve the problems associated with container attack, high thermal gradients and resulting crystal strain, and the need for complex and highly specialized equipment and technique. However, the debit side of the ledger includes the fact that solvent substitution and inclusion can occur and the growth is slower than melt growth, for example. This is due

to the fact that not only must the heat of fusion be dissipated at the interface but solute molecules must diffuse to the interface to crystallize. As a result growth rates from solution may be a factor of 100 slower than melt growth. Another major difficulty is the control of nucleation in solution growth. In melt growth the volume in which nucleation occurs is small (only at the interface). However, the dilution of the desired compound in the solution results in a large volume of potential sites for nucleation which can result in more than a single nucleation site for the crystal. As a result not all the crystallization occurs at a given point. In spite of these difficulties, however, large and high quality crystals of many materials have been grown from solution.

I would like to confine my remarks on solution growth to the GaAs system. Gallium arsenide is the only compound in the GaAs binary system. On either side of the maximum melting GaAs composition, a solid-liquidus area exists consisting of Ga-GaAs on one side and As-GaAs on the other. As in any system of this type one can then use one of the constituents of the compound itself as a solution. In this case the choice is obvious and Ga is a much more preferred solvent than arsenic. As a result of using gallium as a solvent one of the disadvantages of solution growth is somewhat mitigated--that of solvent impurity being present in the grown crystal.

The most frequently used method of solution growth takes advantage of the temperature dependence of the solubility. In most cases the slope of the temperature solubility area is positive--the higher solubility is at higher temperatures. In the usual growth procedure one would saturate the gallium with gallium arsenide solute at a given temperature, perhaps 900°C, and slowly program the temperature downward. In a small interval of temperature the solution becomes supersaturated and nucleation will begin. With the presence of a seed crystal available nucleation will occur preferentially on the crystal, although the gallium arsenide will self-nucleate in other areas of the supersaturated region.

A modification of this solution growth technique was first described by Pfann[1] which utilizes the effect of a thermal gradient within the solvent. In this technique a solvent is placed between a seed at one temperature and a polycrystalline charge at a higher temperature. The polycrystal will dissolve at the higher temperature to give a higher concentration of solute than at the seed. Because of the resulting concentration gradient there is diffusion of the solute from hot to cold until supersaturation occurs at the single crystal seed interface at which point exsolution occurs and the single crystal

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1. Pfann, W.G., J. Metals 7, 961 (1955).

is propagated. The solution zone is kept as small as possible to minimize the effects of convection.

We propose to use a modification of this technique in our zero gravity experiment where the effects of convection will be minimal.

The boundary conditions of the experiment make this a very desirable approach to zero gravity crystal growth. In any form of crystal growth other than solution growth the vapor pressure of arsenic is a problem in that it is necessary to prevent the loss of arsenic. With solution growth where temperature will be maintained below 1000°C, the pressure above the melt will be in the range of 10^{-5} atm.[2] As a result the possibility of pressure build-up and release of noxious vapors is vanishingly small. Another important point is that solution growth will not require constant attention as would melt growth where one must continuously monitor the growing interface. And finally it is possible to operate within modest power requirements by operating at low temperatures and limiting the volume of the growth system. It is also important to note that stringent power (temperature) control is not as critical as in melt growth. If one assumes a variation in delivered power of 1% a temperature change of perhaps 10°C can result. In melt growth this temperature is sufficient to cause degradation of the molten area. In solution growth, a variation in diffusion rate, supersaturation, and nucleation will occur which can cause spurious nucleation or an increase in dislocation density. However, it will not be necessary to terminate the run. In fact, the only apparent disadvantage of this technique is the slow growth rate which, under the conditions of zero gravity, will be diffusion limited.

In our concept of the experiment we have decided against the usual arrangement of an essentially isothermal system and programmed cooling to cause supersaturation and nucleation. The reasons for this are that it will be difficult to prevent spontaneous nucleation in such a run and it will be difficult to isolate the effect of diffusion controlled growth uninfluenced by convection. As a result we have designed the experiment to operate on the principle of a concentration cell where large concentration gradients can be retained over a macroscopic volume as a result of the lack of convective mixing. In principle the scheme is quite simple. We are planning on using a three ampule system, the quartz ampoules being enclosed in a sealed stainless steel cylinder. Within each quartz ampoule is a GaAs polycrystalline source, a quartz baffle plate to prevent motion of the source material, and a GaAs seed, the whole ampoule to be filled with gallium metal. Nichrome resistance wire is wound along two inches of each ampoule at the end where the GaAs source material is located. At the opposite

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2. Arthur, J.R., J. Phys. Chem. Sol. 28, 2257 (1967).

end a high thermal conductivity heat sink will be located. The total length of the ampoule will be seven inches with the solute transport distance to be between 1 and 3 inches. The system will be designed to maintain a thermal gradient of approximately 200-300°C and a concentration gradient of a factor of 10. Due to the absence of convection at zero gravity the rate of arrival of the solute at the seed will be the diffusion rate of GaAs in gallium across the imposed concentration gradient. Depending on our ability to control temperature uniformity longitudinally in the ampoule, the growth interface of the crystal should be flat. One of the main factors of interest is the fact that the diameter of the crystal being grown is limited only by the power limitations and our ability to limit temperature inhomogeneities along the diffusion front to maintain planar geometry. As a result of this experiment we hope to gain information on the diffusion process and its role in solution growth and to demonstrate the crystal perfection and quality obtainable with controlled solution growth.

Future crystal manufacturing and growth experiments should include the scaling up of solution grown crystals and exploration of melt growth.

The solution technique will always have the advantage of requiring minimal operator supervision and only moderate amount of training for operation. This in combination with the general applicability of the technique to many compounds will make this method of growth an attractive one. To fully utilize the potential of the technique for growing large area crystals one must make provision to accommodate larger volume growth apparatus and supply sufficient amounts of well regulated power to run it. Our first exploratory attempt involves 3 ampoules having a total growth and transport area of slightly over 0.5 in^2. With proper design and sufficient power, crystal propagation over areas of 2 in^2 are within our technical capability. This is true not only for GaAs but other materials of technological importance. One point should be emphasized. Although the main thrust of this experiment is toward manufacturing, convectionless growth in zero gravity offers a unique opportunity to gain a fundamental understanding of crystal growth in non-aqueous solvents, something of importance to the many scientists and engineers working with crystals.

Finally one should strongly consider melt growth of selected compounds. I believe that these materials should presently be confined to those having low vapor pressures at the melting point. This will minimize hazard and technical difficulties of growth. One example that comes to mind is of course silicon. The zero gravity environment will be quite beneficial for zone melting from two points of view--convection in the molten zone will be nil and the stability of large zones without gravity will be greatly enhanced. The combination of these factors should lead to large size and more perfect crystals. It

will, of course, be necessary to train operators to perform this growth and the operators will have to be available for frequent monitoring of the growth. However, the potential for rapid growth of high quality crystals makes this attractive.

I think that the potential for zero gravity growth is already large. However, until the preliminary results of crystal growth experiments are evaluated, we can only speculate as to the true future of zero gravity growth.

Acknowledgment

I would like to acknowledge the able collaboration of Dr. M. Rubenstein and Mr. C.S. Duncan in formulating and implementing this program.

N70-20534

TECHNIQUES FOR CHARACTERIZATION AND EVALUATION OF ZERO-GRAVITY GROWN GALLIUM ARSENIDE

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ABSTRACT

Recent proposals concerning the advantages of purifying gallium arsenide and growing its single crystals in zero-gravity environment have led to an investigation into the possibilities of characterizing this material. The present paper discusses briefly several modern techniques which could be utilized to determine the ultratrace impurities and the dislocation-type imperfections and impurities influencing the electronic properties of gallium arsenide.

INTRODUCTION

During the past two decades the semiconductor industry has experienced spectacular growth. Much of the credit for this success can be attributed to the unique and amazing properties of silicon and germanium. The technology has so much advanced that these semiconductors can now be readily obtained at relatively low cost in the form of large, highly pure (to an order of less than one part in 10^{10}) single crystals and the desired impurities can be added to them in controlled manners. However, the rapidly growing industry is now facing a great challange: to grow large single crystals of compound semiconductors, such as gallium arsenide, with a quality which could at least approach, if not exceed, that of silicon and germanium.

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1 Brown Engineering Company, Huntsville, Alabama.

For some time now, especially since the invention of Gunn oscillators [1], it has been felt that gallium arsenide (GaAs) cannot only replace the conventional semiconductors (Si and Ge), but the devices fabricated out of it can far excel in reliability, ruggedness, reproducibility and performance. However, attempts to commercially manufacture single crystals of GaAs for use in microwave devices (such as Gunn or p-i-n diodes) for fast switching diodes, and for laser or sublaser diodes have been mostly unsuccessful. Nevertheless, a small quantity of this material which is of a reasonably pure quality has been prepared in the laboratory. The commercially available material is metallurgically, chemically, and electrically inferior to the semiconductor grade Ge and Si. The difficulties which have generally been encountered during the growth and purification of GaAs are as follows:

1. The chemistry of this material is significantly different and more complicated than that of Si and Ge;

2. It decomposes when melted in an open system;

3. GaAs is easily contaminated (by its) surroundings. Even the use of quartz or graphite boats leads to the addition of contents, such as silicon (donor) and possibly oxygen.

4. The grown crystals are often electrically inhomogeneous and it is not unusual to obtain a portion of the crystal in a highly resistive form [2]. Strong compensation of donors and acceptors is mainly responsible for the formation of this semi-insulating material [3].

5. It is possible to synthesize GaAs by using parent elements. However, the obtained product is often highly disproportionate to the stoichiometric point of view.

6. Any impurity during the solidification operation, submicroscopic solid particles trapped at the solid-liquid interface, condensation of vacancies, externally applied stresses, such as those needed for holding the crystal and the seed or thermal stresses, and turbulent thermal convections might lead to the introduction of possible nucleation sites, which may give rise to twining, dislocations, polycrystallinity, etc. A magnetic field has been used to suppress the thermal convection during the solidification process [4], though this method, as yet, has not shown much promise.

An attempt has been made to overcome most of the above difficulties by employing such modern techniques as liquid encapsulation [5], liquid epitaxy [6],

and vapor phase epitaxy [7]. However, it is now believed that zero-gravity environment during the growth and purification of GaAs can greatly simplify these processes. This matter has been discussed at length by several authors [8]. Plans are now under way to manufacture single crystals of GaAs in space under zero-gravity environment by employing some well established technique (Czochralski, Bridgmann, Chalmers, etc.).

To evaluate the relative quality of the material grown in space over that which has been obtained on earth, using the same technique, and to achieve the required degree of perfection in the crystal growing and purification, it is essential to utilize several methods of analysis and characterization. The role of some of the methods which could be used for the evaluation of GaAs single crystals is discussed in this paper.

CHARACTERIZATION TECHNIQUES

Electrical measurements find a significant place in the evaluation of single crystals of high purity. However, these alone cannot be regarded as a complete characterization, since the chemical nature and the concentration gradients of the inherently present and externally added impurities still remain unknown. In the case of GaAs the measured electrical mobility in the purest available material is found to be much lower than would be expected from the theoretical calculations. This indicates the presence of certain impurity(-ies), presenting a barrier to the achievement of desired purity in terms of the mobility. Furthermore, quite often one observes strong compensation effects of donors and acceptors in the same crystal which, without the knowledge of the chemical nature of these donors and acceptors, interfere with the correct understanding of the situation.

In addition to the above, the dislocations, deformations, etch pits, slips, grain boundaries, etc. play a major role in determining the physical and mechanical properties of crystals. Although the dislocations can show a drastic effect on the electrical properties and their nature can be generally traced back by extrapolation from the electrical parameters, it is wise to make the direct observation of dislocations on the crystal surface.

Therefore the complete characterization of GaAs crystals can be performed in the following sequence:

1. Determination of ultratrace impurities.

2. Study of dislocation type defects.

3. Study of defects influencing electronic properties.

The methods required for these studies are discussed in detail in the subsequent sections.

DETERMINATION OF ULTRATRACE IMPURITIES

There are several well developed techniques that may be used for the direct determination of ultratrace impurities in the electronic materials. However, many of them, such a polarography, spectrophotometry, atomic absorption spectroscopy, etc., need larger samples. The danger of contamination and the loss of material during the process of chemical separation makes the use of these techniques highly doubtful. The ensuing paragraphs give a review of some of the new powerful techniques which have shown great promise in their general applicability to direct and simultaneous analysis of impurities.

Cyclotron Resonance

Cyclotron resonance at microwave frequencies is the most direct way to obtain information on the form of the band edge in semiconductors, but it is difficult to get III-V compounds pure enough for this type of experiment where the relaxation time of the carriers must be longer than about 5×10^{-12} sec. However, this method is helpful only in the quantitative estimation of the impurities. Of the III-V compounds, only Indium Antimonide has been prepared sufficiently pure to observe the cyclotron resonance at microwave frequencies [9]. Thus it appears that the observation of cyclotron resonance will be a criterion for estimating the purity of a GaAs specimen (through the estimation of the relaxation time).

At high magnetic fields used in infrared cyclotron resonance, the separation between the magnetic sublevels is large and the transition between them corresponds to penetration depth into the band. Hence the effective mass obtained is not characteristic of carriers at the edge of the band. Where a band is nonparabolic, such as in the case of the conduction bands of InSn and InAs, the effective mass is some function of the energy above the band minimum, and the measured effective mass varies with the strength of the magnetic field. This suggests that the change in band shape due to lattice imperfections can be studied and will throw light on the crystal characterization.

For crystal characterization on materials, where the free carrier concentration is too large for cyclotron resonance, we may take the help of diamagnetic Landau effect technique. In the case of cyclotron resonance the transitions occur between the magnetic subbands of either the conduction or the valence

band. In Landau effect the transitions are from a magnetic subband of the valence band to a magnetic subband of the conduction band. Because the transitions raise electrons from the valence to the conduction band, the effect does not depend upon the presence of free carriers. The carrier concentration in GaAs will decrease with the extent of purity and one may have to move from the study of Landau effect to that of the Cyclotron resonance.

Activation Analysis

Though the general principles of the activation analysis have not changed significantly, the state of the art in this field has become well developed during the past few years; consequently, this method has found application for the determination of a variety of impurity elements in GaAs [10]. The technique has the unique advantage of freedom from contamination during the course of analysis, because the elements of interest are radioactive.

The fundamental principle of the technique is that a sample is irradiated for a sufficient time to produce adequate radioactive or excited states of elements in the sample. Under identical conditions a known mass of a standard element is also irradiated. A comparison of the induced activity gives the mass of the element to be determined in the sample.

The basic equation for the activation is given by

$$A = f\ \sigma\ \frac{W\phi}{M}\ [1 - \exp\ (-ct)]$$

where A is the induced activity in disintegrations/second at the end of irradiation, f is the flux of particles used in the irradiation in numbers/cm^2/second, σ is the activation cross section for the nuclear reaction concerned in cm^2, W is the weight of the sample in grams, ϕ is the fractional abundance of the particular isotope of the element concerned, M is the atomic weight of the element, c is the decay constant of the induced radionuclide in $second^{-1}$, and t is the irradiation time in seconds. This equation is generally applicable only when the species concerned have half-lives comparable or longer than the time needed for measuring the induced activity after completion of the irradiation. However, there are methods, recently developed and arbitrarily known as "prompt" radiation methods, which involve counting of the irradiation emitted during decay of very short-lived excited nuclear states and thus apparently provide the possibility of infinite sensitivity.

The sensitivity of the activation analysis technique largely depends upon: (1) the selection of optimum nuclear reaction (usually based on the physical, chemical, and nuclear properties of the matrix and trace elements and of their activation products); (2) the choice of a suitable irradiation facility (nuclear reactor, low intensity neutron sources, linear accelerators or cyclotrons, etc., primarily based on the type of nuclear particle required); and (3) the irradiation (slow neutron, fast neutron, gamma photons or charged particles and the optimum length and intensity of irradiation). The average interference-free detection of about 75 elements of the periodic table is approximately 10^{-5} microgram. With the suitable selection of the previously mentioned parameters, it will be possible to evaluate precisely the concentrations of very minute amounts of elements in GaAs.

Emission Spectroscopy

The activation analysis, as previously discussed, cannot in many cases determine certain important impurity elements of semiconductor technology. Moreover, it needs close proximity to a high thermal flux nuclear reactor and also a large number of time-consuming radiochemical separations. As a rapid, easy, and direct method of the trace analysis in the parts per billion concentration range, one therefore often employs emission spectroscopy. The sensitivity of the technique can be further improved by using preconcentration techniques but they are subject to serious errors and are time consuming. With the help of dc/arc excitation, Jones, Andrychuk, and Massengale [11] have been able to determine trace impurities in GaAs with a precision of about 25 percent.

Spark Source Mass Spectrometry

The use of spark source mass spectrometry as a technique for the analysis of solids has increased enormously in the past decade or so because of two inherent advantages. First, its detection sensitivity is high, whether defined in terms of the low concentration of an impurity that can be detected (parts per billion) or in terms of the total amount of sample needed to detect impurities. Second, the mass spectrum reveals that all elements in the sample have approximately the same detection sensitivity, thereby permitting semiquantitative analysis without instrument calibration. The method is particularly attractive from the point of view of its ability to record the spectrum of a whole range of elements from lithium (mass 7) to uranium (mass 238) in a single exposure of the photographic plate.

Mass spectrographic measurements on GaAs have been discussed in detail by several authors [12, 13, 14].

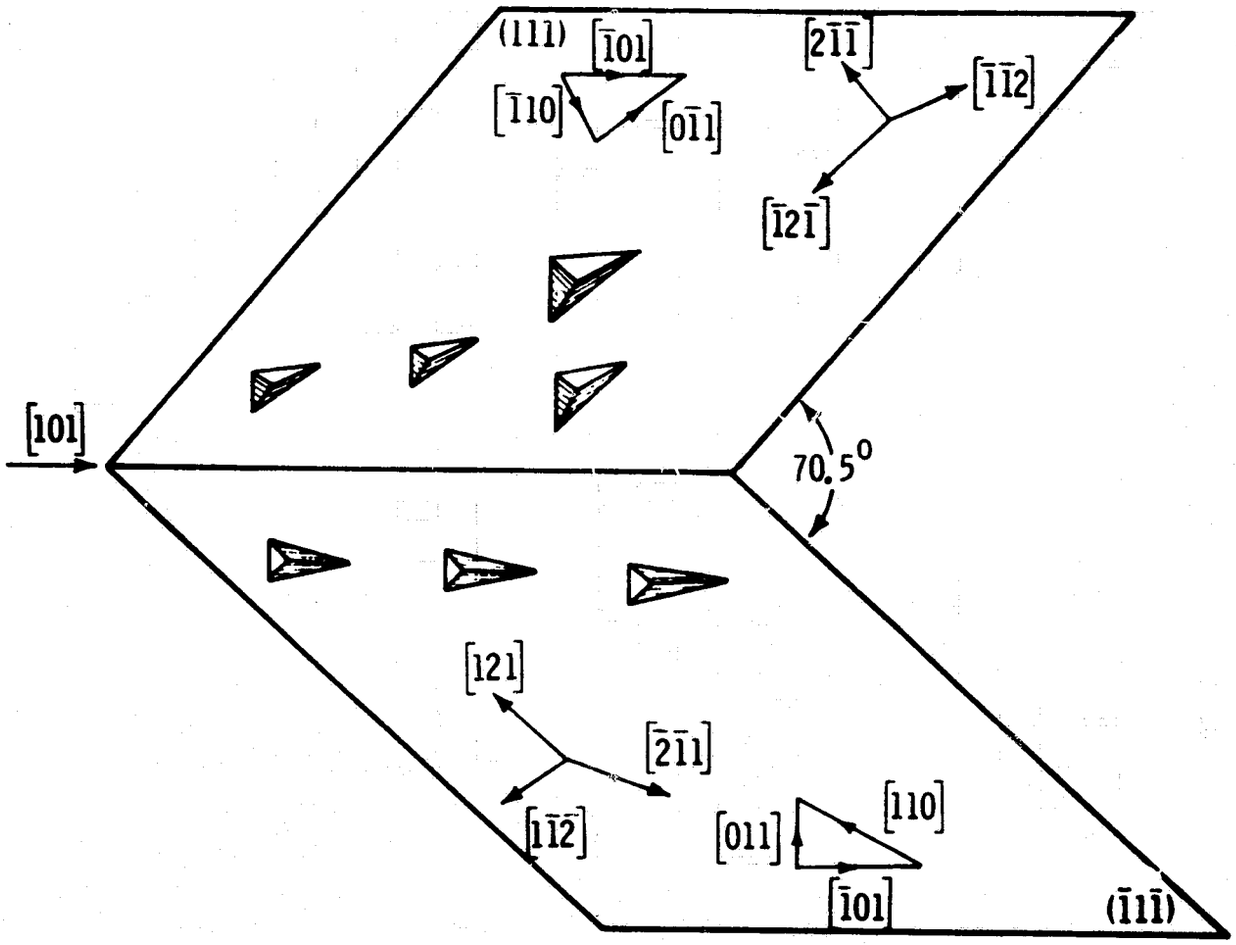
STUDY OF DISLOCATION-TYPE DEFECTS

Physical defects in a crystal can be introduced in several ways. Mechanical surface treatment by means of lapping can introduce damage to a depth of about 5 microns. Rough handling of crystal wafers can create defects to as much as 20 microns below the surface, but these defects can be removed by suitable chemical or mechanical polishing. However, there are other types of imperfections that can be introduced during the solidification process. These include growth pyramids, stacking faults, precipitates, slips, dislocations, etc., as well as local variations in impurity contents, and can be most adverse to the performance of devices made of such defective material. Often these defects cannot be detected by optical means and therefore need special detection techniques, i.e., etch pits, and magnetic and X-ray topographical methods.

As compared to other techniques the etch-pit method is quick and gives a quantitative picture of the dislocation morphology, if suitable etchants are known for the particular material under consideration. Proper etchants for Ge, Si and III-V compounds are very well known. Figure 1 shows the etch-pit development on both [111] faces due to a Schell reagent on GaAs. Plastic bending offers a means for correspondence between etch pits and the intersections of dislocations with the etched surface. The quantitative relationship between radius of curvature and dislocation density has been given by Nye [15]. Though the etch-pit method is quick and provides a quantitative picture of dislocation defect density, it is not as sensitive as other methods, i.e. magnetic and X-ray topography.

Dislocations affect the magnetic properties of crystals in many ways. The strain fields of imperfections have direct influence on the nuclear magnetic resonance. In ferromagnetic materials, dislocations act as a source of internal stress which affects the magnetic properties through magnetostriction, whereas, in antiferromagnetic or covalently bonded crystals they may produce moment-carrying boundaries or uncoupled electron spins.

The effect of dislocations on the nuclear magnetic resonance was first observed and studied theoretically by Watkins [16]. Hon [17] pointed out that the broadening is proportional to the cosine of the angle between the magnetic field and the normal to the slip plane. It is therefore possible that anisotropic effects may be observed. Measurements by Rhoderick [18] on the NMR of



The schematic representation of the etch-pit orientation in a GaAs crystal having both (111) and ($\bar{1}\bar{1}\bar{1}$) exposed. The crystallographic directions associated with the etch pits are shown. (From "Properties of Elemental and Compound Semiconductors," Metallurgical Soc. Conf., Boston, 1959).

Figure 1. Schematic of etch pit orientation.

gallium in silicon-doped samples of GaAs have confirmed that Si enters into the lattice in two ways: (1) at low concentrations, they replace gallium atoms to give a donor level, and (2) at concentrations greater than about 2×10^{18} cm^{-3} they enter in pairs to give neutral centers. The silicon donors produce a broadening of the resonance of Ga^{69} because of the interaction of their Coulomb field with the quadrupole moment of the Ga^{69} nucleus, but there is a further broadening consistent with the distortion of the lattice produced by neutral pairs of Si atoms with a maximum solubility of about 10^{20} cm^{-3}.

From the above discussions it is evident that studies of the NMR on Ga^{69} will provide information about the density of dislocations and their directional effects. This study, in conjunction with existing methods will enhance our capability to quantitatively characterize GaAs crystals grown under zero gravity and to compare the resulting characteristics with those of crystals grown on earth.

The presence of trace imperfections in a crystalline solid can cause small changes in lattice parameters and large changes, usually an increase, in the intensity of X rays diffracted by the material. If the identity of a uniformly dissolved impurity is known, a meaningful estimate of its concentration can be made from precise measurements of crystallographic lattice parameters. On the other hand, transmission and reflection X-ray topography is a strong tool in evaluating the distribution of these imperfections in the interior and on the surface of the crystal, if the crystal is otherwise highly perfect.

The transmission and reflection X-ray topography method, with reference to its application on the characterization of bulk and epitaxial GaAs, has been discussed in great detail by Meieran [19]. Its general principle is concerned with point-to-point variations in the directions and/or the intensity of X rays that have been diffracted by the crystals. A scan of the crystal will provide a one-to-one image which must be enlarged photographically. Since topographic methods can detect only variations of intensity and direction within a broad diffracted beam; a perfectly uniform distribution of impurities has no detectable effect on topography. Actually, however, most crystals have nonuniform distribution of impurities due to slight variations in the crystal growth conditions or due to dislocation type imperfections which may or may not have interacted with the impurities. The X-ray intensity mapping is quite sensitive to such nonuniform distribution.

Some of the observations made by Meieran in his X-ray topographic studies on GaAs crystals are particularly interesting. He has found that boat-grown crystals are more nearly perfect and more homogeneous than Czochralski

crystals with equivalent doping. The major defect in a crystal grown by any method is high density of submicroscopic precipitates introduced during the growth process. A similar type of experimentation on the zero-gravity-grown GaAs will provide a conclusive qualification of the purity of such material.

STUDY OF DEFECTS INFLUENCING ELECTRONIC PROPERTIES

The energy levels which are caused by imperfections of an electronic nature, detected by means of electrical and/or optical means, are shown in Figure 2 [20]. Many of these levels are unidentified; however they are known if they act as electron, hole trap, or recombination center. The wide variety of measurements possible to determine the electronic purity of GaAs include: (1) the electrical measurements; (2) photoelectronic analysis; and (3) optical measurements. Of these measurements, the electrical measurements together with their temperature variation are the most important, because they provide a direct measure of the number of impurities present in the sample. However, when GaAs is of higher resistivity, (and sometimes it is believed that such material will be purer then one of low resistivity), it is preferable to perform the photoelectronic analysis or optical measurements because it is difficult to make accurate measurements of the Hall coefficient in high-resistivity material. Moreover, the results of the measurements cannot be directly compared to those on the low-resistivity material, since the mobilities are much lower because of electron depletion.

Electrical Measurements

The fundamental quantities affecting the electrical measurements are the resistivity, ρ, the concentration of carriers per unit volume, n, and the mobility of carriers, μ. The relation between these quantities is given by:

$$1/\rho = n\, e\, \mu$$

where e is the electronic charge. Mobility is generally calculated theoretically by using the above formula after making the experimental measurements of ρ and n. All these quantities are measured as average over a finite volume of the sample; thus the results may be erroneous if the sample under investigation is very much inhomogeneous. Therefore, to characterize a sample through electrical measurements one should be careful to make thorough cross-checking before making a final conclusion.

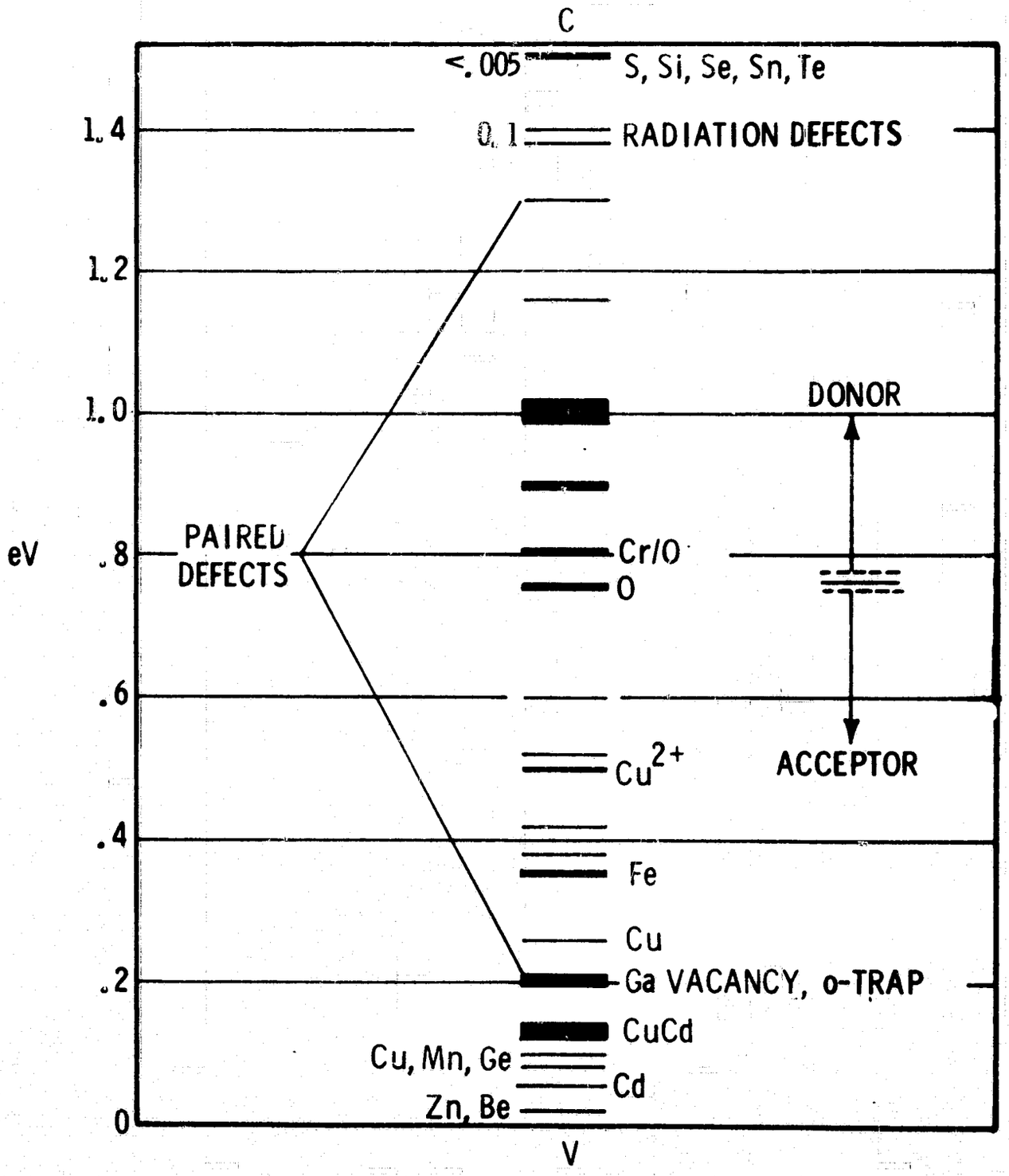


Figure 2. Activation energy levels measured in GaAs.

To quickly determine the order of homogeneity in a grown ingot of GaAs, the current is passed through the sample, as shown in Figure 3, while a probe is allowed to move over a flat surface of the sample. The potential drop may

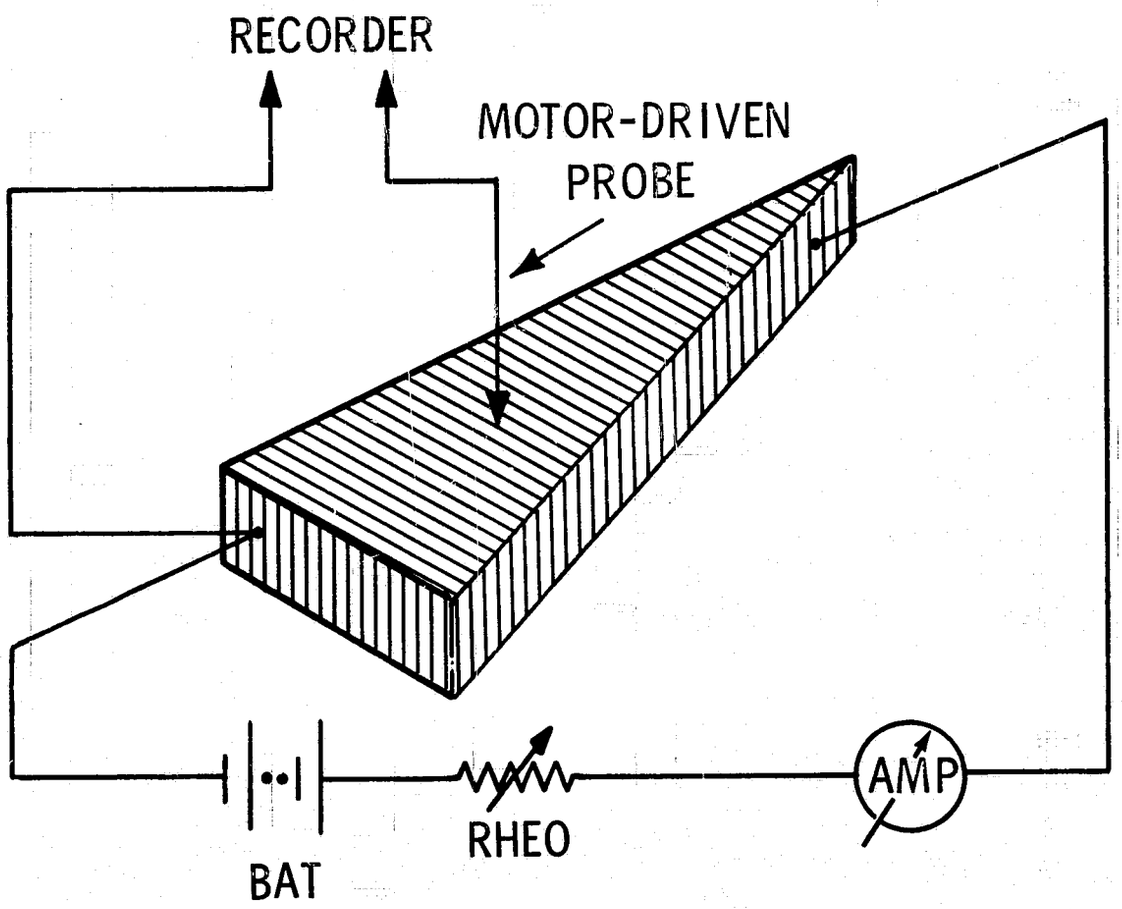


Figure 3. Homogeneity mapping of bulk sample.

be registered on a recorder and the probe may be driven electrically. Any inhomogeneity in the resistivity of the sample will appear as a deviation from linearity of the line drawn by the recorder.

For precise measurements of resistivity, however, one employs the four-probe technique in which the current is passed through the length of a bar-shaped sample and the voltage drop is measured at the two intermediate points along the sample. If negligible current is drawn in the potential leads, contact resistance of the leads will not affect the measurement; thus, the potential difference is measured either by employing a very high input impedance dc voltmeter or by using a null-type detector.

Carrier concentration in a sample is found through measurement of the Hall coefficient and it is effected by applying a magnetic field (about 5000 Gauss)

in a direction normal to the current direction and by measuring the potential drop between two points along the section of the bar specimen in a direction normal to both the magnetic field and the current directions. If it is difficult to make a bar-shaped sample, a disk-type sample of arbitrary shape may be used, and the Hall coefficient and resistivity are determined by application of the van der Pauw method [21]. The detailed formulae for both the cases (i.e., for the bar-shaped as well as the arbitrary-shaped samples) may be found in various textbooks.

While evaluating GaAs through the above measurements it is important to make the measurements at low temperatures, preferably in the liquid helium temperature range. Figure 4 shows the mobility of GaAs as a function of temperature for several samples with varying impurity concentrations. At approximate room temperature there is not much difference in mobility from sample to sample because in this range of temperature the mobility is dominated by thermal lattice scattering. As the temperature is lowered the lattice scattering diminishes and the mobility increases. The maximum mobility at lower temperatures is limited by the onset of impurity scattering. At low temperatures, therefore, mobility basically characterizes a sample.

Gallium arsenide may have low carrier density either because it is very much pure or because of high concentration of charge traps. In the former case the carrier concentration will not change much when the temperature is increased in the thermal scattering range, but the mobility will decrease. Therefore a very pure material would show a positive temperature coefficient of resistivity. In the case of impure material this coefficient would be negative. Generally such material will have both a low carrier concentration ($< 10^{16}$/cc) and a low mobility (< 5000 cm^2/V sec) at the room temperature. At room temperature, theoretically estimated mobilities for electrons and holes in GaAs may be as high as 11 000 and 600 cm^2/V sec, respectively. Carrier concentrations in very pure GaAs may reach values as low as 10^{11} to 10^{10}/cc.

Photoelectronic Analysis

Photoelectronic analysis, discussed in great detail by Bube [22] consists of the following major measurements:

1. Photocurrent dependence on light intensity and its temperature variation

2. Spectral response of photoconductivity and its temperature variation

3. Thermally stimulated currents.

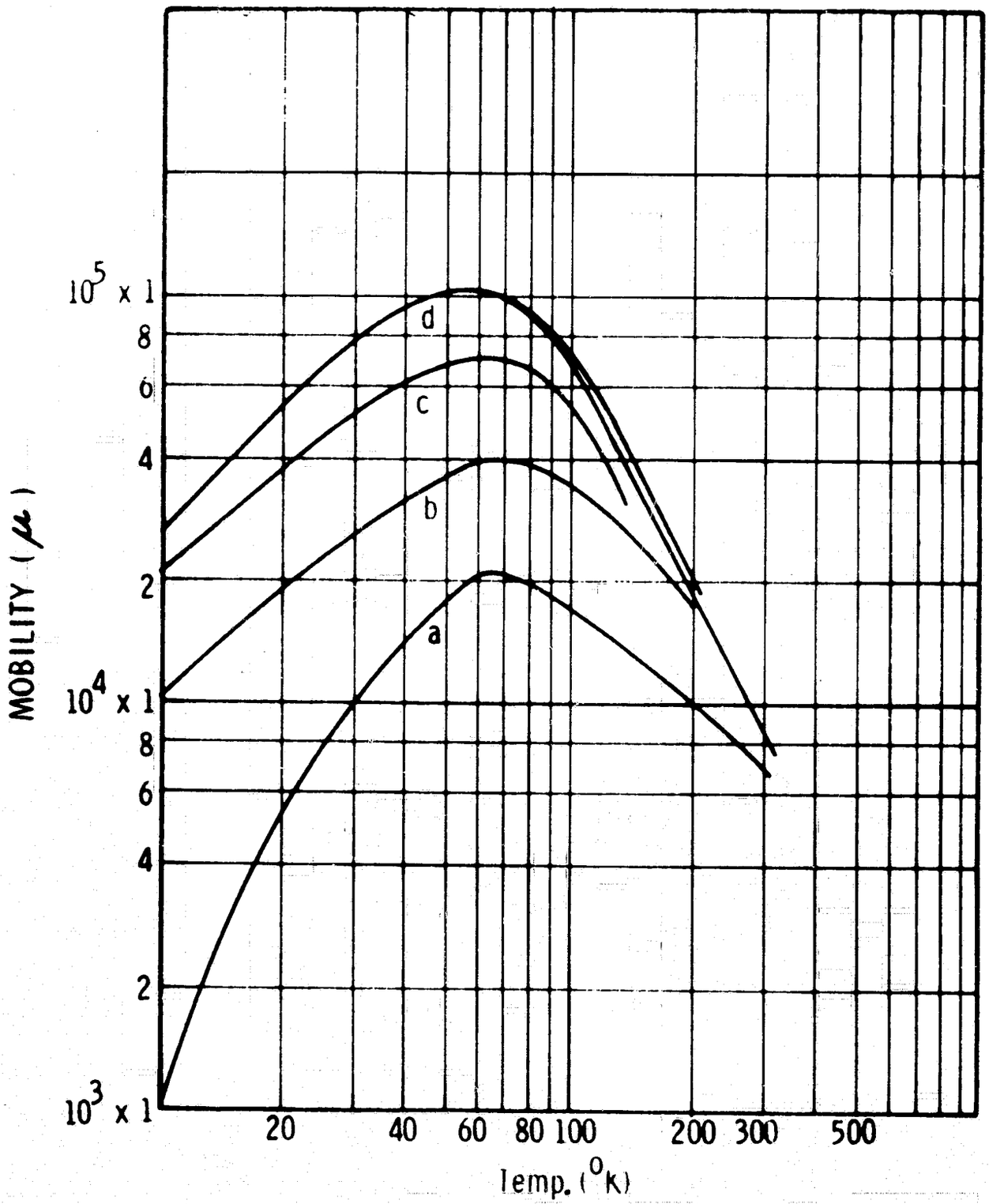


Figure 4. Mobility of gallium arsenide as a function of temperature for samples with increasing purity (a. . . . d)

From these data one can evaluate the following basic quantities: (1) Photoconductive gain, (2) majority carrier lifetime, (3) band gap, and (4) trap activation energies and densities.

Optical Measurements

Optical measurements on GaAs [23] can be performed either by measuring the reflection from a clean, cleaved crystal or by measuring the optical absorption. The latter is generally difficult because it requires very thin slices (of the order of 50 microns) of GaAs and low temperatures to obtain any relevant data. For the measurements of optical reflection, it is desirable to use an ultrahigh vacuum equipment along with a crystal-cleaving and low-temperature facility built into the system. From the optical measurements one can compute the optical ionization energies of the different electrically active imperfections. By comparing the absorption spectra and reflection spectra of two different crystals, one can also determine the relative impurity density.

CONCLUSION

Evaluation of zero-gravity grown GaAs can be performed in three different stages; namely, the determination of ultratrace impurities (in the range of parts per million to parts per billion), the study of dislocation type imperfections, and the study of defects affecting the electronic properties of the material. Although several methods exist to carry out such investigations, many of them are either obsolete, are time-consuming, or have other relative disadvantages. In the present paper it is the authors' intent to familiarize the reader with only those techniques which can be readily applied for the characterization purpose. The technical details have been omitted in the interest of brevity. However, attempts have been made to provide specific information about the application of a particular technique in evaluating the purity of GaAs.

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ZERO-GRAVITY FLAMMABILITY

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ABSTRACT

A study of flammability in a zero-g environment, based on results obtained during aircraft flight, is discussed. The need for long-duration zero-g testing to study inflight spacecraft fire propagation, safe spacecraft designs, and methods of fire extinguishment is shown. The objectives of Apollo Applications Program Experiment M-479 (which concerns flammability in zero g and the equipment needed for the experiment) are discussed.

INTRODUCTION

A two-phase series of experiments was conducted to study the effects of weightlessness or zero g on a flame. This program was undertaken so that the seriousness of an accidental fire in a spacecraft could be evaluated and the means of controlling such a fire could be developed.

Available literature contains only two references regarding flammability in zero g. In 1956, Kumagai and Isoda (ref. 1) reported on the combustion of droplets in a falling chamber. Their data showed that, as the droplet diameter decreased, the flame diameter increased. The maximum test time was 0.32 second. In 1963, Hall (ref. 2) observed a burning candle in aircraft tests with zero-g intervals lasting as long as 25 to 28 seconds. On the basis of some thermocouple data and the change of the flame coloration to deep blue, he concluded that the flame was somewhat hotter than characteristic of one g. Both works indicated that a steady-state condition existed.

ZERO-g FLAMMABILITY — PHASE I

A comparison between flames in one- and zero-g environments is shown in figure 1. When a hydrocarbon is burned in one g, several events occur simultaneously. Solid material is converted to hot gases, thereby absorbing energy. The gases mix with the surrounding atmosphere and, in chemically reacting with the oxygen, liberate energy. Hot gas products are formed, including carbon dioxide, carbon monoxide, water vapor, and numerous minor constituents ranging from hydrogen to complex acids, alcohols, and other organic compounds. These products are formed through various intermediates, including atoms and free radicals. The high temperature of these gases contributes to the low density. The gases rise from the flame zone, allowing more oxygen to enter and mix with the fuel gases. Thus, a steady-state combustion process, in which gas flow-in can be equated with gas flow-out, is made possible.

An idealized concept (based on experimental results) of zero-g combustion is shown in figure 1 as the flame achieves a maximum degree of burning. It should be emphasized that the depicted condition is transitory. As the films of combustion in a zero-g environment show, the flame builds up to a maximum size and brilliance soon after ignition, then quickly recedes, and darkens. The experimental flame never achieved the total envelopment depicted for two reasons: The igniter localized the burning to a few spots and the products of combustion tended to subdue the flame before the fuel could be enveloped.

Several aspects of the zero-g flame are noteworthy. The gas that is formed by an overheated material in zero g is ignited and burns in the oxygen with which the gas is initially mixed. The fuel-to-air ratio, therefore, changes during combustion from lean to rich as the ambient oxygen is depleted. This depletion occurs much more rapidly than the diffusion process can supply oxygen. Eventually, oxygen starvation occurs and the flame begins to cool by radiation and conduction. What results is a blanket of unburned flammable gases adjacent to a solid or molten fuel that, in turn, is covered with a layer of both solid and gaseous combustion products with a very low oxygen content. The result is that the fire is diminished to the extent that light is no longer visible, which indicates that steady-state combustion was not achieved. Thus, oxygen can be less than an inch away from warm flammable gases, yet be unable to react with the gases. These conclusions were based on the pictures showing the flame darkening and diminishing less than 1.5 seconds after ignition. In the familiar one-g environment, the flame temperatures invariably increase over a brief period to a peak heat when steady-state combustion is achieved. Zero-g burning is hampered because only the fuel gases generated within extremely brief periods can burn. In many instances, the flame itself is apparently too cool to generate additional flammable gases.

In several instances of paraffin burning, the light disappeared for several seconds and reappeared when an acceleration returned and convection developed (e.g., when weightlessness ceased because the experiment chamber came into contact with the aircraft). It is assumed when the light is no longer visible that the fire is extinguished with respect to energy emittance, because neither the color nor the infrared film used in the experiments revealed any evidence of combustion during these intervals. With respect to chemical unbalance, however, the system is better described as dormant, with the intermediate free radicals remaining where formed. When convection was renewed, molecular oxygen reacted with these free radicals as the hot, light gases flowed away from the fuel and the process resumed.

The data pertinent to most of the tests shown in the motion-picture film are listed in table I; 26 burnings were photographed. Fuels included spacecraft materials and paraffin (selected because of the relatively simple chemical structure and kinetics). The atmospheres used included pure oxygen, air, and other oxygen-nitrogen mixtures. Pressures varied from 5 psia, as used in manned spacecraft, to 14.7 psia. Styrene, white foam rubber, and paraffin were used as fuels in the nine burnings shown in this presentation. Excess oxygen was present and the fuel was burning during the return to level flight in all instances.

The equipment designed for the experiments is shown in figure 2. These flammability chambers were designed for use in aircraft tests. The 15 chambers were designed to be charged with a selected fuel and atmosphere under controlled conditions so that the inflight time could be used to the best advantage and so that gas products could be analyzed after the flight.

The equipment used in the first series of tests consisted of a shell of anodized aluminum with a volume of 0.75 cubic foot (which provided a region 10 inches in diameter for the flame), a glass window to permit photography of the combustion, and a fuel support that allowed positioning of the fuel without obstructing the atmosphere or flame. The support was made of glass beads threaded on a wire. A filament made of 20-gage Nichrome wire was positioned horizontally from two brass electrodes. Twenty-four volts dc were passed through the wire to ignite the fuel; the voltage overloaded the wire and caused a break in approximately 2 seconds, which opened the circuit. The fuel could be contacted at a single point or in several places. The points of contact appeared to start separate fires, some of which united. A grid 5 inches behind the fuel provided 0.25-inch parallel lines for reference. No supplemental light was used; in fact, the aircraft cabin was usually dark during the tests.

FILM NARRATION

Zero-g flammability was observed by using a Wright-Patterson Air Force Base aircraft equipped for weightless flight. The first scene shows the interior of the C-131. The camera and ignition plugs of the control cable are shown being connected to a flammability chamber by an engineer. A sample "float" lasting 8 seconds is shown next. Some floats lasted slightly longer than 8 seconds; the maximum measured time in this series of tests was 12 seconds.

Several tests showing ignition and combustion during zero g are shown next. These scenes, photographed at 200 frames per second, are being shown in slow motion at one-eighth the actual time. The horizontal member is the ignition wire.

Styrene

First, styrene was ignited in zero g in 100 percent oxygen at 5 psia. The fires started at several points. The flame increased rapidly and then began to darken and diminish before the wire parted. The fire spread slowly, causing some of the smaller fires to unite. Meanwhile, the rate of combustion continued to diminish with the passage of time until the chamber struck the aircraft cabin, ending the test.

Foam Rubber

Foam rubber in the same atmosphere is shown next. The foam rubber took longer to ignite and the ignition wire parted less than 1 second after ignition. A very uniform flame corona can be seen, with flowing particles of carbon passing through a sharp interface in a completely random distribution. The dark shadow in the center of the flame is unburned fuel. Again, the corona diminished and darkened before the period of weightlessness ended.

Paraffin

Paraffin was used as a control fuel. The paraffin was ignited in zero g in 21 percent oxygen at 14.7 psia. The heated gas quickly ignited and then appeared to be extinguished. The wire can be seen to part and cool approximately 0.5 second after ignition. The actual time that passed before the flame reappeared was 5.7 seconds (for this showing, no blank film has been deleted). Little information about what occurred during this interval is available. No emitted energy is detectable in the color film used here nor in the infrared film used in the final scene. It is evident that the region containing the fuel cooled by both radiation and conduction. The Nichrome wire darkened and eventually became invisible. When the period of weightlessness ends (in any direction or magnitude), the hot products of combustion flow from the flame zone as

fresh oxygen flows in. In this series of tests, the flame invariably reappeared as the force field was renewed so that in every case except for Teflon, the fuels were burning during the return to level flight. Whether this reignition occurs because of the heat load or because the gases remain reactive or chemically hot — that is, contain numerous free radicals with unpaired electrons that reacted with the molecular oxygen — has not been determined. Another possibility is the presence of a "cool flame," but a cool flame is usually detectable by the deep purple color. Regrettably, the zero-g time was not of sufficient duration in this series of tests for a fire, once extinguished, to remain extinguished. Several other paraffin-fuel flammability tests were similarly documented. Most tests exhibited the same self-extinguishment seen here.

Paraffin was again ignited as before, except that in this test pure oxygen was used. The corona was small, as in the first two scenes, which also were photographed in a 100-percent-oxygen environment. The higher oxygen pressure seemed to make very little difference as compared with the 5-psia pressure. The flame diminished, darkened, and appeared to be extinguished as before. The appearance of the flame at the upper portion of the fuel resulted from the location of the igniter wire, not from an induced motion at the time of ignition.

Next, paraffin was ignited in an atmosphere of 50 percent oxygen/50 percent nitrogen at 10 psia, which equates to the same partial pressure of oxygen as in the first two scenes of styrene and foam rubber. Again the flame had the darker, less well defined corona that diminished very rapidly, apparently because of the presence of the inert gas. The fire appeared to be extinguished, but when the package was struck, convection resumed momentarily; then weightlessness reoccurred and again the fire appeared to be extinguished until the effect of the final impact with the aircraft was observed.

Another combustion of paraffin in a 100-percent-oxygen atmosphere at 14.7 psia is shown for comparison. This portion of the film shows the dramatic effect of several impacts on the molten fuel.

Paraffin in a 50-percent-oxygen/50-percent-nitrogen mixture at 10 psia was again ignited.

Infrared film was used to record two burnings in an attempt to obtain a qualitative temperature measurement. This burning (and the next) used paraffin in 100 percent oxygen at 5 psia. The pictures were taken at 100 frames per second. Thus, the viewing speed has been doubled to one-fourth the actual time of the two scenes. The same coronal diminution occurred until an acceleration (as indicated by the vibration) was imposed.

In this last test of paraffin burning in oxygen, the atmosphere was the same as used before. Again, the fire appeared to be extinguished very shortly after ignition, as can be seen quite easily in these infrared views.

DISCUSSION OF AIRCRAFT TESTS

The temporary extinguishments seen in the film indicate the possibility that a dormant, fairly cool envelope of chemically reactive gases remains in the flame zone; the gases ignite only if the oxygen contacts the fuel. In time, if left undisturbed, oxygen slowly entering this zone by diffusion could combine with the reactive products without increasing the temperature. In many tests, gas samples were removed and analyzed. One gas of special concern was carbon monoxide. Although not detected in samples burned in one g, carbon monoxide was found in three of the 18 zero-g test analyses for this gas. This incidence of carbon monoxide is not surprising, however, when one considers the over-rich condition resulting from the zero-g environment. Results of the Phase I test series are discussed in reference 3.

ZERO-g FLAMMABILITY — PHASE II

The burning rates of various materials investigated in the second series of tests are shown in table II. Five polymeric materials were selected as fuels. Four materials (neoprene, silicone, Teflon, and polyurethane) represent electrical insulation; the fifth material (Dacron thread wrapped around polyurethane) was tested for possible use in space suits. All fuels were tubular to eliminate variations caused by geometrical shape. Three test atmospheres were selected — ambient air, pure oxygen at 5 psia, and pure oxygen at 15 psia. One- and zero-g data are compared.

The equipment used in the Phase II tests was basically the same as that used in the Phase I tests except for the fuel configuration. Ignition was provided by a resistance wire closely wrapped around one end.

It should be noted that, despite the variety of burning rates in one g, the zero-g rates are approximately 0.1 in/sec for oxygen atmospheres (table II).

CONCLUSIONS

1. Ignition during periods of weightlessness is essentially unchanged compared with ignition in one g.

2. Burning rates are reduced to approximately 0.1 in/sec for a wide assortment of solid hydrocarbon fuels.

3. Self-extinguishment can occur in some fuel-atmosphere systems.

4. Introduction of an acceleration renews convection promptly.

5. A distinct gas interface exists at the edge of the corona, which implies a phenomenon analogous to surface tension, with characteristics varying according to the presence of inert gases.

The need for exploring the effects of longer periods of weightlessness is obvious. Several methods have been proposed, including free-fall drops from towers or aircraft and the use of rockets, X-15 aircraft, or unmanned Apollo spacecraft.

The current approach of sharing equipment with other experiments is described in reference 4. The objectives of this experiment are the following items with respect to burning various materials in pure oxygen at 5 psia.

1. Extent of flame propagation, flashover to adjacent materials, et cetera

2. Rates of surface- and bulk-flame propagation under zero-g convection

3. Self-extinguishment

4. Extinguishment by vacuum or water spray

Only one atmosphere is to be used in the tests, although a variety of atmospheres have been proposed for future use, and despite the fact that the most interesting results in the aircraft tests were noted in two-gas atmospheres. Similarly, relatively few materials can be selected for test fuels and only limited fire-extinguishment data will be obtained. Thirty-seven tests are proposed. All tests will be photographed with 16-millimeter motion-picture film at the rate of 24 frames per second.

Although the presently scheduled test program is severely limited in scope, it is recognized that a more thorough program is desirable. Much valuable information could be derived from tests of wider scope. For example, ignition energies and spectral patterns during the initial period of self-extinguishment should provide very useful data. Tests using gaseous fuels and metals (which produce only solid ash instead of gaseous combustion products) burning in zero-g conditions could also be conducted. The apparent surface tension existing between the luminous plasma and the surrounding gas also should be investigated further. All these test objectives, of course, cannot be included in the M-479 Experiment.

Hopefully, space flight will afford many hours of zero-g environment for testing and will provide engineering data that can be used not only for designing future spacecraft, but also for solving some of the mysteries of the combustion mechanisms on earth.

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1. Kumagai, S.; and Isoda, H.: Combustion of Fuel Droplets in a Falling Chamber. Proceeding of the Sixth International Symposium on Combustion, Reinhold Pub. Co., 1956, pp. 726-731.

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3. Kimzey, J. H.; Downs, W. R.; Eldred, C. H.; and Norris, C. W.: Flammability in Zero-Gravity Environment. NASA TR R-246, 1966.

4. Kimzey, J. H.: Experiment Inplementation Plan for Manned Space Flight Experiments — Zero Gravity Flammability, Experiment M-479. Aug. 8, 1969.

TABLE I.- ZERO-g FLAMMABILITY EXPERIMENTS

Test no.	Fuel	Weight, gram	Oxygen atmosphere, percent	Nominal pressure, psia	Zero-g time, sec	Photography
16	Styrene	1.0003	100	5	--	Color
15	Foam rubber	.2706	100	5	6	Color
35	Paraffin	.7213	[a]21	14.7	10	Color
19	Paraffin	.1084	100	14.7	5 to 8	Color
56	Paraffin	.1636	[b]50	10	7 to 12	Color
28	Paraffin	.1244	100	14.7	5	Color
36	Paraffin	.1551	[b]50	10	3 to 8	Color
22	Paraffin	.1524	100	5	--	Infrared
10	Paraffin	.5680	100	5	3	Infrared

[a]Atmosphere consisted of air of 60 ± 10 percent relative humidity.

[b]Dry nitrogen constituted the remaining 50 percent of the atmosphere.

TABLE II.- BURNING RATES IN ONE g AND ZERO g

Fuel (b)	Rate of burning, in/sec (a)					
	One g			Zero g		
	Air at 15 psia	Oxygen at 5 psia	Oxygen at 15 psia	Air at 15 psia	Oxygen at 5 psia	Oxygen at 15 psia
Neoprene	0.0	0.2	0.4	--	0.10	--
Silicone	.04	.5	1.1	0.0	.08	--
Teflon	.0	--	--	--	.00	--
Polyurethane	--	.6	.7	.0	.08	0.15
Dacron[c]	--	.6	.7	--	.08	.15

[a]Ignition was provided by electric resistance coil; the temperature of the atmosphere was 65° ± 5° F.

[b]Fuel was tubular (no. 10 American wire gage i.d.) and threaded over a steel or ceramic mandrel.

[c]Dacron thread was wrapped around polyurethane.

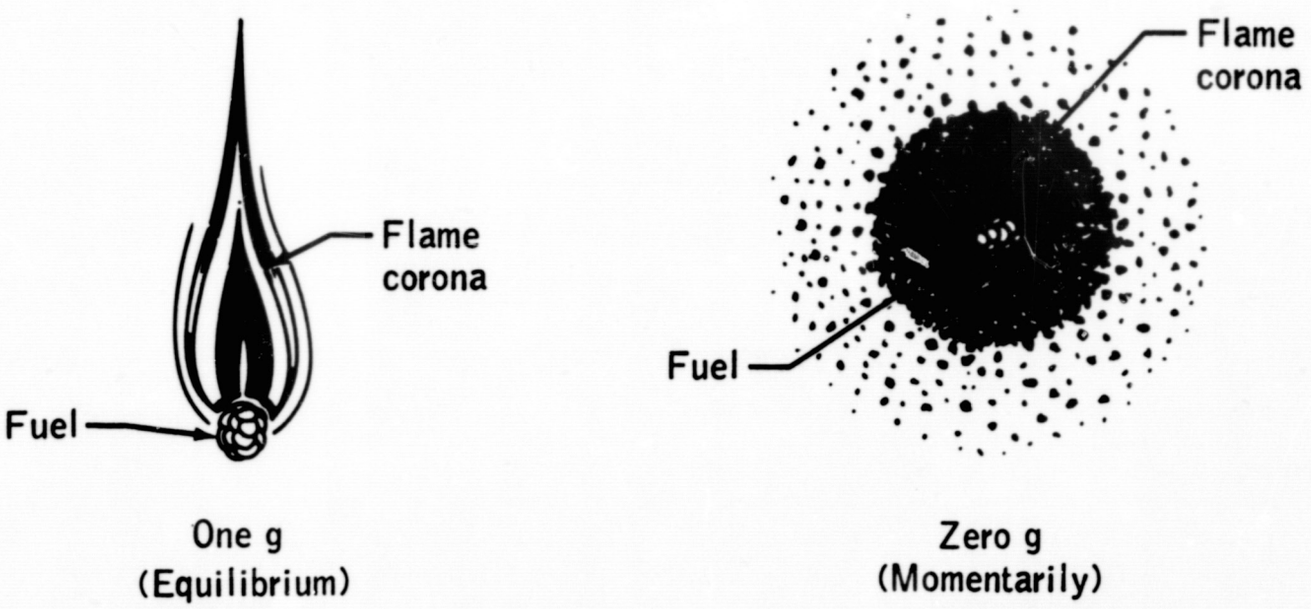


Figure 1.- Comparison of fuel burning at one-g and zero-g in oxygen atmosphere.

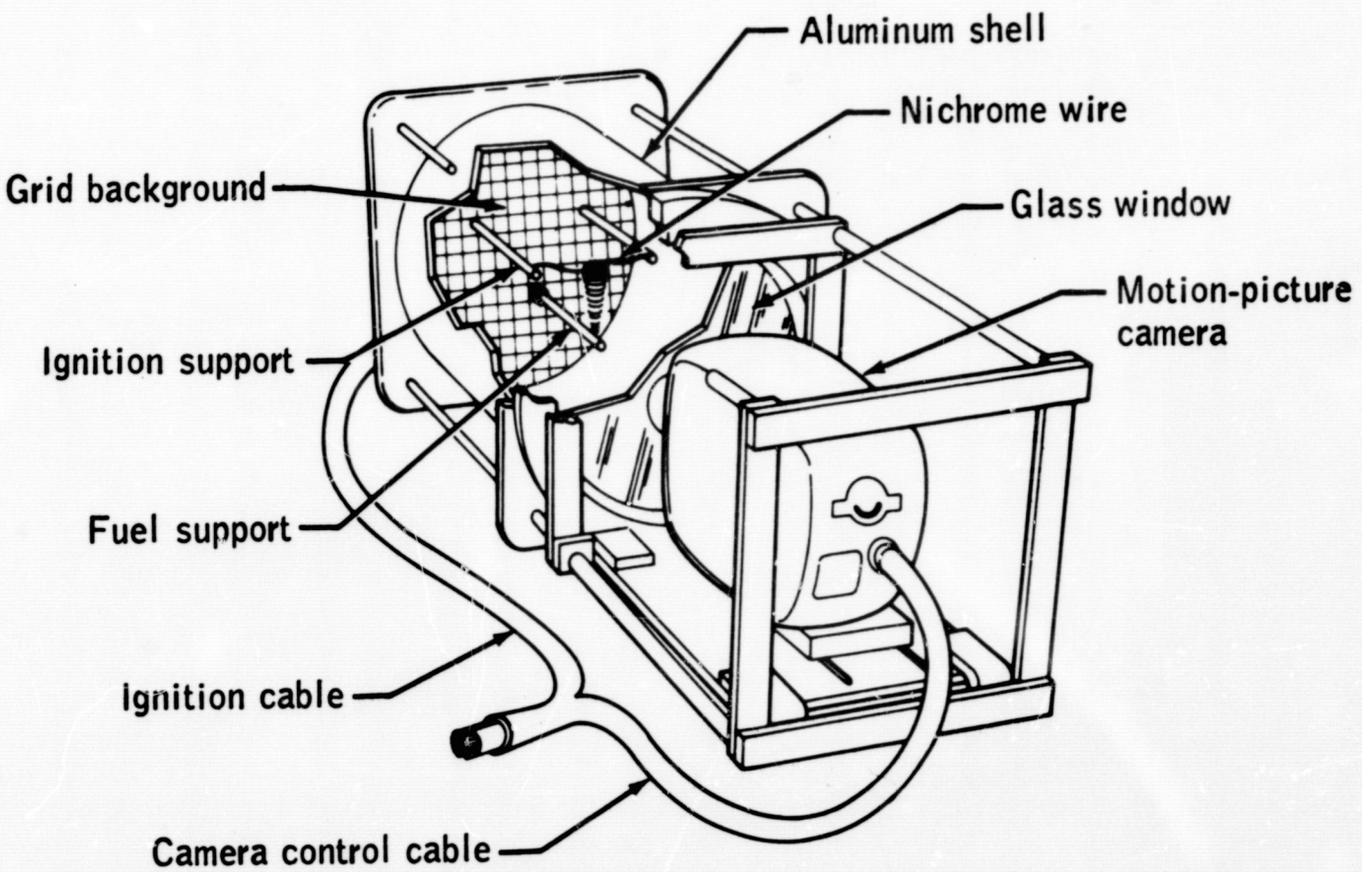
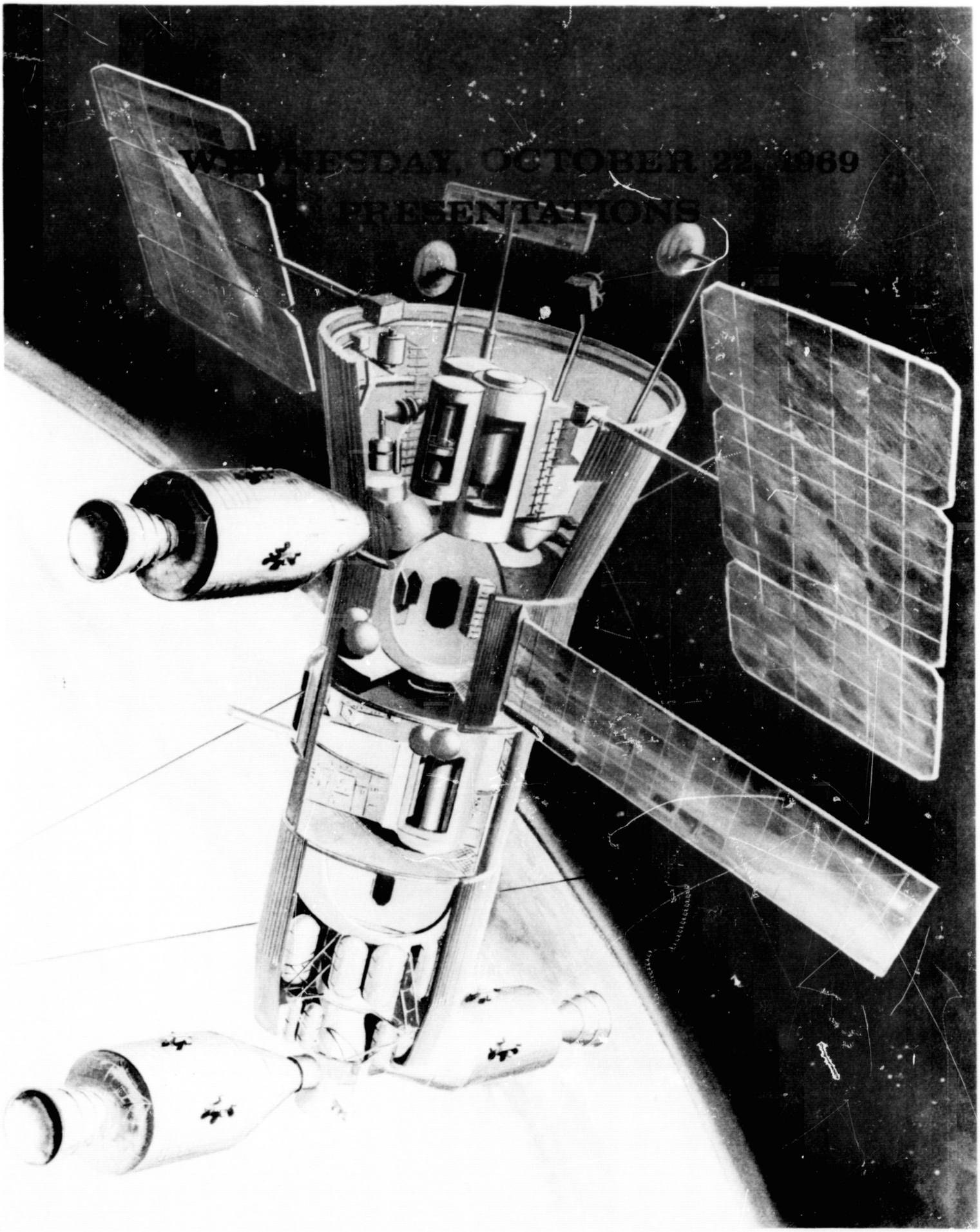


Figure 2.- Zero-g flammability chamber.

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N70-20536

NEW DEVELOPMENT IN SPACE MANUFACTURING

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ABSTRACT

The progress in space manufacturing development is reviewed. The possibilities of processes in zero and low "g" environment have been considered in industry, at universities and research institutes, and government agencies. Areas of interest stimulated conceptual studies and evaluation of economical aspects. In-depth assessment of feasibility is underway.

The tabulation of unique space processes is brought up-to-date. New processes which have emerged are discussed. The present coverage by research and technology development toward space experiments is assessed, and recommendations for future development areas are given.

We have learned recently how to leave the mechanically closed system of the earth. Rocketry has opened an escape hatch from our highest order terrestrial environment. We can describe it as the earth being completely enclosed in an Ocean of Gravity. The freedom from the ever-present gravity here impacts our thinking. It sounds at first like a trivial, easy to handle change. But be on guard; it is a change completely abstract to our experience.

It impacts the microscopic and the macroscopic technology. It even amplifies our terrestrial idea of full scale things--because the disappearance of the dead weight will allow us to build things of truly extraterrestrial dimensions.

A million years ago, our "Darwin relatives" left the Ocean of Water. We learned to escape the Ocean of Air only 300 years ago. The air-free environment--the technical utilization of the vacuum--is the basis of today's technology. Without processes in pressures below one atmosphere and all the way down to the zero atmosphere level, we would not have changed and mastered the "dark age". No steam or combustion engine, no vacuum tube and electron beam, no liquefication of gases, nor the 20th Century technology would yet be developed. The significant step, 300 years ago, was this discovery of the vacuum and its subsequent utilization for laboratory and manufacturing processes. And how easy it is to talk about all the drastic developments it brought about, like playing the Monday morning quarterback.

Let's wake up now to the fact that we are witnessing another historical event--the discovery of permanent weightlessness. We must learn and become accustomed to the many novel things about the processes in environment below one "g", all the way down to the zero "g" level. The advent of zero "g" technology is the significant step into a new age of technology and we are the original participants; let's learn how to master this challenge of the Century.

How can we learn it? What does learning mean? Learning means doing something wrong. Otherwise doing it right immediately means you knew it already; you did not have to learn it in the first place. Let's wake up and go to work.

The major importance of the weightless environment lies in the fact that liquid materials become objects in their own right. From our terrestrial experience, liquids alone practically do not exist. They always need a container, and buoyancy and thermal convection during the interaction with other liquids, solids and gases are overshadowing, preventing many processes. Furthermore, on macroscopic scale, the molecular forces such as cohesion and adhesion are a set of rather disturbing influences versus the large gravity forces and rarely considered to be process determining factors. Weightless environment removes all these barriers from liquids.

In Figure 1, unique space processes which are presently under investigation are tabulated. Under A, processes are listed which use the buoyancy and thermal convection free environment and under B, the processes which are controlled by the inherent cohesion and adhesion forces. Also shown are the materials groups presently involved and the potential product groups which might emerge during follow-on space manufacturing activities.

S&E-ME-DIR 109	SPACE MANUFACTURING UNIQUE TO WEIGHTLESS ENVIRONMENT	SUMMARY

SPACE PROCESSES UNDER INVESTIGATION		MATERIAL GROUPS	PRODUCT GROUPS
A. BUOYANCY AND THERMAL CONVECTION			
FREE PROCESSES: TOTAL 28			
1. FREE AND CAPTIVE SUSPENSION	2		
2. MIXING	1		
3. SEPARATION & PURIFICATION	5	METALS	BALLS, SOLID AND HOLLOW, PRECISION PARTS
4. ALLOYING & SUPERSATURATION	2	CERAMICS	HIGH STRENGTH-TEMPERATURE COMPONENTS,
5. COMPOSITE CASTING	3	GLASSES	FILAMENTS, MEMBRANES, COMPOSITE
6. SOLIDIFICATION	6	BORON	STRUCTURES, COATINGS
7. DEPOSITION	2	ORGANICS	OPTICAL BLANKS AND COMPONENTS, ABRASIVES,
8. NUCLEAR	1	COMPOUNDS	ISOTOPES, NUCLEAR FUELS
9. CHEMICAL	3	CULTURES	ELECTRONIC COMPONENTS AND CRYSTALS,
10. BIOLOGICAL	3		SUPERCONDUCTORS
			VACCINES
B. COHESION AND ADHESION CONTROLLED			
PROCESSES: TOTAL 14			
1. SURFACE TENSION CASTING	6		
2. SURFACE TENSION DRAWING	3		
3. ADHESION CASTING	1		
4. BLOW CASTING	1		
5. CONTROLLED DENSITY CASTING	3		
TOTAL A AND B: 42			

FIGURE 1

A1 is the most typical of all weightless process: the Free and Captive Suspension of Materials. On earth, we help ourselves with levitation melting, which is limited to very small amounts of certain metals and high temperature ranges. How large and involved the possibilities of operation in zero "g" environments really are is shown in Figure 2. Here is a detailed definition of Free Suspension. There are presently two specific studies underway. More investigations are planned.

Process A2 concerns just the operation of mixing or blending in weightless environment, and there is one investigation specifically in this direction.

Process A3, Separation and Purification, is a newcomer since last year's meeting. Five investigations have developed in this area, and Figure 3 shows the involvement. Here is the present state of definition for zero "g" separation.

Processes A4 and A5, Alloying and Supersaturation and Composite Casting, are well covered throughout these presentations.

Process A6, Solidification in Weightless Environment, is one of the most attractive areas where basic improvements or even achievement of new type materials look promising. There are new operations seen in amorphous solidification, controlled crystallization, single crystal solidification, directional solidification and supercooled solidification or coining.

Process A7, Deposition in Weightlessness, carries the promise of dislocation free plating and even improved diamond deposition.

Process A8, the Making of Isotopes and Nuclear Fuels, will be discussed later in another presentation.

Process A9, the Chemical Processes in Zero Gravity, is a new area under recent consideration, and you will hear about these potential processes in other presentations. The last chart in this presentation will help to make you aware of the extreme vacuum which can be achieved even in the relatively low orbit of our future Space Station.

Process A10, the Biological Process area, is new as well, and there have already been three special presentations about it.

S&E-ME-DIR 109	FREE AND CAPTIVE SUSPENSION PROCESSES IN WEIGHTLESS ENVIRONMENT	PROCESS A1 DEFINITION

ENVIRONMENTAL CONDITIONS

a. FREE SUSPENSION IN INDIVIDUAL ORBIT

b. CAPTIVE SUSPENSION
- STING POSITIONING
- DIFFERENTIAL GAS PRESSURE POSITIONING
- ELECTROMAGNETIC FIELD POSITIONING

MATERIAL CONDITIONS

STATE OF MATTER:
- SOLID POWDERS, FIBERS, PARTS
- LIQUID
- GASEOUS

PROCESS CONDITIONS

SUSPENSION IN ONE PIECE, LIQUID OR SOLID

IMMISCIBLE LIQUID MATERIALS
LIQUID AND SOLID MATERIALS
LIQUID AND GASEOUS MATERIALS

SOLID MATERIALS PARTICLES MIXED IN VACUUM
SOLID MATERIALS PARTICLES MIXED IN GAS
SOLID + LIQUID + GASEOUS MATERIALS MIXED

FIGURE 2

S&E-ME-DIR 109	SEPARATION AND PURIFICATION IN WEIGHTLESS ENVIRONMENT	PROCESS A4 DEFINITION

CENTRIFUGAL SEPARATION
(FREE OR IN CONTAINER)

VELOCITY SEPARATION
(CONTINUOUS CONDENSATION; SELECTIVE MEMBRANES)

ELECTROSTATIC SEPARATION
(ELETROPHORESIS)

MAGNETIC SEPARATION
(MASS SPECTROMETER)

HIGH VACUUM REFINEMENT
(FREE CENTRIFUGATION)

FIGURE 3

The processes under B use the molecular forces as process controlling factors. Here the list actually has not changed since last year, but the utilization of the surface tension or free casting of precision bodies and high temperature materials has found large interest as evident from the six experiments under investigation, which have already been presented. The casting means putting under consideration the total process to the solidified component, while the free suspension, the mixing, separation and purification are either the subject of an experiment in itself or are playing only then a supporting role within the total casting process.

Surface tension drawing has found application in filament making and proposals for directional solidification. The actual drawing of membranes from inorganic materials is still an area of the future.

Adhesion casting has as well not yet found application beyond preliminary study of the process. This is true for the blow casting, which essentially will produce the hollow precision shapes, and the controlled density casting.

The material groups presently involved are metals, ceramics, glasses, boron, and organic compounds and cultures. The product groups which can be visualized in future space manufacturing activities are as follows:

Balls, solid and hollow, precision parts
High strength-temperature components, filaments, membranes, composite structures, coatings
Optical blanks and components, abrasives, isotopes, nuclear fuels
Electronic components and crystals, superconductors
Vaccines

Figure 4 demonstrates that extreme high vacuum of high pumping capacity can be made available in the wake of a rarefied flow shield. Air-free chemical preparation proposals might be greatly enhanced by this new approach.

The presentations which follow will interpret the presently known processes and cover science and technology aspects. We will also look at some more advanced processing prospects and have a grandiose look into the far future, for instance by visualizing a space factory for providing the earth with nuclear fuel. This is the end of the introductory presentation. In the beginning, you were reminded that today's technology started just 300 years ago with the discovery of zero pressure--the vacuum. So we have since then brought energy under control and established a closed cycle in food production. This is what distinguishes us from the apes, that we do not only harvest--we

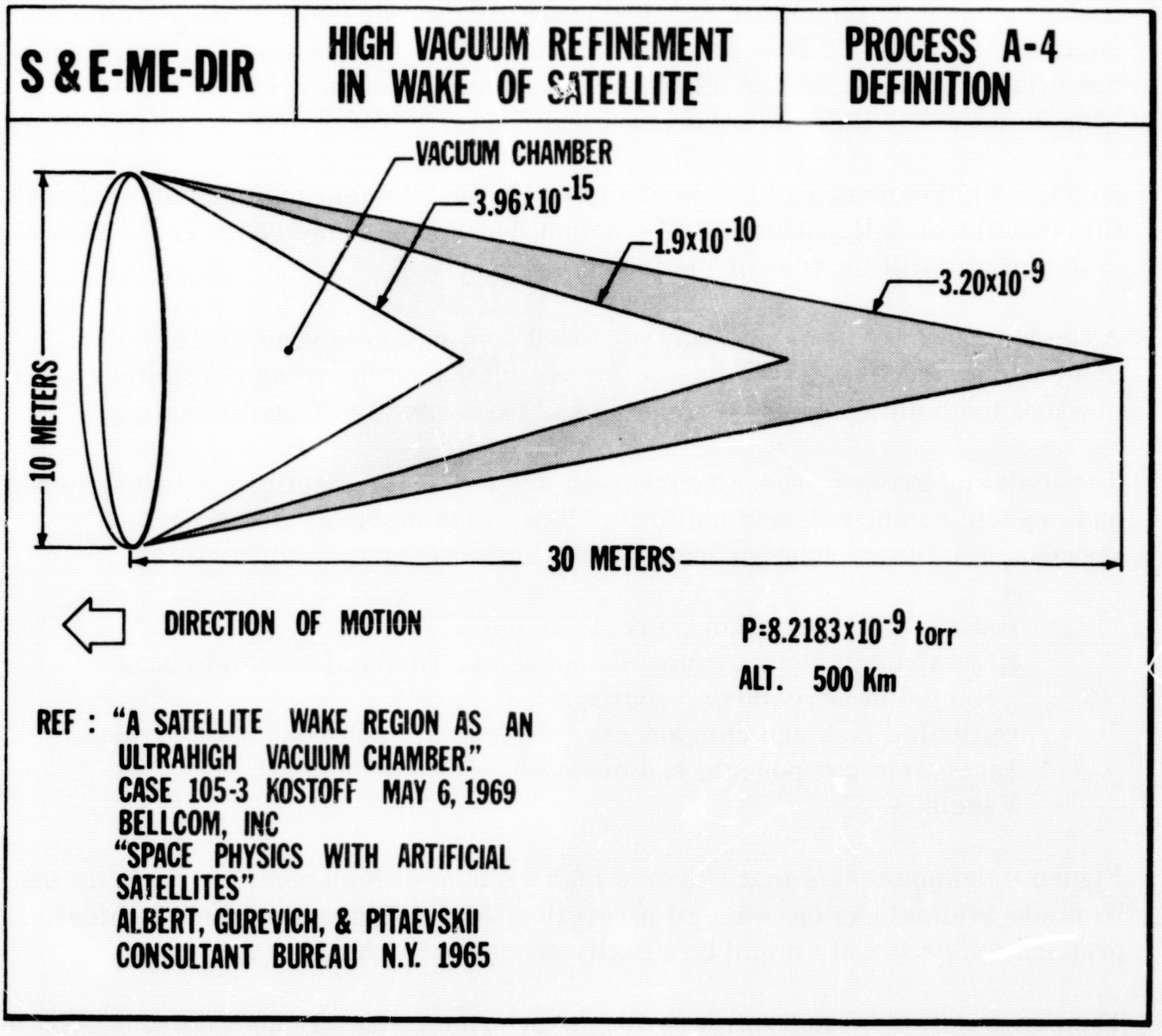

S & E-ME-DIR
HIGH VACUUM REFINEMENT IN WAKE OF SATELLITE
PROCESS A-4 DEFINITION
VACUUM CHAMBER
3.96x10-15
1.9x10-10
3.20x10-9
10 METERS
30 METERS
DIRECTION OF MOTION
P=8.2183x10-9 torr
ALT. 500 Km
REF : "A SATELLITE WAKE REGION AS AN ULTRAHIGH VACUUM CHAMBER."
CASE 105-3 KOSTOFF MAY 6, 1969
BELLCOM, INC
"SPACE PHYSICS WITH ARTIFICIAL SATELLITES"
ALBERT, GUREVICH, & PITAEVSKII
CONSULTANT BUREAU N.Y. 1965

FIGURE 4

produce what we need as well. There is only one gap left open, that is in the open loop fuel economy. We cannot reproduce the fuels we take from the earth. Maybe we are now on the way toward learning how to someday replenish our fuel needs from space.

You should test your daily processes to discover the very often hidden and indirect role which gravity plays. Review attractive concepts of the past which failed, and toy with what zero "g" can change. New developments start with the discovery of new concepts--that is the "non-mathematical" portion of science and engineering. Newton had to postulate first the concept of general gravitational attraction just from watching the apple fall. Einstein had to postulate the concept of matter-energy equivalence first. Mathematics comes later and works only if we are lucky enough to have a concept that is right, and most of the simple concepts are right. Zero "g" has the beautiful effect of simplification of involved terrestrial processes. Just think about it.

Don't hesitate--the timing now is right. Let's go to work on the exploitation of space--an area of great promise and even greater challenge.

N70-20537

THEORETICAL INVESTIGATION OF GAS MANAGEMENT IN ZERO-GRAVITY SPACE MANUFACTURING

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ABSTRACT

The proposed research has as its objective the management of gases in liquefied materials in a free suspended position in zero gravity environment. The investigation shall mainly center on the degassing of liquefied materials, which shall be accomplished by accelerating the material. Also the gas-liquid-interaction, as well as methods to distribute gas properly in liquefied materials of various viscosity and surface tension shall be studied.

INTRODUCTION

The advent of space flight and the availability of large boosters which can carry large payloads into an orbit make it possible to put a workshop in space in which intriguing manufacturing processes could be performed. The lack of gravitation and the vacuum are the basis for the development of unique technologies which are absolutely impossible in an earth bound workshop. It is believed that one is able to cast perfect optical lenses, to produce perfect ball bearings and even more, to create unique materials, alloying various metals or by mixing gas in any ratio into liquefied materials. For such applications the gas bubbles have to be managed in a certain fashion according to the purpose of the process.

In most manufacturing processes the degassing of the material during the liquid phase is a basic requirement for obtaining a useful engineering material. On earth this is aided by buoyancy forces which cause the entrained gas bubbles to rise to the surface and escape. This process can be accelerated and enhanced by degassing into a vacuum. In an orbital workshop, however, buoyancy forces are not available and the elimination of gas bubbles from the molten material

may be a serious problem. In order to introduce forces which move the gas bubbles, the molten material is placed in an acceleration force field. The centrifugal force field will create a migration of the bubbles towards the rotational axis and shall finally give the total gas bubble as well as the spinning free floating material a certain shape which depends upon the angular velocity, the volume, the viscosities, densities and surface tensions involved. The stability of the system is also of importance.

Taylor[1] treated the behavior of a gas bubble in an infinite liquid region and determined the shape of a bubble in an axisymmetric electrical field under the action of surface tension, neglecting gravitational effects. He found that due to the electric field the originally spherical bubble was deformed into a convex body of revolution. The shape of a rotating drop under the influence of capillary force was treated by Lord Rayleigh[2], while Rosenthal[3] investigated the shape of a bubble in one liquid inside a denser body of liquid which rotate rigidly together. In both studies gravity has been neglected. The stability of the system has also been discussed. It was found that the bubble length increases almost linearly with its volume and that it increases proportionally to the four-thirds power of the angular velocity. With increasing angular velocity the bubble flattens at the equator and the length, (measured along the spin-axis) increases. For constant speed of rotation and increasing bubble volume, the bubble elongates, its radius approaches a limit value and its length increases.

Habip, Siekmann and Chang[4] investigated the effect of an electric field upon a uniformly rotating drop in a dielectric liquid mass under the influence of surface tension. The axisymmetric relative equilibrium shape of the bubble in such a uniform axial electric field has been determined. The shape of the bubble is a function of the dielectric constants, the surface tension as well as the rotational speed of the system. In another study Pao and Siekmann[5] investigated the oscillations of a vapor bubble in a rotating cylindrical container in zero gravity.

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1. G. I. Taylor, "Studies in electrohydrodynamics. I. The circulation produced in a drop by an electric field." Proc. Royal Soc. A, Vol. 291, pp. 159-166 (1966).
2. Lord Rayleigh, "The Equilibrium of Revolving Liquid under Capillary force." Philos. Mag. S.6., Vol. 28, No. 164, pp. 161-170 (1914).
3. D. K. Rosenthal, "The shape and stability of a bubble at the axis of a rotating liquid." Journal of Fluid Mechanics 12, pp. 358-366 (1962).
4. Habip, L. M., Siekmann, J. and Chang, S. C., "On the Shape of a Rotating Liquid Drop in an Electric Field." Acta Mechanica, Vol. IV, 1, pp. 107-114 (1967).
5. Pao, S. K. P., Siekmann, J., "Oscillations of a vapor cavity in a rotating cylindrical tank." J. Fluid Mechanics, Vol. 31, Part 2, pp. 249-271 (1968).

Since the stability of the bubble depends largely upon the rotational speed of the system, the influence of it upon the shape of the bubble and the natural frequencies of the liquid system have been determined. It was found that the rotational speed had a profound effect on the dynamic response of the liquid-gas-interface. Under the presence of a small gravity field the response of a gas-liquid system in a cylindrical container has been investigated[6]. Small amplitude free oscillations of an incompressible liquid of arbitrary depth have been treated, and the natural frequencies have been determined for small and very large angular velocities. A similar investigation has been performed for a harmonically excited rotating system[7], where wave form of the liquid surface as well as the response of the system have been determined.

DISCUSSION OF THE PROGRAM PLAN

The proposed program of research in theoretical investigation of gas management is planned in three phases:

Phase I: Degassing of materials during their liquid phase.

Phase II: Migration of a bubble during the action of a centrifugal force field.

Phase III: Distribution of gas in a liquefied material.

PHASE I: DEGASSING OF MATERIALS DURING THEIR LIQUID PHASE

The objective of this phase is the determination of the shape of a gas bubble as well as the shape of the liquid containing this bubble under the influence of surface tension, chamber pressure of the material, and the rotational speed of the system. The study will consider the critical velocity and the critical volume under which the system starts to disintegrate. In this phase the effect of the gravity gradient shall be neglected. The treatment of such a doubly-connected liquid-gas-geometry is based on the interaction of the contribution of pressure due to surface tension and centrifugal force. On the gas-liquid-interface one must consider the potential of the surface tension σ_{ij}. Furthermore, the internal pressure should equilibrate the external pressure, which is

6. Bauer, H. F., "Liquid Oscillations in a rotating container." Project B-906, NASA-Research Grant No. NGR-11-002-028 (1966).

7. Bauer, H. F., and Chang, S. S., "Dynamics of Propellant in a Spinning Container," (in preparation).

assumed constant. The shape of the interface is then governed by the following expression:

$$p_i = p_{i-1} + \frac{1}{2}\rho_i \Omega^2 r^2 + \sigma_{i-1i}\left(\frac{1}{R_{i-1i}} + \frac{1}{R'_{i-1i}}\right) \quad , \quad i=1,2,3$$

where R_{ij} and R'_{ij} are the radii of curvature of the surface of the interface of medium i and j . Medium 1 represents the interior gas bubble, medium 2 the liquefied material and medium 3 the chamber gas. The angular velocity of the system is denoted by Ω, while r represents the distance of a particle to the axis of rotation. σ_{ij} is the surface tension of the interface (ij) , while ρ_i (i = 1, 2, 3) represents the mass density of gas, liquid and chamber gas respectively. These equations determine the equilibrium of the gas-liquid-interface as functions of the parameters of the system. They have to be solved for a given volume of material for various amounts of entrained gases.

Location and geometric shape of the gas bubble as well as the geometrical shape of the liquefied material and the critical rotational speed shall be determined.

PHASE II: MIGRATION OF A BUBBLE DURING THE ACTION OF A CENTRIFUGAL FORCE FIELD

A free suspended liquid material contains a gas bubble. In order to move those bubbles to a proper degassing position, the system is put into rotation. Before attacking the dynamic problem of the migration of a gas bubble under the influence of surface tension, viscosity and centrifugal forces, the time involved for the motion of the gas under the sole effect of Newton's gravitational attraction force shall be studied first. The objectives of the second part of this phase is then the investigation of the flow of the total system under the action of centrifugal forces of various magnitudes. Thus the time necessary to move gas from a certain location in the liquefied material to the degassing position should be determined. Critical speed and volume shall be taken into consideration as limit factors of such a process, in order to obtain reasonable time durations for the migration of the gas bubble. In the first approximation the bubble during its migration is considered as a perfect sphere, of which, of course, the volume change during the motion of the bubble shall be observed.

PHASE III: DISTRIBUTION OF GAS IN A LIQUEFIED MATERIAL

In this phase the response of a gas bubble in a rotating system under the action of harmonic excitation of the total system shall be attempted. Some thought will be given to the even distribution of gas bubbles in a liquefied material. For this reason the action of an electric field may be of benefit.

N70-20538

COMPOSITE CASTING
SUPERIOR STRUCTURAL MATERIALS THROUGH THE COMBINED APPLICATION OF UNIQUE ZERO-G EFFECTS

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ABSTRACT

Composite casting is of particular interest for the demonstration of space manufacturing capabilities in early experiments, since it (1) permits the application of basic zero-g processing concepts in a variety of effective combinations, and (2) has a high assurance of experiment success. In conceptual terms, composite casting has been adequately defined in previous presentations and papers. The purpose of this discussion is to assess the effectiveness of various modifications and to propose specific experiments.

The basic process, which employs primarily the zero-g phenomenon of mixture stability, comprises two methods: mold casting and free casting. The attainable end-product properties are determined by proper selection of matrix and reinforcement materials and by optimization of reinforcement shape, size and packing. Further improvement of properties may be achieved by the individual or combined application of the following modifications:

1. Modifications for strength optimization: Variable reinforcement distribution; and controlled reinforcement orientation.

2. Modifications for the improvement of ductility: grain refinement by the use of closely packed microsize reinforcements, acting as nucleation sites; and further matrix microstructure control by finely dispersed micro-particles.

Potential techniques and expected capabilities for each modification and various combinations are discussed in detail. Fundamental and technological problems for mold and free casting are identified, together with potential ways of solution in either laboratory investigations or in the context of other space experiments.

An experiment program is proposed, specifying individual experiment conditions (materials, batch size, mold shape), equipment requirements (design, vehicle arrangement, support requirements), operations (controls, astronaut assistance) and expected results. The proposed experiment schedule, providing for a gradual increase of capabilities and an effective correlation with other experiments, is based on presently planned vehicle availability (workshop, space station) and on anticipated experiment hardware leadtimes.

INTRODUCTION: BACKGROUND

The concept of composite casting as a unique space manufacturing process has been introduced in earlier reports (Ref. 1, 2, 3). Its ultimate objective is the production of high-performance structural materials and components directly from the melt, circumventing the long and expensive sequence of processing steps necessary for non-reinforced metals, such as ingot production, rolling, forging, and machining.

The potential of composite materials is undisputed; numerous types of polymer-matrix composites such as "fiberglass" have become common construction materials, in aerospace engineering as well as in consumer goods. At the same time, whiskers whose mechanical properties exceed the presently used polycrystalline or amorphous fibers by at least one order of magnitude, have never been successfully integrated into metal-base composites, simply because they do not lend themselves to the mating with the matrix in the solid state dictated by gravity in terrestrial production.

This confinement led to the use of single crystals in the form of comparatively thick filaments, such as boron filaments. Even though highly attractive for specific applications, such filamentary composites have inherent limitations:

1. The preferred orientation of reinforcement and, consequently, properties limits the application to specific shapes, and presents serious joining assembly problems.
2. In polymer-base filamentary composites, the low shear strength of the matrix prohibits full exploitation of the filament strength.
3. In metal-base filamentary composites, the high shear strength and stress-redistribution capability of the matrix is fully effective only at lower packing densities; the desirable high packing densities are impaired by the difficulty of achieving reliable diffusion bonds in the matrix and by extensive filament damage resulting from the high diffusion bonding pressures.

An ideal material, therefore, would be a metal whisker composite with a continuous matrix and isotropic property distribution. Manufacturing such a material in the solid state by diffusion bonding is unfeasible: manufacturing it in the liquid-matrix state is precluded under terrestrial conditions by the gravity-induced whisker segregation. The phenomenon of absolute mixture stability characteristic to zero-g, therefore, offers the unique opportunity to produce homogenous metal-whisker composites by means of casting; it further permits fabricating complex components from these materials in a single operation. As will be shown later, further material improvements may be attainable by various combinations of zero-g processing techniques.

DEFINITION OF "COMPOSITE CASTING"

The term "composite casting" is used here in a broad sense and comprises the following methods and materials:

Casting methods:

1. Mold-casting.
2. Free casting of ingots, primarily in the form of spheres.
3. Free-formed shapes with the use of induced forces.
4. Adhesion casting.

Materials

1. Matrices reinforced with whiskers, fibers, flakes, ribbons, etc.
2. Matrices with dispersed particles.
3. Combinations of (1) and (2).

ATTRACTIVENESS FOR SPACE EXPERIMENTS

Composite casting has been selected for this discussion for six reasons:

1. It is unique to the zero-g or a low-g environment.
2. While already attractive in its basic form, it offers a variety of combinations of typical zero-g phenomena. It therefore, permits the demonstration of a variety of zero-g effects.
3. The basic concept is straightforward and its tooling requirements comparatively simple; thus it offers a high assurance of success.
4. It involves a number of typical zero-g methods and tooling problems and may serve, thereby, as a general testbed for zero-g manufacturing engineering.
5. Extensive use can be made of the advanced state of the art in conventional composites, resulting from their intensified promotion during the last decade (Ref. 4 to 11).
6. The products have immediate applications (customers) and will result in a substantial advancement in high-performance structures.

PROCESS CONCEPTS

The basic process of composite casting has the objective to produce high-strength materials and components consisting of a metal matrix and random-oriented reinforcements of various materials, forms, and packing densities. Preferred reinforcement orientation or variable distribution may be achieved by means of induced forces. By proper material selection, the reinforcements may further act as nucleation sites, producing grain refinement associated with improved ductility. Grain refinement may be increased by orders of magnitude by the dispersion of micro-particles of appropriate materials throughout the matrix; this may be used in the conjunction with fiber reinforcements for high strength and ductility, or without reinforcements with the potential of producing polycrystalline components of essentially mill-product quality directly from the melt (Ref. 1).

The basic process may be further modified by generating gas bubbles in the interfiber matrix, producing a high-stiffness, low-density material. Consequently, composite casting comprises the following processes and products:

1. Casting metal matrix-random fiber composites with isotropic high strength and stiffness.
2. Casting metal matrix composites with controlled fiber orientation or distribution.
3. Casting fine-grain polycrystalline materials by means of finely dispersed micro-particles.
4. Casting fiber-reinforced composites with high ductility by combination of (1) and (3).
5. Casting high stiffness-low density materials by introducing a partially foamed matrix in (1) or (4).

Table 1 identifies the five versions of composite casting in terms of the employed zero-g effects, together with several other space manufacturing concepts for comparison. The prime effect, common to all process modifications, is that of mixture stability.

Table 1. Zero-g effects employed in selected processes.

PROCESS/PRODUCT		NO CONTAINER	INTERMOLEC. FORCES		NO MASS ACCEL.		INDUCED FORCES	
			INTRINSIC	CONTACT/ CAPILLARITY	MIXTURE STABILITY	ZERO CONVECT.	FORM CONTROL	POSITION CONTROL
COMPOSITE CASTING	MOLD			Ⓣ	●	○		
	FREE	●		Ⓣ	●	○	○	Ⓣ
	DISPERSION			Ⓣ	●	○		
	ORIENTATION			Ⓣ	●	○		
	LOW DENSITY		●	Ⓣ	●	○		
ADHESION CASTING			●	●				
LIQUID FORMING		●	●	Ⓣ			●	Ⓣ
BLOW FORMING		○	●	Ⓣ			○	
FOAMS		○	●	Ⓣ			○	
GLASSES		●	○			○	○	Ⓣ
SINGLE CRYSTALS	FROM GAS					●	○	
	FROM MELT	●				●	○	Ⓣ
SUPERCOOLING		○				○		
SUPERSATURATION					●	○		
METAL COMPOUNDS					●	○	○	

● PRIMARY FUNCTIONAL
○ SECONDARY FUNCTIONAL
Ⓣ TOOLING REQUIREMENT

MATERIALS AND COMPOSITE SELECTION

In view of the absence of terrestrial limitations to composite fabrication, composite casting offers a wide spectrum of potential matrix and reinforcement combinations. The applicable data for several matrix and reinforcement materials are listed in Tables 2 and 3.

Table 2. Applicable properties of selected matrix materials (in order of increasing melting temperatures).

PROPERTIES/MATERIAL	Sn	Mg	Al	Ag	Cu	Ni	Fe	Ti
MELTING TEMP (°F)	450	1202	1220	1761	1981	2650	2800	3300
DENSITY (GM/CM^3)	7.30	1.74	2.36	9.26	8.96	8.90	7.87	4.54
HEAT R.T. TO FUSION (BTU/LB)	241.2	300.5	254.1	95.7	180.5	265.1	308.2	362.3
HEAT OF FUSION (BTU/LB)	25.6	154.2	166.7	45.6	88.1	133.6	115.4	169.1
SPECIFIC HEAT/LIQUID (BTU/LB/°F)	0.06	0.33	0.26	0.07	0.12	0.15	0.15	0.12
VISCOSITY/LIQUID (DYNE-SEC./CM^2)	0.017	0.011	0.029	0.039	0.034	0.05	0.040	
SURFACE TENSION/LIQUID (DYNE/CM)	550	542	900	1140	1280	1930	1500	1510

Table 3. Properties of potential reinforcements.

MATERIAL	MELTING TEMP. (°F)	DENSITY (G/CM^3)	DIAMETER (MICRONS)	LENGTH (MICRONS)	STRENGTH (10^6 PSI)	ELASTIC MODULUS (10^6 PSI)	COST ($/LB.)
WHISKERS							
Al_2O_3-α (SAPPHIRE)	3780	3.97	1-30	50-2000	0.5-3.5	60-150	9000
Al_2O_3-α/Al N	4000	3.6	3-30	30-600	0.5-2.0	50-100	900
SiC	4200	3.21	1-10	20-400	2-6	80-150	3000-11,000
SiC/Al_2O_3-α	4000	3.6	2-30	20-1000	2-6	60-150	900
Si_3N_4	3450	3.1	1-10		0.7-2	55	
BeO	4650	2.78			1.8	50	
GRAPHITE	6700	2.22	0.5	1 CM	2.8	~100	MILLIONS
OTHERS							
GRAPHITE FIBERS	6700	2.22	7	ANY	0.5	~100	350
BORON FILAMENT	4200	2.3	100	ANY	0.3-1.5	60	300
Be CHOPPED WIRE	2340	1.82	100	ANY	0.18	40	2000

For initial space experiments, selection of materials was based on the following criteria:

Matrix-whisker compatibility

Expected composite properties

Whisker availability, state-of-art

Typicality (representative of a group of materials)

Minimum secondary material problems

Minimum processing and tooling problems

Product usefulness (applications)

Material cost

The evaluation of various feasible matrix and reinforcement combinations indicated the best overall experiment effectiveness for the following material systems:

1. Aluminum matrix, reinforced with sapphire whiskers or mixed whiskers of sapphire and aluminum nitride.
2. Nickel matrix, reinforced with silicon carbide whiskers.

The two selected systems are representative of two major material groups, so that the data and processing experience gained in experiments will be useful for a wide spectrum of composite casting applications.

The aluminum system is typical of light-metal matrices aimed at high strength and stiffness to weight ratio. Processing temperatures are moderate and the cooling rates by radiation to space environment rather low. The nickel system is primarily aimed at superior high-temperature components with high creep strength and oxidation resistance. It serves as a model for a wide variety of nickel, cobalt, and ferrous alloys as matrix materials. Its high processing temperatures require a modified line of tooling. Heating requirements in terms of Btu/lb. are essentially the same for both systems; on the basis of equal volume (which may be more meaningful for casting of components), they differ by a factor of 2.5.

BASIC PROCESS

The "basic process" refers to casting random mixture of matrix and reinforcements only. Attainable mechanical properties are determined by (1) properties of component materials and (2) the reinforcement content.

The beneficial effect of low whisker contents in Al and Ni matrices has been demonstrated by work carried out by the Mitron Research & Development Corporation under the sponsorship of OART and MSFC (Ref. 12). It was shown that sapphire whiskers, coated with Ni for weldability, assume random positions across the grains, producing a mechanical interlocking effect (Figure 1a). The gains in mechanical properties obtained at whisker contents of less than 0.1% are summarized in Table 4. While these gains are moderate, they support the basic concept of strengthening with random-oriented reinforcements.

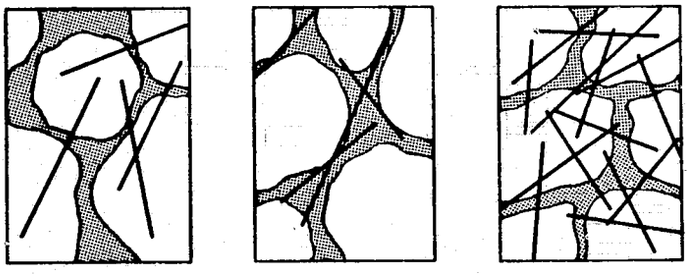


Figure 1. Effect of random-oriented whiskers on microstructure.

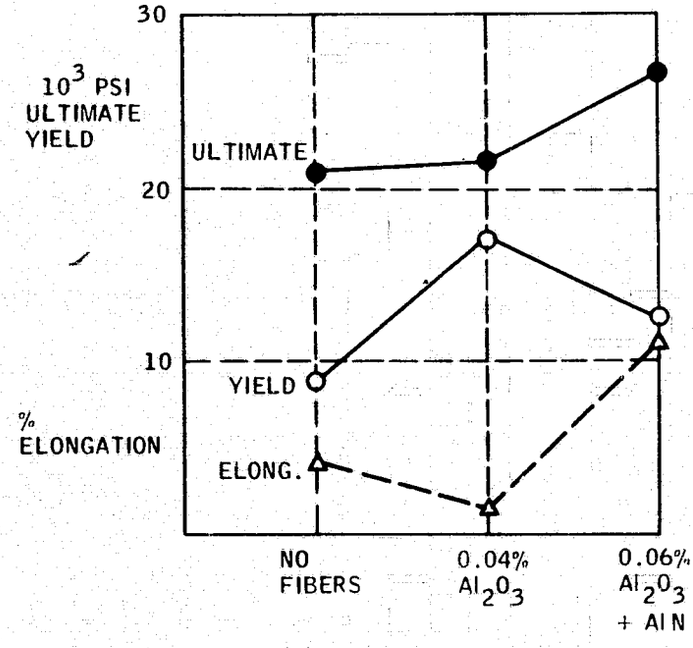


Figure 2. Effect of two whisker materials on mechanical properties of cast aluminum alloy 2024.

As illustrated in Figure 2, the mechanical properties may be controlled by reinforcement modifications. While sapphire fibers reduce the ductility (elongation), a full recovery and increased strength is obtained by addition of Al-N whiskers.

Nonwetting whiskers tend to position themselves in the grain boundaries (Figure 1b); this has no effect upon room temperature properties, yet increases creep resistance at high temperatures.

At high reinforcement contents (Figure 1c), the increase of stiffeners (elastic modulus) is adequately determined by the rule of mixtures; i.e., it is proportional to the reinforcement/matrix ratio. The strengthening effect is quite complex, yet is primarily the result of mechanical interlocking, deformation constraint and multiaxial stress distribution in the interfiber matrix.

Table 4. Effect of small fiber contents on mechanical properties of cast aluminum alloy (2024).

FIBERS			MATRIX	STRENGTH			YIELD		ELONGAT.	
MATERIAL	STRENGTH (10^6 PSI)	VOL. %	POST-CAST TREATMENT	PREDICT. X	10^3 PSI	X	10^3 PSI	X	%	X
–	–	0	AS CAST		21.0	1	8.7	1	4.0	1
Al_2O_3	1.5	0.043		1.015	21.7	1.03	17.3	2.0	1.0	0.25
Al_2O_3 + Al N	1.2	0.063		1.02	26.8	1.28	12.5	1.44	11.6	2.9
–	–	0	SOLUTION HEAT TREATED & AGED	1	33.0	1	26.1	1	3.8	1
Al_2O_3	1.5	0.043		1.01	33.9	1.03	25.5	0.98	1.0	0.26
Al_2O_3 + Al N	1.2	0.063		1.01	32.4	0.98	25.5	0.98	2.5	0.63
		0.230		34.4 1.04	43.0	1.31	29.2	1.12	2.5	0.63

FIBER DIMENSIONS: Al_2O_3:DIAM. 10-30μ LENGTH 125-2,500μ
ALN :DIAM. 3-30μ LENGTH 30-600μ
1 MIL 5-100 MIL
1 MIL 1-24 MIL

The maximum attainable reinforcement contents have been determined by tests with equal-density models. It is primarily dependent upon the length-to-diameter ratio (L/D) of the whiskers. As shown in Figure 3, the maximum density for random-oriented fibers of high L/D, which are of prime interest, is in the order of 25%. It may be increased by vibrations. However, it is expected that, in view of the complex strengthening mechanism, highest fiber contents may not even be desirable and that an optimum condition is achieved at a specific content for each system. Preliminary data on the effect of packing density are the subject of laboratory experiments presently in progress; the final answer can, however, only be obtained in space experiments.

While this implies that accurate strength predictions are impossible at this time, a tentative assessment of the strengthening effect has been made with the rule of mixtures and an estimated composite effectiveness factor. The expected mechanical properties of the two selected composite systems are presented in Figure 4 for various whisker types and contents. In Figure 5 the strength is compared with conventional monolithic materials on the basis of equal weight. Even at low whisker contents, the expected strength-to-weight ratio substantially surpasses any present, high-strength structural alloy.

The uniform mixture distribution attainable under zero-g, together with the high fluidity of molten metals, permits the movement of individual fibers with small induced forces. Both variable fiber distribution (fiber concentration) and fiber orientation as alignment are most effectively achieved by the combined

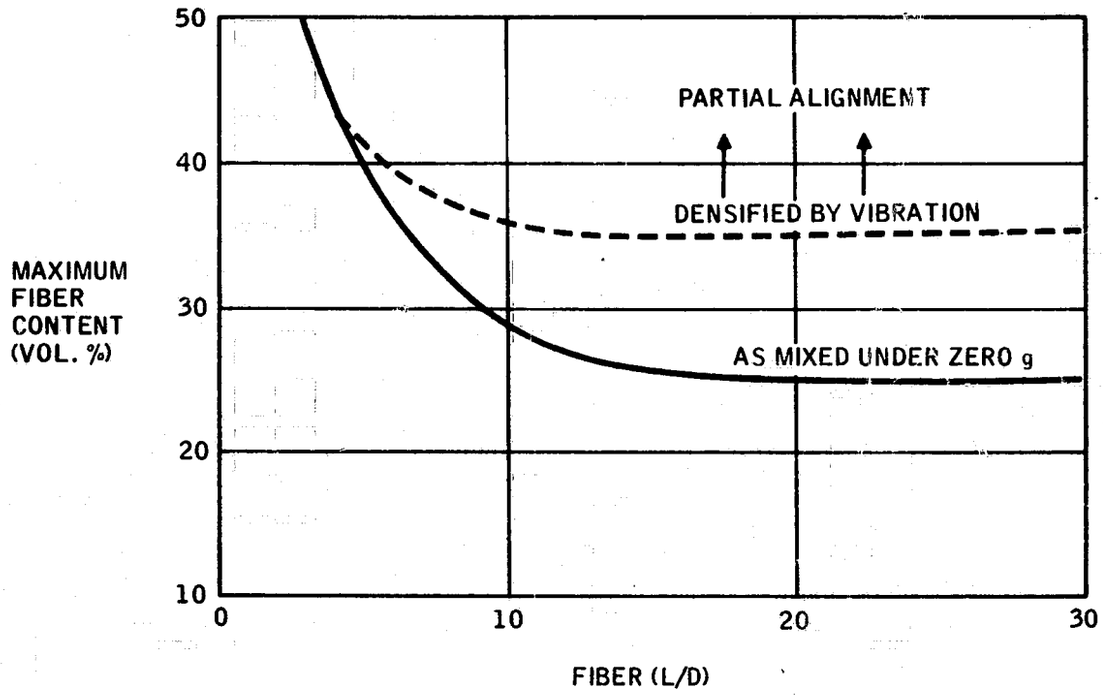
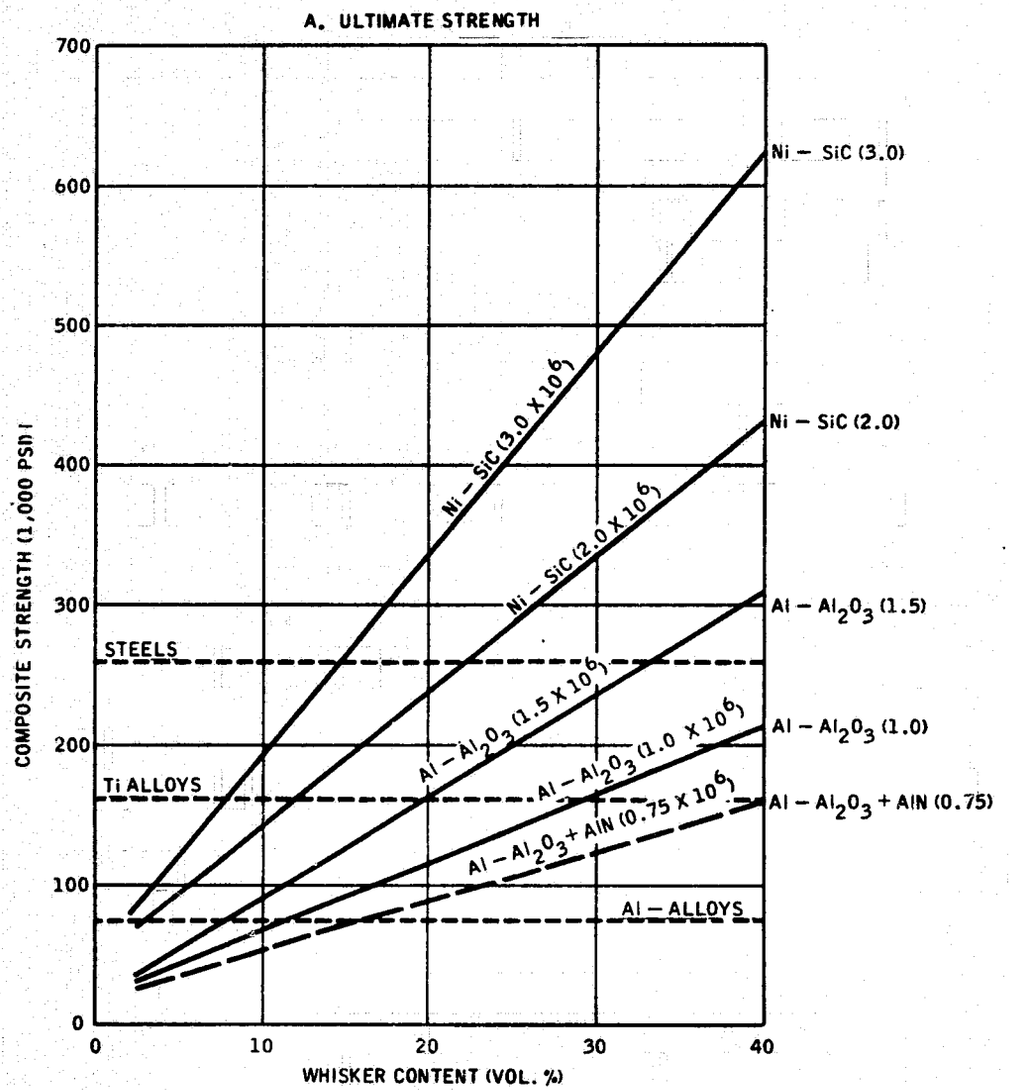


Figure 3. Highest attainable fiber contents for random orientation.

action of vibrations and a directional force. The vibrations, generated either mechanically or by an alternating electromagnetic field, have the purpose to free the fibers from their interlocked position and to ensure high mobility. The directional force is provided by either an electromagnetic or an electrostatic field. Both are applied simultaneously after casting prior to solidification. The effect of various moves can be well demonstrated and evaluated with equal-density models.

By combination of the basic process with zero-g methods of nucleation and crystallization control, products may be achieved that exhibit not only superior strength and stiffness, but also high ductility. Improved ductility may already be obtained in the basic process, as the individual whiskers will undoubtedly generate grain segmentation during solidification or act as nucleation sites. The resulting grain size will be substantially smaller than obtainable in conventional casting (Figure 6a).

A considerably higher degree of grain refinement and, consequently, ductility may be achieved by the generation of a high number of nucleation sites in the form of finely dispersed microparticles whose uniform distribution is assured by the zero-g phenomenon of mixture stability (Figure 6b). Effective particle materials for the Al-matrix are titanium carbide or titanium boride, which will



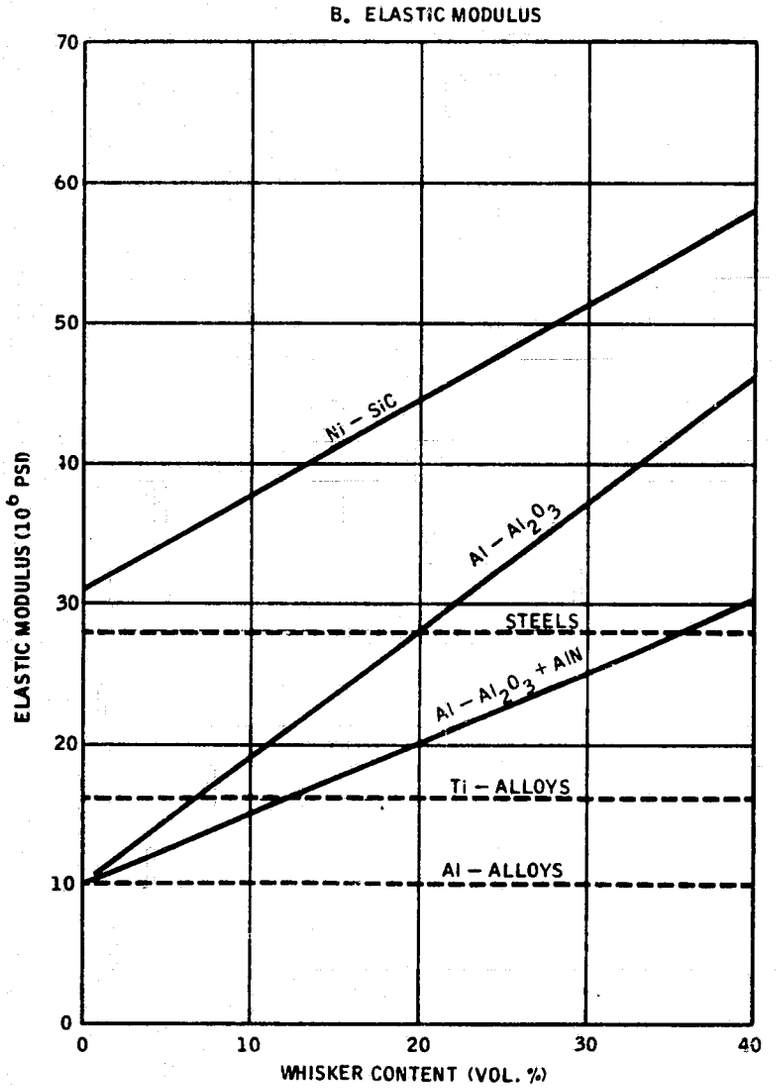


Figure 4. Expected mechanical properties of cast whisker composites in comparison with monolithic materials.

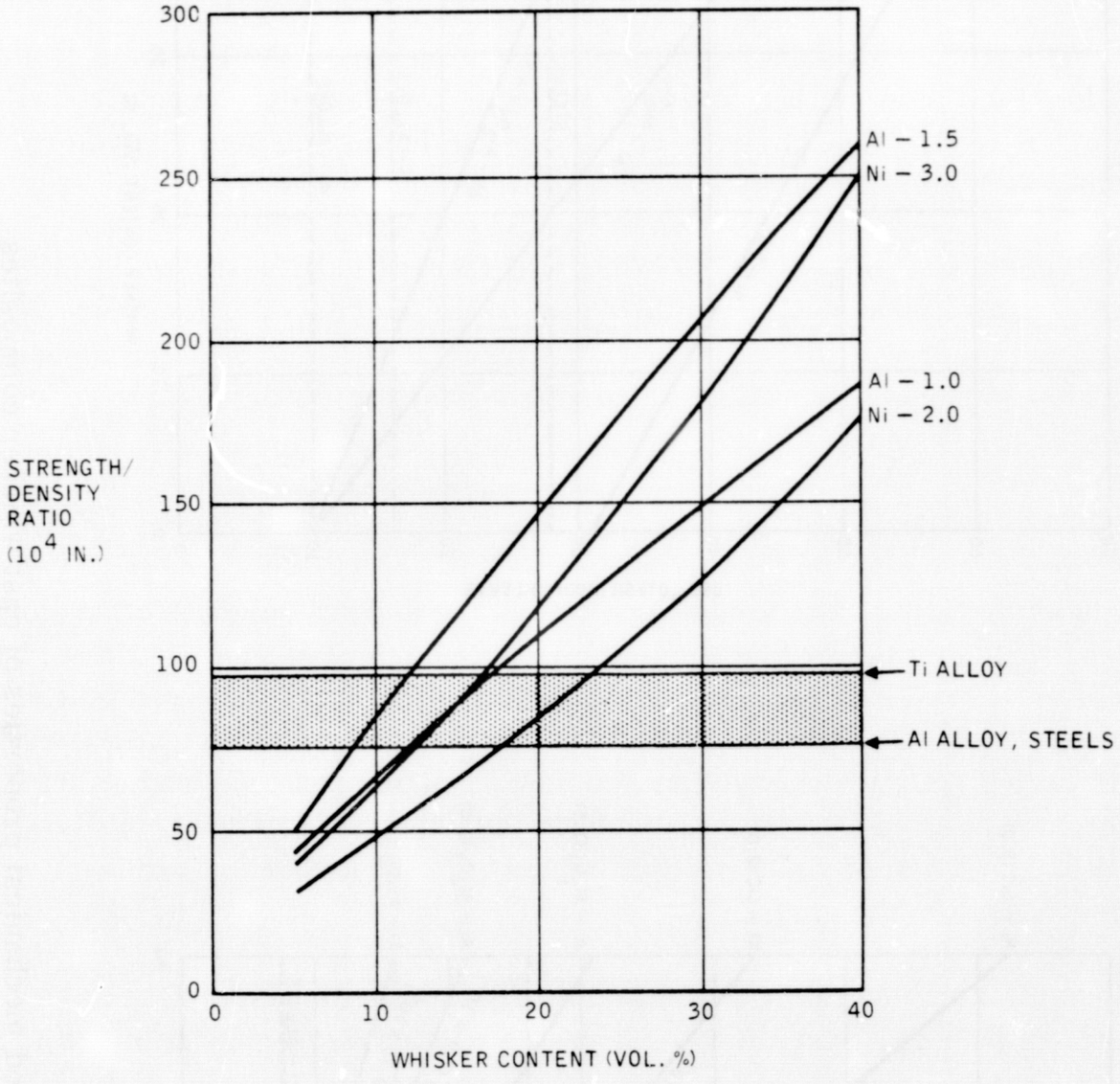


Figure 5. Strength comparison of composite castings with high-strength forgings on equal weight basis.

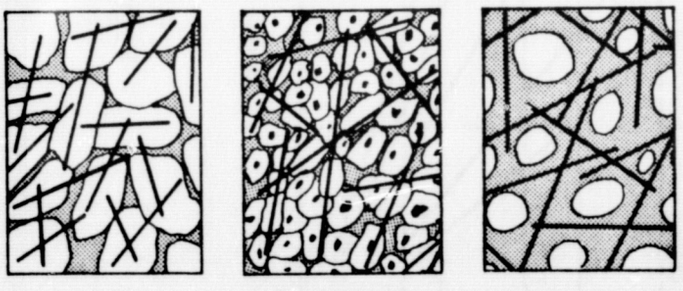


Figure 6. Microstructure of modified cast composites.

be in solution and precipitate during cooling as discrete particles a few degrees above solidification temperature. For the nickel matrix, alumina particles are expected to be effective catalysts for the achievement of a fine-grain microstructure.

These fine-grain casting techniques may be used in connection with fibers as a dual-composite, or without fibers

as a single-phase "particulate composite" with the ultimate objective of producing fine-grain polycrystalline materials and components directly from the melt.

The third modification of the basic process consists of the injection of an inert gas into the liquid matrix, to form a foamed low-density composite as illustrated in Figure 6c. The gas may be introduced during mixing or, preferably, by continuous dispersing shortly before entrance into the mold.

On the basis of equal weight, foaming will increase stiffness, while the strength remains unchanged. The low-density composite will, therefore, find application primarily in stiffness-critical structures. A foamed nickel-base composite may serve as an effective core material for lifting surface panels operating at high temperatures.

TOOLING REQUIREMENTS AND CONCEPTS

Tooling studies carried out for composite casting and a number of other zero-g processes indicate clearly that the primary problems of space manufacturing lie not in the validity of processing concepts, but rather in the required tooling — which is the key to practical application. The researcher often tends to overlook these problems mainly because they appear — at first glance — rather trival. How, for instance, can we move a liquid in the absence of gravity; or, how can we prevent formation of voids and gas bubbles in a heated liquid which on earth rise conveniently to the surface?

The solution of such problems calls for a complete disassociation from terrestrial methods, as has been pointed out repeatedly by Wuenscher (Ref. 13). It is the art of space manufacturing to take advantage of typical zero-g phenomena, rather than to attempt an awkward reproduction of the terrestrial behavior of matter.

The same necessity of departure from conventional concepts applies to equipment and operations. Methods and facilities have to be adapted to the absence of weight and preferred orientation, as well as to the space confinement and high degree of automation in orbital vehicles. This precludes the in-space development and gradual assembly of experiment equipment, starting with a "simple laboratory experiment." The low earth-orbit traffic frequency in the initial experiment period and the difficult in-space vehicle integration further precludes the successive deployment of single-purpose units with increasing complexity. Rather, for each family of experiments conventional laboratory facilities must be replaced by a single experiment machinery with a high degree of automation and remote control, fully assembled and checked out on earth and acceptable to a multitude of experiment modifications.

On the basis of these ground rules, a single experiment "apparatus" is proposed for composite casting experiments in the advanced orbital workshop. It has to combine the following major functions:

1. Containing solid and liquid material.
2. Heating and melting.
3. Transfer (moving) liquid material from the melting chamber to the mold.
4. Mixing liquid-matrix material.
5. Cooling the mold and casting solidification.
6. Environment (gas, pressure) control for open-mold casting.
7. Gas injection for foaming.
8. Contact -free generation of forces in casting material (electromagnetic, electrostatic).
9. Remote control of all functions and settings (such as temperature, pressures).
10. Minimized heat input into the vehicle.

Once conceptual design of the composite casting apparatus, which combines these functions, is shown in Figure 7. It consists of a closed system of melting chamber, melt transfer and mold, uniformly heated to the material processing temperature by radiation or induction. The mold is cooled by retracting (swing-away) the mold-heating units and radiation into deep space, supported by a small sure-pointing shadow shield. Major functional details are discussed below.

Vehicle integration and the deployment procedure are illustrated in Figure 8. Apparatus preparation, charging with material, and setting controls are carried out in position 1 inside the vehicle, with full 360-degree access. For deployment, the apparatus is moved into a vehicle-attached tube by means of telescoping rails (Position 2). After the inside hatch is sealed and the external hatch is opened, the apparatus is moved into Position 3, at least 20 feet from the vehicle, followed by the deployment of the shadow shield. Experiment performance is monitored by the astronaut via the control unit attached to the inside hatch. After cooling of the entire unit, it is retracted into the vehicle in a reversed sequence of deployment steps.

In the fully deployed Position 3 the apparatus may be removed from the guide rails by a serpentuator and carried into a favorable processing position, such as the workshop vacuum wake.

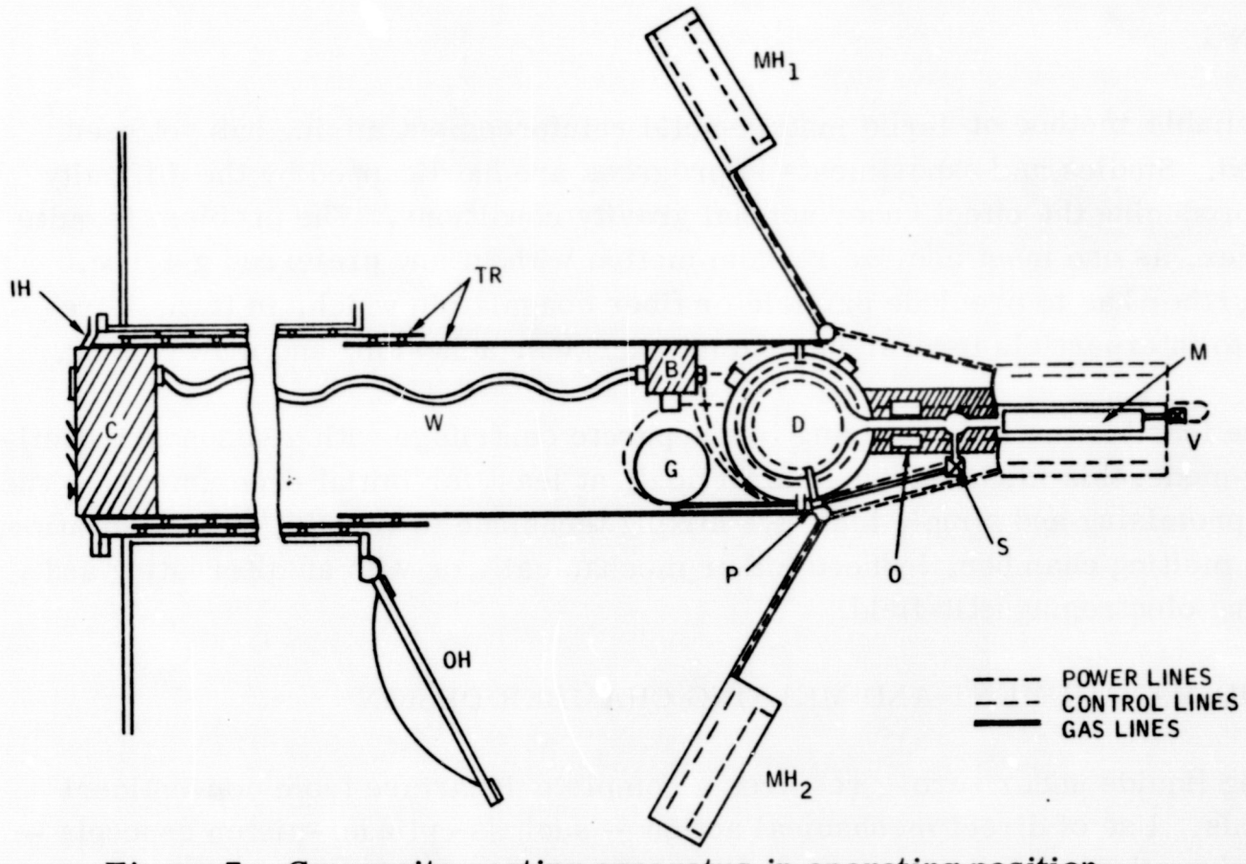


Figure 7. Composite casting apparatus in operating position.

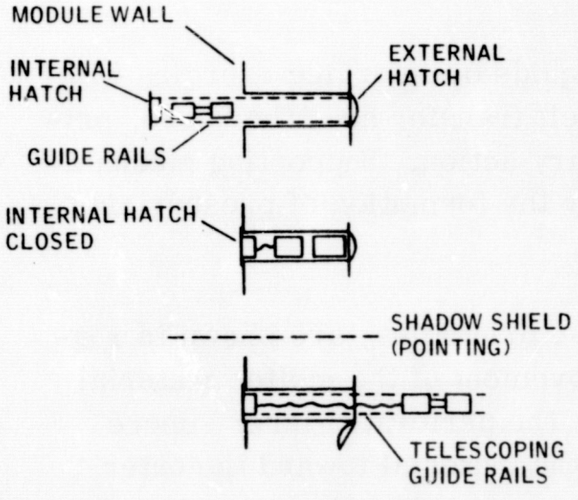


Figure 8. Experiment operations.

RAW MATERIAL FORM

Four methods of raw material supply are being considered. For large melting chambers, raw material may be provided in form of either a prepressed powder-reinforcement mixture or a precast mixture. In both cases, the reinformcement content is accurately adjusted, while the distribution across the ingot is not critical as final mixing will be accomplished upon melting in zero-g. For continuous melting, powdered metal and reinforcements are supplied either separately or premixed.

Compacted powder "ingots" will have the shape of the inner melting chamber space. For series of experiments, a number of ingots would be prepared: one for each material composition and reinforcement content. Melting chamber and ingots are dimensioned to provide sufficient material for repeated casting experiments at one composition.

For initial experimentation it may be preferable to supply for each material type a complete heating chamber-ingot assembly.

MIXING

No reliable method of liquid matrix-solid reinforcement mixing has yet been defined. Studies and experiments in progress are handicapped by the difficulty of reproducing the effect under normal gravity conditions. The problem is quite complex, as one must achieve random motion without any preferred g-force. One further has to preclude particle or fiber coagulation which, in turn, is related to interparticle forces, interfacial energies, adhesion, and matrix drag.

One feasible method is mixing in a separate centrifuge with a secondary oscillating mode; this is, however, impractical, at least for initial experiments. The most promising and simple tentative mixing technique is variable-mode vibrations of the melting chamber, induced either mechanically or with an alternating and rotating electromagnetic field.

LIQUID MANAGEMENT AND MELTING CHAMBER DESIGN

Moving liquids under zero-g requires a complete departure from conventional methods. Use of direct mechanical action — such as cylinder-piston concepts — has to be ruled out from the outset, since it is incompatible with molten metals and unnecessarily clumsy. Moving by induced g-forces, even though feasible, is similarly ruled out since it interferes with mixture integrity and represents just another attempt to reproduce terrestrial conditions in orbit.

Zero-g offers the unique capability to move liquids by interface energies with no induced forces. The suggested concepts of melt transfer are, therefore, primarily based on controlled wettability and capillary action. Supporting mechanical action is introduced only in an indirect way by the formation of pressurizing bubbles, primarily using surface tension effects.

Two melting chamber designs, employing these principles, are shown in Figures 9 and 10. In the spherical chamber, the movement of the molten material is facilitated by high wettability to all surfaces. The perforated inner sphere and its capillary effect will ensure movement of the material toward the outer sphere wall and the mold passage. Movement is supported by the pressure-controlled formation of a bubble in the center space; this bubble cannot move through the perforated inner sphere, since the small radii of any bubble-bulges at the perforation are not compatible with the bubble pressure. The second function of the bubble is absorption of vapors from the melt as they move to the liquid-gas interface.

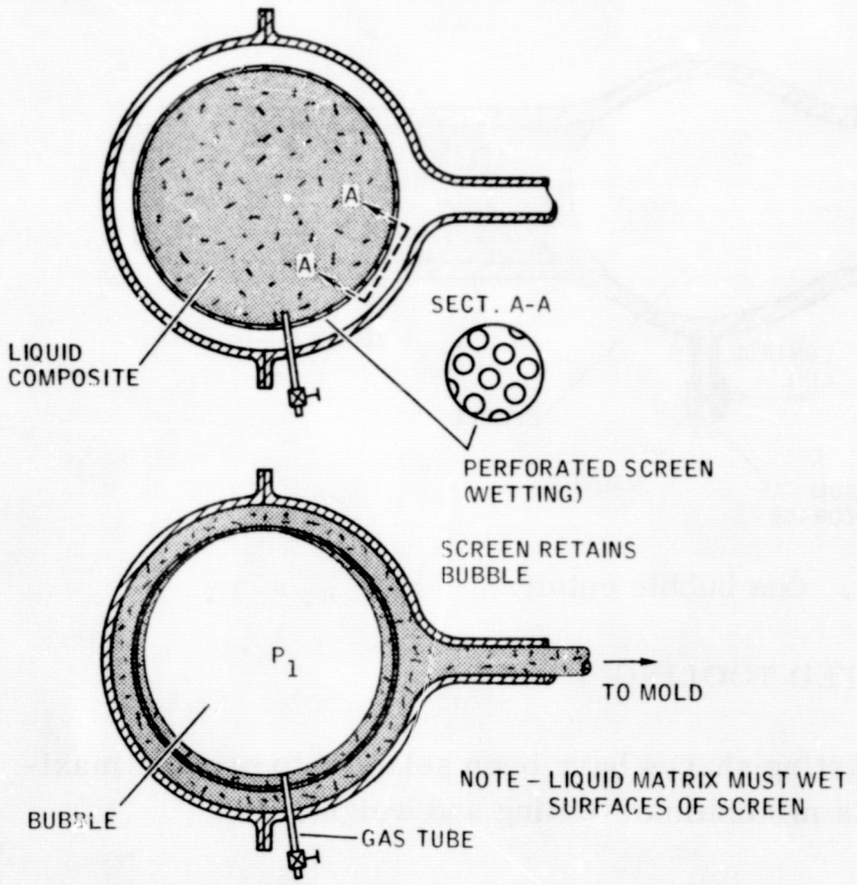


Figure 9. Spherical melting and dispensing unit.

The ellipsoidal chamber, Figure 10, employs the same principles; the function of the holes in the perforated sphere are provided by the chamber shape and the presence of two exits: the decreasing bubble radii toward the exits and the necessity of pressure balance will keep the bubble centered; movement of the bubble into the exits is impossible as long as there is any melt present. While this design has the advantage of simplicity, it is somewhat more difficult to open for charging with material.

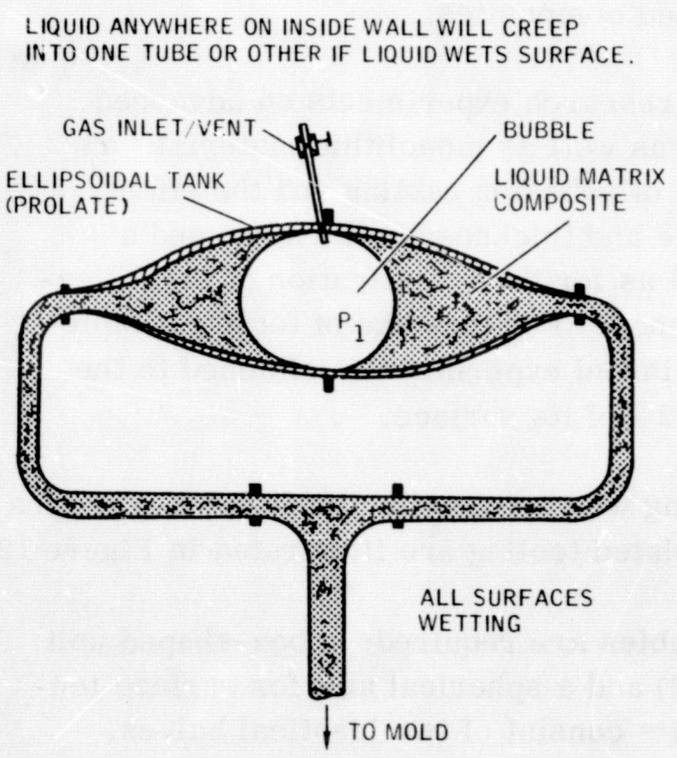


Figure 10. Ellipsoidal dispensing unit.

The design of a small melting and mixing chamber for continuous raw material supply (metal powder and reinforcements) and continuous electron-beam melting are presently under study.

For convenient removal of the casting after solidification, a clear separation from the material supply system near the mold entrance is desirable. A mechanical cutoff before solidification is impractical as it will freeze in. Instead, the generation of a gas bubble, as illustrated in Figure 11, in a bulged section of of the transfer tube ("bubble valve") not only provides an effective separation, but also is a typical application of liquid management techniques unique to zero-g.

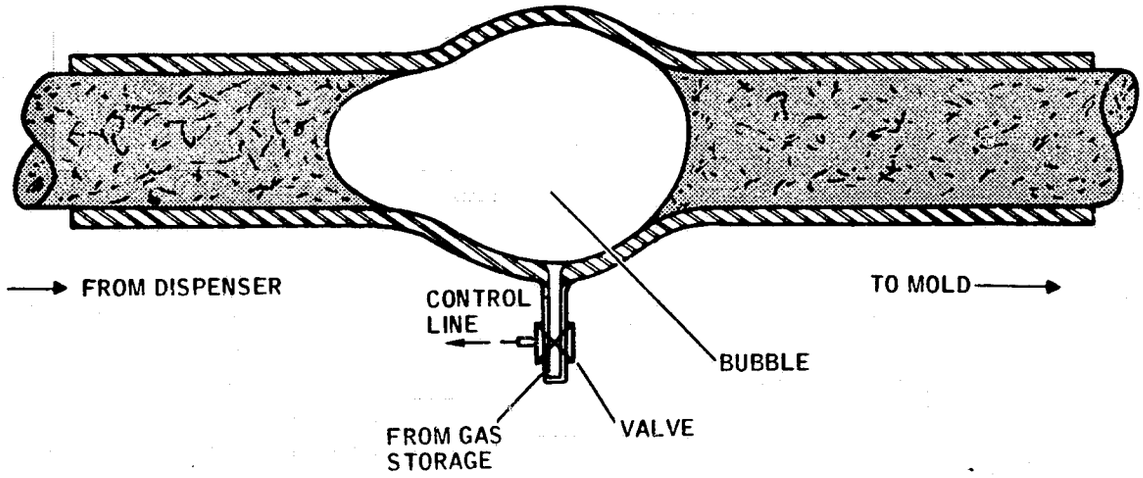


Figure 11. Gas bubble cutoff.

CASTING SHAPES AND RELATED TOOLING

For the initial exp riments, casting shapes have been selected to provide maximum data and experience with a minimum of tooling and weight.

For general casting applications, three basic configurations are proposed for testing materials, shape effects, and casting procedures: A full cylinder, for basic casting tests and materials data; a tubular shape, representing more complex "thin"-wall castings; and a flat plate, for investigation of material flow and reinforcement uniformity, as well as foamed composites.

Two additional shapes are designed for research experiments on advanced zero-g casting techniques with composites as well as monolithic material: a disk with a raised section for investigation of adhesion casting and the effect of shape discontinuities upon spreading rate and thickness uniformity; and a sphere for surface tension casting, as well as for the investigation of solidification phenomena without mold wall interference. For the sake of tooling simplicity, the sphere remains — at least in the initial experiment — attached to the dispensing nozzle, which covers less than 2% of its surface.

The dimensions and the maximum casting weights for the discussed five shapes are identified on Table 5; the molds and related tooling are illustrated in Figure 12.

For heating, two interchangeable assembles are required: a box-shaped unit for the closed molds (A, B, C of Figure 12) and a spherical unit for surface tension and adhesion casting (D, E). Both units consist of two identical halves, which swing away for radiation cooling. The spherical unit, in closed position, provides complete sealing against environment to permit pressurization and melt evaporation control.

Table 5. Experimental casting shapes & weights.

MOLD TYPE	CASTING SHAPE	CASTING DIMENSION (IN.)	CASTING WEIGHT (LB.)*	
			AL-BASE	Ni-BASE
A	CYLINDRICAL	2 DIA. X 10	3.8	10.2
B	TUBULAR	2.5 I.D. X 1.75 O.D. X 10	3.0	8.1
C	FLAT PLATE	4 X 10 X 3/4	3.6	9.6
D	SPHERE	4 OD, MAX.	3.8	10.4
E	MODIFIED DISK	DISK DIA. 7	2.4	6.4

* MAXIMUM; VARIES WITH REINFORCEMENT CONTENT.

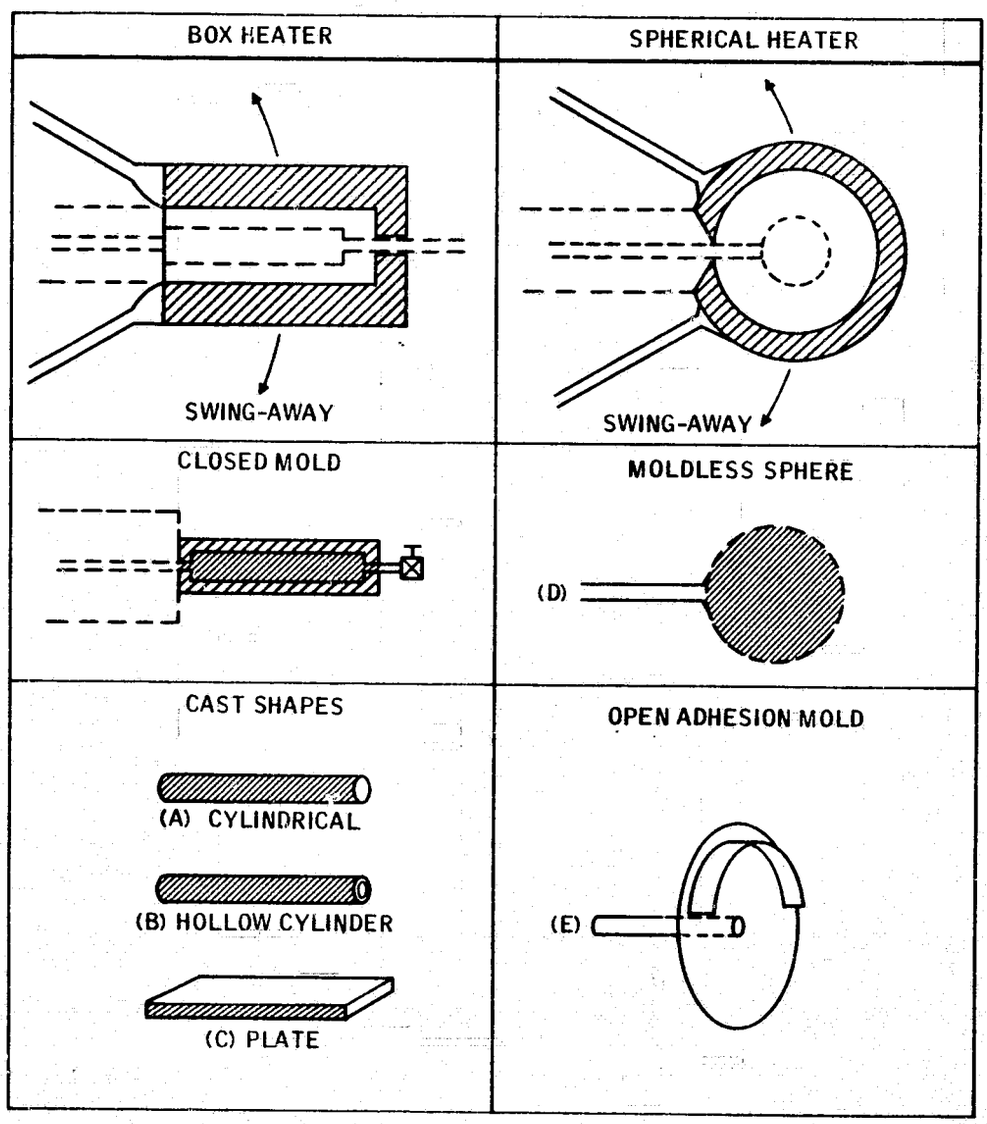


Figure 12. Molds and casting shapes.

EXPERIMENT PERFORMANCE

The major processing and operational steps of each individual casting experiment are identified in Figure 13. Each step is activated and observed by an astronaut, while all processing details are preset and controlled automatically. Experiment preparation and retrieval of the casting after experiment completion requires two men. Approximate power requirements for individual experiments are:

Al-Base 2 kw for 2 hours + 0.5 kw for 1 hour

Ni-Base 2 kw for 3 hours + 1 kw for 1 hour

EXPERIMENT PROGRAM

The concept of composite casting is aimed at an early use as a space manufacturing process. This calls for an early availability of conclusive engineering data. As pointed out earlier, this can only be achieved with a versatile experiment facility similar to the one proposed earlier. This facility, supported by the extensive capabilities of the advanced orbital workshop, permits performance of series of individual casting experiments in which a well-planned variation of materials, processing details, and product shapes generates a maximum amount of reliable engineering data.

An example for such a program is presented in Table 6, which integrates the material types, process modifications, and casting shapes defined earlier in this discussion. It consists of 16 experiment series arranged in four groups:

1. Aluminum-whisker composites.
2. Aluminum-whisker-particle composites.
3. Nickel-whisker composites.
4. Nickel-whisker-particle composites.

Each series represents one material composition to facilitate the potential use of premixed ingots as raw material. The seven individual experiments of each series provide for the most effective variation of processes and casting shapes.

The rather systematic program can be arranged timewise in various more or less ambitious schedules. One could, for instance, emphasize in a first phase the evaluation of materials, reducing the variation in processes and product shapes. If, on the other hand, each material composition is supplied in form of

Table 6. Experiment program - definition of individual experiments.

MATERIALS				CASTINGS - SHAPES*					
MATRIX	WHISKERS		PARTICLES	AS CAST	ORIENTATION CONTROL	VARIABLE DISTRIBUTION	FOAM 20%	FOAM 50%	EXP. (NET)
Al	Al_2O_3	5%	—	ADE		BC		AC	7
	Al_2O_3	15%	—	ACD	BC		AC		7
	Al_2O_3	25%	—	ABC	BC		AC		7
	Al_2O_3+AlN	25%	—	ABC	BC		AC		7
Al	—		0.01%	ADE		BC		CD	7
	—		0.1 %	ADE		BC		CD	7
	Al_2O_3	5%	0.1 %	ACE		BC		AC	7
	Al_2O_3	25%	0.01%	ABC	BC		AC		7
	Al_2O_3+AlN	25%	0.01%	ABC	BC		AC		7
Ni	SiC	5%	—	ADE		BC		AC	7
	SiC	15%	—	ACD	BC		AC		7
	SiC	25%	—	ABC	BC		AC		7
Ni	—		0.01%	ADE		BC		CD	7
	—		0.1 %	ADE		BC		CD	7
	SiC	5%	0.1 %	ACE	BC		AC		7
	SiC	25%	0.01%	ABC	BC		AC		7
TOTAL EXPERIMENTS				48	18	14	18	14	112

*CASTING SHAPES, DIMENSIONS & WEIGHTS ARE IDENTIFIED IN FIGURE 12 & TABLE 5

one ingot, the completion of horizontal series in Table 6 is almost mandatory; it is even feasible to carry out each series in one single heat, so that it could be considered as one experiment. This approach would further generate early experience in process engineering and tooling as a basis for potential program revisions.

To convey an overall picture of the magnitude of the program, the total number of individual experiments and the related net material weights to be shipped to and from orbit are summarized in Table 7, arranged in three phases with increasing complexity and processing temperature. While the total program may appear ambitious in terms of experiment number, it turns out to be rather modest in terms of material weight.

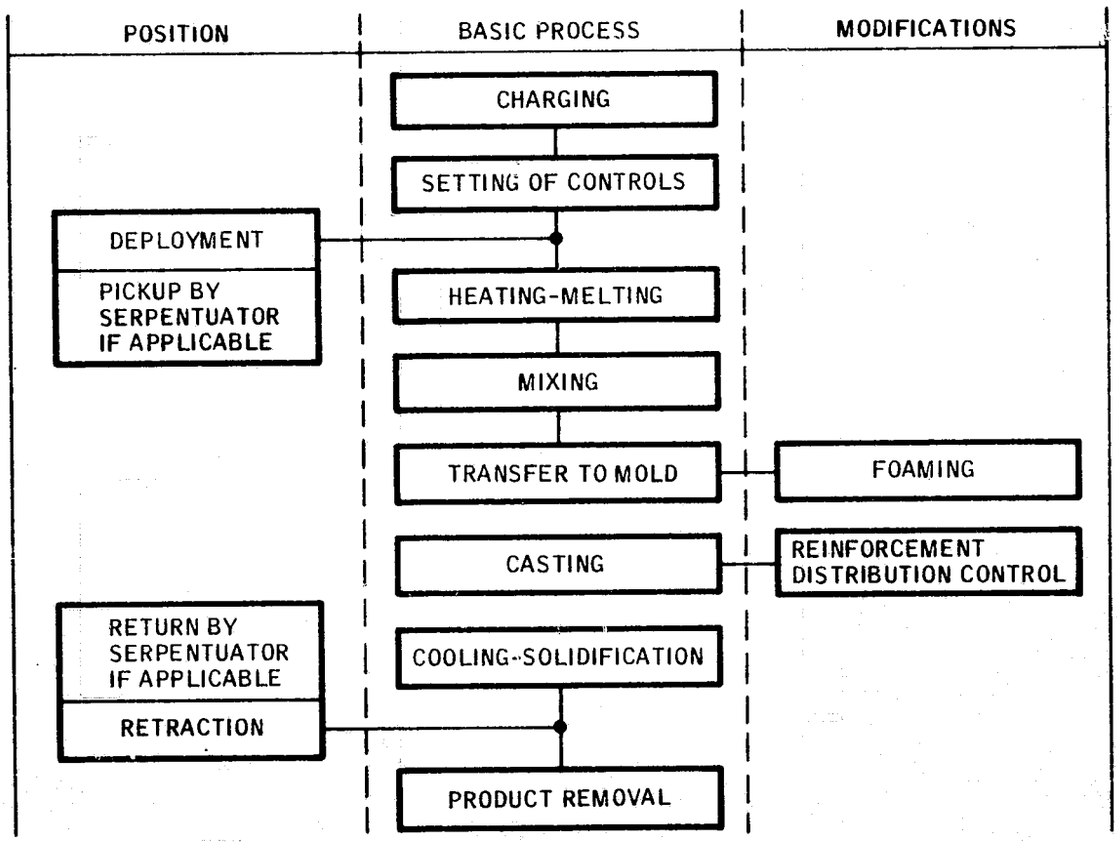


Figure 13. Sequence of major processing steps.

Table 7. Experiment program summary.

EXPT. PHASE	OBJECTIVE	NUMBER OF			MATERIAL WEIGHT (LB.)	
		INGOTS	CHECK EXP.	CASTG. EXP.	DEPLOY.	RETURN
I	HIGH-STRENGTH ALUMINUM-WHISKER COMPOSITES	4	6	28	250	110
II	HIGH-STRENGTH Al-WHISKER COMPOSITES WITH MICRO-STRUCTURE CONTROL	5	5	35	310	135
III	HIGH-STRENGTH & CREEP RESISTANT NICKEL-WHISKER COMPOSITES; MICROSTRUC-TURE CONTROL	7	6	49	1,150	450

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N70-20539

HEAT SOURCES FOR SPACE MANUFACTURING PROCESSES

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ABSTRACT

This paper examines the various possible heat sources for manufacturing processes requiring heat in the environment of space and zero-G and makes a rough analysis of the usefulness of the heat sources with respect to weight, bulk, power requirements, reliability, safety of operation, and cost where applicable to any of the various manufacturing process experiments proposed for the AAP program.

The analysis of the heat sources is not too detailed or accurate because not enough is known at this time about which materials are to be processed.

This paper also assumes that a primary source of electric power is available, large enough to meet the demand in each instance.

INTRODUCTION

Almost everyone recognizes that space offers some unique properties for certain manufacturing processes. These are zero-G and a vacuum pump of infinite capacity. Accordingly, various experiments have been proposed to determine if these properties can be exploited for manufacturing unique products. We should also recognize that it is the liquid state

of matter that offers the best properties for the zero-G environment. Gases and solids are not affected very much by zero-G.

It should be made clear at this time that the heat sources referred to in this paper, except for solar radiation and hot gases, are not primary. For the purposes of this paper, we shall assume that there is a prime source of electric power available. Obviously, the electric power source, for the first experiments at least will be severely limited, therefore, the heat source chosen should be the most efficient for the particular process involved.

We don't know at this time which processes will be the most fruitful and therefore a series of experiments have been proposed to determine this. A test chamber has been designed and built which utilizes an electron beam gun for a heat source and it is intended that this will be orbited on the AAP-1 flight. This chamber has facilities for several manufacturing experiments. The experiments approved for this flight are:

1. Exothermic Brazing (Exp. #492)
2. Electron Beam Welding (Exp. #493)

Additional proposed experiments are:

1. Single Crystal Growth
2. Casting of Composite Materials
3. Casting Spheres
4. Manufacture of Amorphous High Index Glass

In the meantime the design of a second generation manufacturing chamber has been started. This chamber is to have many more manufacturing capabilities than the first chamber including multiple heat sources, hence the need for our examination of various heat sources for their greatest usefulness.

This new chamber, which is a prototype, will teach us what we need to know about the final design of such a chamber. It will certainly allow us to make empirical experiments to determine exact heat requirements, heat transfer rates, cooling requirements and contamination potential of each experiment. The chamber is designed with a jacket which can be pumped down to a vacuum for insulating purposes or filled with liquid nitrogen to provide a cold wall. The interior of the chamber will be pumped by a 6 inch diffusion pump and the jacket by a 2 inch diffusion pump. The dimensions inside will be approximately 4 ft. long by 26 inches in diameter since the shape will be cylindrical.

Every BTU must be accounted for because a space station is a closed environment and if the heat generated by the manufacturing process is not radiated off into space or dumped into a heat sink which is thrown

away, the heat will appear in the space station. Insulating the chamber merely delays the matter. It is mandatory that calculations and experiments be undertaken to determine if the space station will radiate this heat away without making the environment uncomfortably hot for the astronauts. If it will not then the heat must be rejected by some method yet to be determined.

First slide.

Since most manufacturing processes require the use of heat as a necessary adjunct to the process itself, let us take a hard look at various sources of heat to select the best candidates for use in space.

Slide #1

1. Induction Heating
2. Electron Beam Gun
3. Electron Beam Plasma Gun
4. Laser
5. Electric Arc
6. Hot Gas
7. Electrical Resistance
8. Solar Radiation
9. Chemical
10. Ultrasonics
11. Infra-red Radiation
12. Microwave Radiation

The sources shown were examined, when significant, for their weight, efficiency, bulk, time to product the heat required, power requirements ancillary equipment needed, complexity of operation construction and control, contamination hazards, reliability, training required to use, operator skill and cost. We don't consider this list as final. Other heating methods will be examined when they become candidates.

The sources best suited for space use turned out to be-

Induction Heating
Electron Beam
Electrical Resistance
Chemical

The chemical heat is good for short term heating because it makes no demand on the spacecraft power system.

Electrical resistance and the electron beam are efficient and are practical to use from the standpoint of cleanliness and their adaptability to vacuum use.

Induction heating is important because the coils used for heating can be also used for levitating the object to be heated and thus give us management of position and movement except with non-conductors. The process is also about 70% efficient.

When the coils are properly spaced, this system of heating has the possibility of producing convenient temperature gradients in experimental materials.

It is impossible in the time alloted to go into the calculations which were used to evaluate each heat source. All we can do is give some evaluation of the results.

The heat sources eliminated were rejected for the following reasons:

The electron beam plasma gun is more complicated to operate than the electron beam gun and gives no special advantage for the present proposed experiments. It may be used on some later experiment which requires it.

The laser was rejected because of its poor efficiency. The most efficient laser is the CO_2 laser and it is only 14% efficient. On these first experiments, we have no power to waste. Also that energy which doesn't go into the laser beam will largely appear in the spacecraft, which is highly undesirable.

The electric arc was rejected because, so far, all the experiments proposed are to be done in a vacuum, and of course, the electric arc will not work in a vacuum.

The use of a hot gas, which means fuel and oxidizer gases, was rejected at this time for safety reasons.

Solar radiation would be very awkward to use unless the spacecraft maintains a constant orientation to the sun. At the very least, it would require a rather elaborate optical system to place the heat at the spot where it is needed.

Ultrasonics are also very inefficient and require a rubbing contact. They were rejected for these reasons.

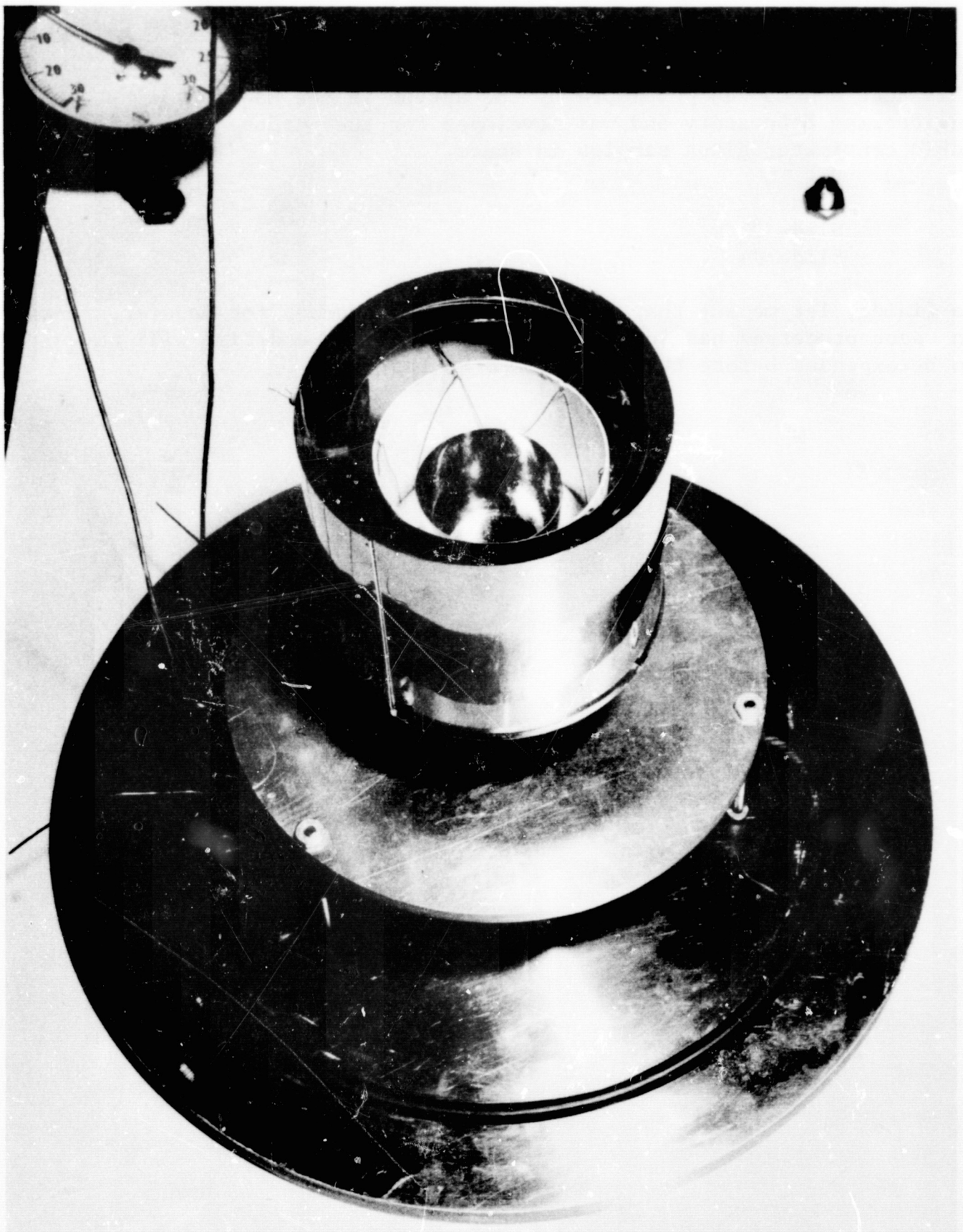
Infra-red radiation from lamps may prove to be a good heat source for later experiments particularly where heat is required over a large area, but for high temperature work where metals are to be melted, the lamps are too awkward to use.

Microwave radiation requires a powerful transmitter for heating so its weight efficiency is poor but it may be used at a time when the heating of non-metallic substances is required.

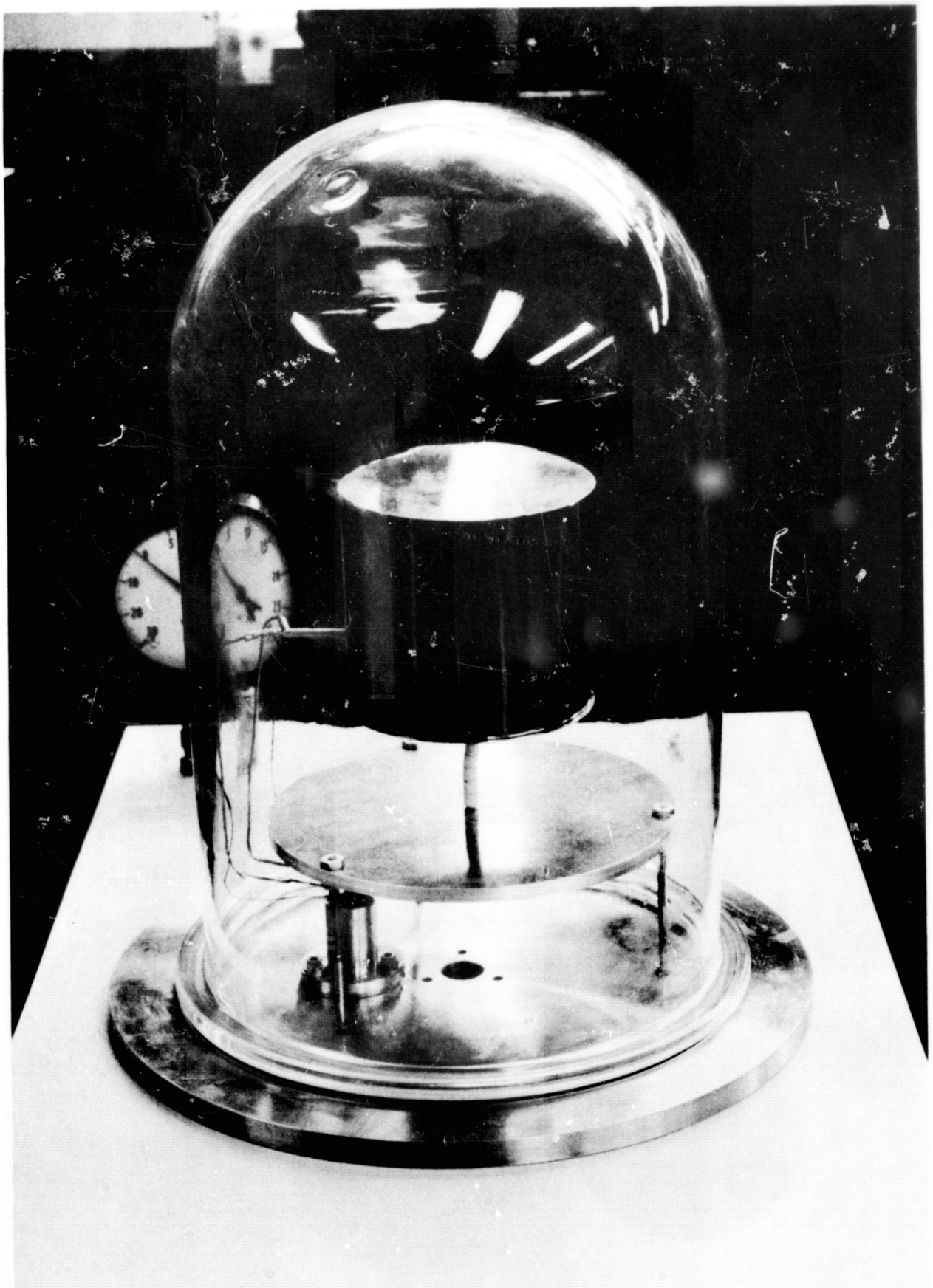
Let us take a look at a typical heat source in its prototype stage. This heat source was developed by the author in the Manufacturing Engineering Laboratory and was developed for the purpose of melting 5 cubic centimeter glass samples in space.

Slide #2
Slide #3
Slide #4

To finish, let me say that the study of heat sources for manufacturing in space processes has just started. Much effort and time will have to be expended before the art becomes routine.



SLIDE 2



SLIDE 3



SLIDE 4

N70-20540

CRYSTAL GROWTH FROM MELTS IN 0-G ENVIRONMENT

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ABSTRACT

The value of highly perfect single crystals to technology is discussed. Many crystals used sell in the range $10,000 - $100,000 per pound. Many potentially useful crystals which cannot be grown on earth because the melt cannot be contained could be grown from containerless melts in 0-g. Very desirable increases in perfection of other crystals currently being used could probably be achieved in 0-g. The factors limiting perfection and their relation to gravity are discussed. Different techniques of growth in 0-g are discussed and a very versatile crystal pulling apparatus which combines the advantages of float zone refining and Czochralski growth is schematically described.

PROMISE

Of the many possibilities which have been suggested for space manufacturing it seems to us that crystal growing offers the most promise of rapid economic success. Many crystals now used in technology for such purposes as lasers, laser modulators, semiconducting devices, transducers, substrates for large scale integrated circuits, etc., sell for prices in the range of $10,000 - $100,000 per pound. The fact that these prices are paid gives a measure of the technological value of the crystals.

Many potentially useful crystals have not realized their promise because it has not proven possible so far to produce them of suitable size and perfection. In a number of cases this seems to be solely due to the unavailability of a crucible material that will hold a melt from which the crystal can be grown. Noteworthy examples of difficult to contain melts are transition metal oxides including rare earth iron garnets and compounds with high alkali and alkali earth content.

We believe crystals of this class can be grown relatively easily from containerless melts in space and that the economic rewards from such an accomplishment would clearly be great.

In many other cases the crystals currently used in technology are limited in perfection by fluctuations in composition and/or the accompanying strains. Semiconductors, for example, are very sensitive to dopant levels (carrier concentrations) and even small fluctuations can render the device useless. Ferroelectric crystals used for laser modulation, second harmonic generation, and other nonlinear effects are extremely sensitive to fluctuations in stoichiometry which induce domain structure and/or result in birefringence variations. This effect causes detrimental optical losses in the device.

There are at least three well recognized causes for these composition fluctuations in melt grown crystals[1] 1) Faceting results from the irregular nucleation of new growth along low index planes in a low temperature gradient. 2) Constitutional supercooling results from the instability of the growth front to a perturbation in the composition of the melt under conditions of high temperature gradient. In extreme cases this leads to the formation of trails of precipitated solute. 3) Temperature fluctuations leading to compositional fluctuations result from turbulent[2] or oscillatory[3] convection in the melt.

These convective thermal oscillations during growth have long been known to lead to oscillations in the carrier density of semiconductors.[4] Growth striations due to this cause have also recently been positively identified in[1,2] rare earth doped CaF_2, Nd-$CaWO_4$, $Ba_2NaNb_5O_{12}$, Nd-$Y_3Al_5O_{12}$, Cr-Al_2O_3, and Cr-$MgAl_2O_4$.

Convection and the associated oscillations would of course be absent in 0-g. Absence of convection and the constraints imposed by a melt container in 0-g also offer the possibility of arranging the heater and insulation geometries in such a way that the freezing isotherm is not near parallel to any low index crystal planes and at the same time the temperature gradients are small. This would minimize problems due to both faceting and constitutional supercooling. Therefore, there is real promise that better quality crystals of these materials can be grown in o-g.

Modest improvements in crystal quality resulting in devices with improved characteristics or higher yields of acceptable devices could again have a tremendous economic importance.

TECHNIQUES

Conceptually the simplest way of growing crystals in 0-g is from a seeded free floating melt. This possibility was mentioned by several speakers last year. Consideration of surface energies indicates that the seed and growing crystal would always stay inside the spherical melt until the maximum dimension of the crystal corresponded to the diameter of the melt. Perfection of crystals obtained by this technique would be limited by faceting and constitutional supercooling as are other melt grown crystals.

The cooling time necessary to grow high quality crystals would certainly be measured in hours. Clearly some method of keeping the melt centered in the furnace for this length of time would be needed. Magnetic induction and gas jets have been suggested as means for positioning such a melt. Both would probably lead to temperature fluctuations in the melt and hence imperfections in the crystal.

In addition the constant attention of an operator would be necessary to keep the melt centered. Alternatively, a servo system could possibly be devised but this would involve an additional development of sensors and control circuitry. It might be difficult to design sensors and positioning devices compatible with a furnace which will provide the necessary temperatures and temperature gradients.

All of this is not to say that good crystals could not be grown from a free floating melt. It is only to convince you that the modified Czochralski method which we propose is actually simpler as well as far more versatile.

A schematic drawing of our design is shown on slide 1. It can also be looked at as a modification of the floating zone principle to incorporate the advantages of the Czochralski method. These are the use of a well crystallized seed and the ability to neck down the crystal to prevent the propagation of twin boundaries, dislocations, etc.

The basic equipment would be two opposing crystal pullers with reversible and varying pull rates and a suitable heating arrangement with controls and programmer. The insulation would be designed and fabricated from suitable materials for the specific crystal pulled. A versatile puller would have interchangeable containers for a variety of atmospheres, i.e., reducing or oxidizing. This design would not require positioning of the melt.

Slide 2 shows the operation of the puller. The end of a large, prepared ingot or crystal would be positioned and melted in the furnace. The ingot could be prepared by pressing and/or sintering a combination of materials yielding the right chemical composition. After the melt is obtained and thermally stabilized, the opposite puller would introduce a seed into the melt. The melt and seed could be simultaneously moved within the furnace to establish the proper gradients, etc. The seed puller would then "pull" the crystal as in the Czochralski technique. As the material is removed from the melt, the feed rod puller could replenish the supply at a steady rate. We believe a crystal puller of the type described here could be engineered, built, and tested within a year, and hence could easily be ready to go on a 1973 flight. Space Manufacturing Process Chamber #2 appears to have enough room for equipment designed along fairly conventional lines.

One final subject must be discussed. That is the source of heat which will be used. This has two aspects, the type of heating element in the furnace and the ultimate power source. Each useful crystal produced by melt growth will require from several kilowatt-hours to several tens of kilowatt-hours of energy. The only ultimate sources of power which appear practical are solar power and nuclear power. If nuclear power is used, the heating elements could be of any conventional type, i.e., resistance, electron beam, glow discharge, induction, etc. This has obvious advantages.

If solar power is to be used, it seems that high priority should be given to design of such a furnace and a Space Manufacturing Process Chamber compatible with it. A polar orbit would probably be required for the successful use of solar power. Solar power might have advantages for certain refractory insulating materials, but glow discharge heating should also be considered.

Since in the 1973 tests only battery pack power will be available, experimental runs should be made with a relatively low melting point material to limit power consumption. The material should also have been thoroughly studied on earth so that the results can be interpreted unambiguously. Many materials qualify, for example, KCl.

Production of say 100 crystals with a value of several million dollars would require of the order of 1000 kilowatt-hours of energy. Assuming this power is available, quantity production could begin in the 1975 space station.

A real evaluation of the cost effectiveness of crystal growth from melts in space depends on a realistic assessment of the power cost.

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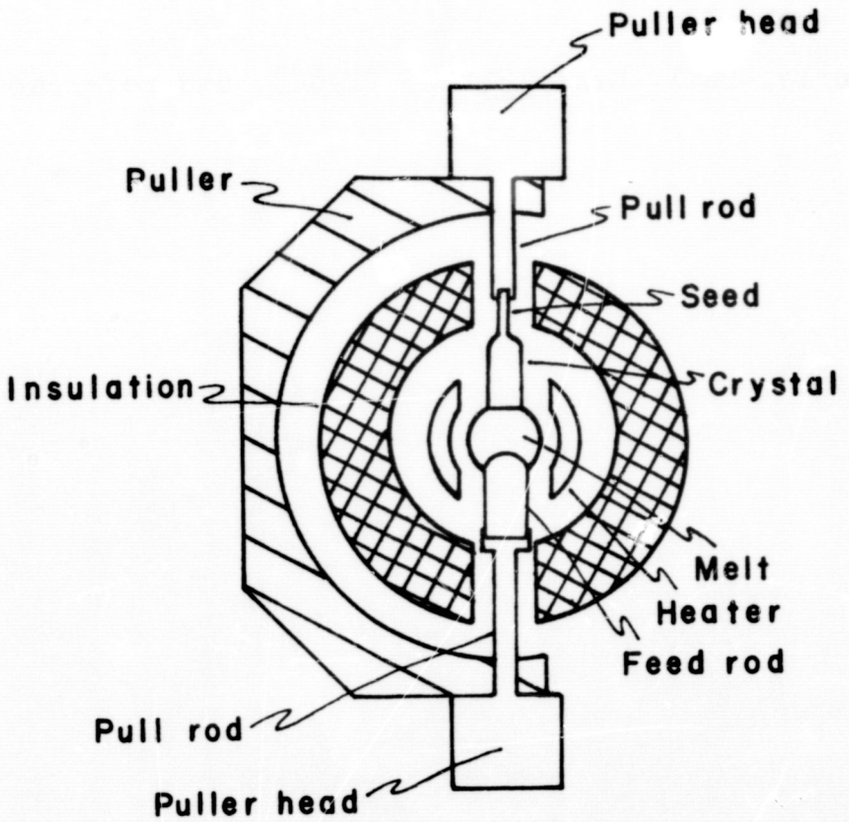


Fig. I Pull for O-Gravity Environment

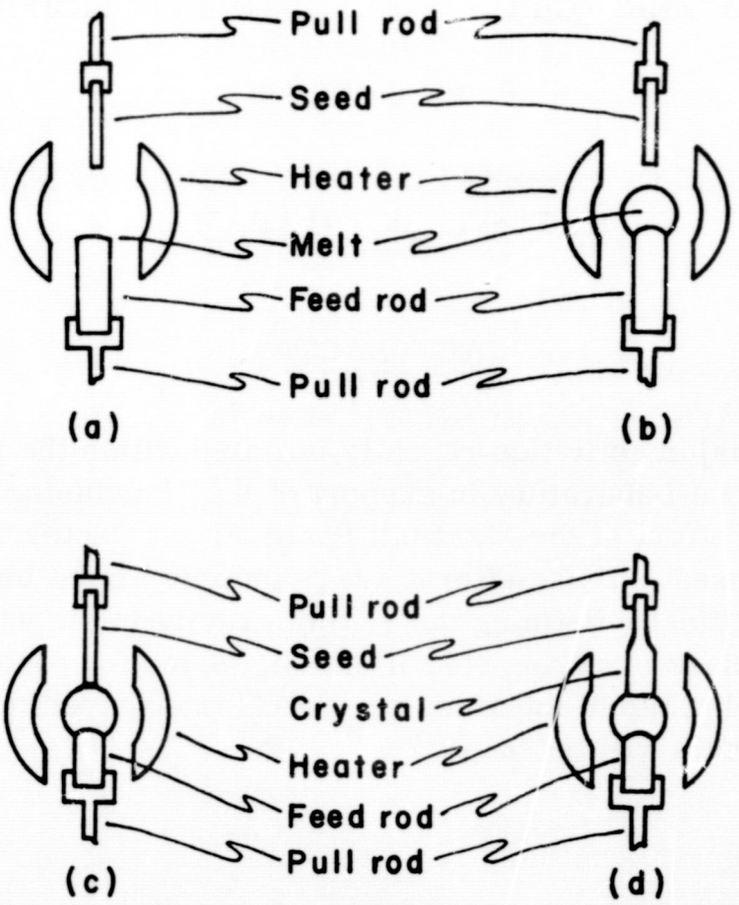


Fig. 2 Procedure for Crystal Growth in O-Gravity Puller

N70-20541

STUDIES OF ZERO-GRAVITY EFFECTS ON SOLIDIFICATION

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ABSTRACT

The major activities recently initiated within the Space Sciences Laboratory in support of the Manufacturing in Space effort at the Marshall Space Flight Center will be discussed. These efforts are primarily aimed toward scientifically defining the role of gravity in the various processes involving solidification. A motion picture of the solid/liquid interface of several transparent freezing materials will be shown.

INTRODUCTION

The Manufacturing in Space Program presently being formulated within NASA is a concept having tremendous potential. It covers a broad spectrum of ideas and tasks to manufacture products in the unique environment of space where several definite advantages are inherently present. Many disciplines are required to formulate, evaluate, design, and develop a sound and complete program. The disciplines vary from commercial hardware to material science to space science to spacecraft engineering. These must be integrated suitably to produce the very best program possible. This program should 1) define the products to be manufactured in space on a continuous basis, 2) define, analyze, and develop zero-g technology and its associated problems, 3) define the research and development that is required in space, and 4) plan, develop, test, and fly manufacturing-in-space modules and payloads. A strong scientific research program is required and will be a vital part of NASA's overall Manufacturing in Space Program.

The unique space environment of zero gravity, vacuum with infinite pumping speed, solar radiation, solar wind, and low vibration are of most interest. Of these, zero gravity is the most unique and important boundary condition of space. The effects of these special environments on such solidification properties as nucleation and supercooling, freezing stability criteria, contamination, diffusion, etc., poses a fundamental problem in evaluating potential space manufacturing processes. Most of the subject effects are presently in the speculative stage. This research program will initiate analytical and experimental definition of these effects. The experimentation should initially be earthbound and later culminate in space flight experimentation. The following is quoted from the Proceedings of the 1968 Winter Study on Uses of Manned Space Flight:

> "The initial emphasis should be upon research to understand how materials behave during zero-g processing and to identify new materials and fabrication methods to be used later. It does not appear that early emphasis should be placed upon actual fabrication of specific products."

This approach is particularly important because it means that a logical, planned, and coherent research program must be initiated toward the understanding of space environmental effects on the basic mechanisms (rather than researching every aspect of only one product which could possibly not be attractive to the industrial and scientific community in a few years). Nevertheless, a candidate list of highly potential processes and materials to be formed in space is still an essential guideline in studying the effects of the space environment upon basic properties.

There are many candidate tasks and associated problems in the Manufacturing in Space Program that can be properly evaluated only by scientific research and development. This is especially true in the area of crystal growth, perhaps the most important single area of the Manufacturing in Space Program.

More nearly perfect crystals are possible. Artificially grown single crystals are being produced in large quantities to satisfy the needs of solid-state electronics, optics, and structural engineering research (by utilizing the full bonding forces between adjacent atoms in nearly perfect single crystals). Crystal growth is accomplished in a variety of ways for the production of piezoelectrics, semiconductors, laser crystals, whisker crystals, etc.

ZERO-GRAVITY CRYSTAL GROWTH

To ascertain the effects of the space environment upon solidification processes and crystal growth and to determine how these unique boundary conditions can be used to improve the size and perfection of crystals, it is useful to begin by considering the whole field of crystal growth as presented by M. Schieber at the 1966 International Congress of Crystal Growth:

"I. THEORY OF NUCLEATION AND GROWTH

- A. Interface versus Diffusion Process
- B. Mathematical Growth of Crystals
- C. Kinetics of Growth
- D. Morphological Stability Criteria
- E. Three-Dimensional Nucleation
- F. Perturbation of Impurity Flow

"II. EXPERIMENTAL CRYSTAL GROWTH

- A. Melt Growth of Semiconductors
- B. High-Pressure Growth
- C. Vapor Growth
- D. Strain Anneal Growth of Metals
- E. Flux Growth of Ferrites
- F. Zone Melting of Organic Crystals
- G. Automatic Plasma Torch-Verneuil

"III. CHARACTERIZATION OF CRYSTALS

- A. Electrical
- B. Solid-State Physics

C. Perfection of Crystals

D. Properties of Crystals

E. Segregation Coefficients

F. Stoichiometry Magnetism Purity

G. Crystallography of Structure"

Obviously, all three areas are of interest in the Manufacturing in Space Program. In Area I, one expects to find the functional dependence of the subject processes on the imposed boundary conditions, i.e., gravitational perturbation of impurity flow, etc. In Area II, the techniques to be employed in space must be analyzed for adoption to space flight conditions and constraints. In Area III are the techniques by which the crystals are evaluated and characterized.

It is often stated that crystal growth is an art. To some extent this is true. The work in Area I has lagged behind the tremendous advances which have been made in Areas II and III. On the other hand, the volume of knowledge in Area I is fairly extensive and is growing rapidly. The technical status in the field of crystal growth strongly influences the approach which must be taken in developing crystal growth technology for manufacturing in space. A strong ground-based program is required that has initial thrust in Area I, supplemented with carefully planned ground-based experiments in Area II. (The experimental data are evaluated using the approaches listed in Area III.)

The ground-based program approach must recognize that each of the fields listed by Schieber are in themselves broad fields of scientific study. Thus, the program defined here represents a multidisciplinary approach which includes in-house, contractual, and academic personnel. The definition of objectives stated herein utilizes academic consultations. A strong in-house effort is particularly desirable for the following reasons:

1. Research flexibility

2. Contact and communication with the scientific community

3. Task evaluation independent of commercial interests

4. Scientific monitoring of out-of-house contracts

5. Direct assistance to project engineering in the Manufacturing in Space on such missions as the Saturn Orbital Workshop

6. Immediate access to existing information on the space environment

7. Definition of critical problem areas

8. Long-range research continuity

With these factors in mind, Space Sciences Laboratory (SSL) has initiated a ground-based research program whose objectives are to answer, insofar as technically possible, the following basic questions by analytical and experimental study and by personal contact with various experts within the scientific community:

1. What are the effects of gravity on solidification and crystal growth?

2. How can these effects be utilized to improve the size, quality, and purity of industrial-type crystals?

3. What are the observable dependent parameters affected by gravity?

4. What are the synergistic effects of gravity with other boundary condition changes?

5. What theoretical and analytical predictions are possible on gravitational effects?

6. What supporting ground-based experimentation is required?

7. What flight data are required?

In the ensuing pages, studies initiated to answer these questions in the areas of solidification, single crystal growth (bulk crystals), and single crystal growth (whisker crystals) are discussed.

ANALYTICAL STUDIES

A continuing effort is being made to keep abreast of the literature and to perform pertinent analysis. At present, considerable effort is spent on this aspect of the program by SSL personnel and in contractual studies being performed by Dr. Grodska of Lockheed. The inhouse studies are

concentrating on defining the influence of thermal convection and fluctuations upon parameters such as diffusion which affect the deposition of impurities and dopants in crystal growth.

For example, Burton, Prim, and Slichter have shown that a relation can be established between the interfacial distribution coefficient k and properties of the liquid melt:

$$k_{eff} = \frac{k}{k + (1-k)\, e^{-\frac{f\delta}{D\,\frac{\rho_s}{\rho_L}}}}$$

where

$k = C_s/C_L$

C_s = impurity concentration in the solid

C_L = impurity concentration in the liquid

δ = effective thickness of the diffusion layer

f = growth rate

ρ = density

D = effective diffusion coefficient of the impurity.

The term k_{eff} determines the rate at which impurities (or dopants) are deposited during solidification. Both δ and D are usually very susceptible to the smallest fluctuations [1] in the liquid melt, meaning they are influenced by gravity-induced convection. It is noted that several expressions exist in the literature [2] for k_{eff}, depending on particular material properties such as anisotropic growth rate. The above expression is given as an example of this type of relationship.

It may be asked why solidification in zero-g cannot be simulated on earth by maintaining the lower densities upward where gravity-induced convection is eliminated. The answer is that laminar flow, as described by Rayleigh, for all intents and purposes, is eliminated. However, the types of flow that hinder crystal growth are thought to be fluctuations, turbulences, and eddy currents that are present because of various driving forces such as thermal gradients, surface tension, and capillarity, all of which give rise to flow such as Marangoni flow and Benard cells. These fluctuations do not occur homogeneously and are perturbated by gravity. Thus, crystal growth in zero-g is unique.

The Lockheed effort is aimed toward the broader goal of defining space environmental effects on solidification, emphasizing the role of gravity upon interface shape, dislocation formation, component segregation, growth rate, nucleation, etc., and to predict the effect of these factors on the solidification of semiconductors, superconductors, ferroelectrics and other candidate space processing materials. This effort requires a short precursory study to assemble a list of the present candidate materials to which this knowledge must be applied. The principal investigator is Dr. P. Grodska, who is speaking at this meeting.

ZERO-G DROP TOWER

This project is a joint experimental effort of the Space Sciences and Manufacturing Engineering Laboratories to generate data on the solidification in zero-g (in vacuo) of small drops of high melting point metals. The research objectives are divided into the following:

1. Geometry and shape of drops. The degree of roundness which a freely falling drop will attain due to cohesion, surface tension, and viscosity upon freezing is to be analyzed. Most models used for defining this roundness are functionally dependent upon the initial distortion and the average radius of the sphere. Thus, the results obtained from the spheres formed in the drop tower should provide useful data applicable to the larger spheres to be formed in space on AAP-2. Of particular concern here is the comparison of the time for this initial distortion to dampen with the time to nucleation. A variety of shapes will be obtained if the initial distortions are not dampened.

2. Grain structure. Among the factors influencing grain structure are a) quenching after freezing, b) rate of freezing, c) nucleation, and d) heat transfer within the sphere during freezing (reference is made to personal conversations with M. C. Fleming of MIT). We intend to make comparative

analyses on drops frozen in 1-g and 0-g in which (a) and (b) are made the same. We hope that nucleation effects will be sufficiently repeatable to make deductions concerning (d). As a later project, a second-generation catching device will be designed to prevent rapid quenching after the sphere is frozen.

3. Hollow areas. It is not unlikely that thermal contraction effects, together with small thermal asymmetry effects, can cause the appearance of hollow regions during freezing in free fall. Some thermal asymmetry can be expected because the initial nucleation sites are random, and, as growth progresses from these sites, the latent heat is liberated asymmetrically with respect to the center of the sphere.

4. To observe possible supercooling effects by varying the time of fall.

The SSL/ME drop tower is located in Building 4331 (Figure 1). The tower is designed to obtain the desired spheres without the use of a falling canister; only the sphere falls. This approach eliminates the problem of positioning the sphere relative to a canister. To elimate air drag, gaseous convection, and oxidation, a vacuum of at least 10^{-5} torr is required in the drop tube. The drop distance ℓ was established at 4.9 m (16 ft) [extension to 6.1 m (20 ft) may be accomplished later] where 1-sec drop time t is attained; that is,

$$t = \sqrt{2\ell/g} \quad .$$

Sphere diameters of the order of millimeters are possible as illustrated in the following calculation:

For a metallic sphere having the following geometrical and material properties,

r = radium (m)

ρ = density (kg/m^3)

Q_F = heat of fusion (kcal/kg = cal/g)

ϵ = emissivity

T = temperature of freezing (°K)

M mass (kg)

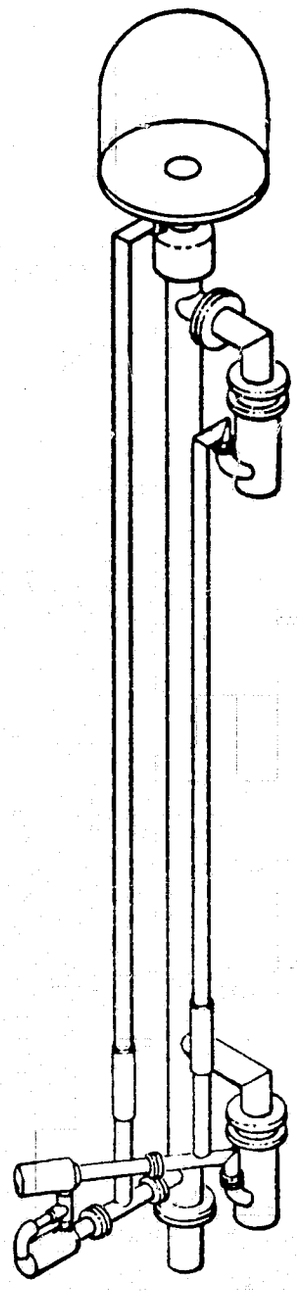


FIGURE 1. Joint SSL/ME zero-g drop tower for space processing ground-based studies

other parameters:

Q = heat energy (joules)

t = time (sec)

A = surface area (m^2)

σ = Stefan-Boltzmann constant ($W/m^2 \cdot K$)

T' = temperature of the tube.

The amount of heat energy to be radiated away from the sphere to accomplish total freezing is

$$Q = (4.18 \times 10^3)\, Q_F M$$

$$\cong 5\pi Q_F \rho r^3\, 10^3 \qquad (1)$$

This quantity is also equal to the time integral of the dissipation rate by the Stefan-Boltzmann relation for a freely falling sphere in vacuo

$$\frac{dQ}{dt} = A \epsilon \sigma (T^4 - T'^4) \quad ,$$

Now

$$T^4 >> T'^4$$

$$\therefore \frac{dQ}{dt} \cong A \epsilon \sigma (T)^4$$

or

$$\frac{dQ}{dt} = \pi r^2 \epsilon \sigma T^4 \quad .$$

Upon integrating from t=0 to t=t,

$$Q = \pi r^2 \epsilon \sigma T^4 t \quad . \tag{2}$$

Combining equations (1) and (2),

$$r = \frac{\epsilon \sigma T^4 t}{5 Q_F \rho 10^3} \quad .$$

Finally, for a sphere having

$$Q_f = 10 \text{ kcal/kg } (=10 \text{ cal/g})$$

$$\epsilon = 0.1$$

$$T_f = 2000\,^\circ\text{K}$$

$$\rho = 7 \times 10^3 \text{ kg/m}^3$$

$$r = \frac{(10^{-1})\ (5.67\ \ 10^{-8})\ (2)^4\ (10^{12})\ 1}{5\ (10)\ (7)\ (10^3)\ (10^3)}$$

$$= 3 \times 10^{-4} \text{ m} = 0.3 \text{ mm}$$

or $d = 0.6$ mm.

It is anticipated that $\epsilon = 0.1$ is a worst case and $\epsilon = 0.4$ is probably more reasonable for the materials, in which case, $d = 2.4$ mm.

EXPERIMENTAL CRYSTAL GROWTH

The experimental growth presently encompasses three tasks. Each of these tasks has been defined to obtain data on a specific aspect of zero-g crystal growth, and the approach that is used is to perturbate a boundary condition causing a change similar to that caused by zero-gravity environment. Each of these tasks is supported analytically and is designed as the first-step, ground-based experimentation toward defining the designated objective.

The first task is a contractual study entitled "Effect of Zero Gravity on Single Crystal Whisker Growth," being conducted at the University of Alabama; the principal Investigator is Dr. J. Davis, who is also speaking at this meeting. Single-crystal whiskers have tremendous industrial potential because of their high degree of crystalline perfection which gives them tensile strength two orders of magnitude higher than the bulk crystal.

The second task in the area of crystal growth experiments is entitled "Bulk Crystal Growth in Zero-g." The Principal Investigator is Dr. U. Roy of the University of Alabama at Huntsville. Dr. Roy's group is working very closely with SSL in-house efforts. Primarily, he is attacking the question of zero-g effects on the growth of large single crystals by defining and performing specially selected experiments in the laboratory that will elucidate the role of gravity. Dr. Roy will discuss this in greater detail in another presentation at this meeting.

The third task is an in-house effort defined to experimentally determine the effects of the magnitude thermal convection on impurity deposition in semiconductors. This task was defined in SSL and will be performed in Marshall's Astronautics Laboratory where the required equipment is available. By holding all boundary conditions constant except the thermal gradient in the crucible, it is anticipated that single crystals can be grown and characterized according to growth condition. We plan to use the Czochralski growth method, as it is one of the better techniques for growing high-quality semiconductors. However, this technique, in its present form, is not attractive for space flight because of the amount of machinery required. It is very possible that a modified approach will materialize that will be compatible with space flight. The material chosen for this study is In Sb which exhibits impurity banding, has a melting point of 525° C, and no vapor pressure problems. [3] Compared with Ga As, In Sb experiments should yield vital information, be easier to grow, and should provide a basis for in-house capability necessary for this type of project.

FLIGHT EXPERIMENT

A flight experiment presently under development in SSL is T-038, "Zero Gravity Crystal Growth." This experiment is designed to study the solidification of materials in orbit whose behavior is highly observable and whose handling is relatively simple. The experiment is also designed to visually and photographically observe through a microscope the freezing of transparent materials. Laboratory movies (time lapse) are presently available in which studies are documented on the behavior of such materials as

hexadecane, lithium nitrate trihydrate, and water. Bubble formation, convection, nucleation, autonucleation, and growth rates are easily observed. (Similar studies have been made in a centrifuge where smaller grain sizes were observed.) We propose to perform these experiments in zero-g to obtain data for analysis. The flight configuration is designed to accommodate several materials including a low melting point metal and perhaps a whisker experiment.

Space Sciences Laboratory is also involved in the M512 crystal-growing experiment approved for AAP-2 as alternate investigator and alternate COR. The Solid State physics group of SSL-TR has been considering post-flight analysis of the crystals resulting from this experiment. Dr. Kulshreshtha will expand on this subject later in this meeting.

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SINGLE CRYSTAL GROWTH FROM MELT UNDER SPACE ENVIRONMENT

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ABSTRACT

A brief outline of the methods of single crystal growth from melt under 1-g is presented and their relative merits discussed. The role of near 0-g environment and other practical parameters important to the growth of perfect single crystals is considered. The effect of interface shape, high-g, gamma-ray irradiation and electromagnetic body force is reviewed. The experiment to study the growth kinetics under various equivalent gravity fields is discussed in more general terms and a partial list of the candidate materials suitable for space crystal growth is presented.

INTRODUCTION

The age of solid state electronics was inaugurated by the large scale availability of highly pure and superior quality single crystals of germanium and silicon. The crystal growth, in return, has been vastly benefited by the availability of sophisticated control electronics. Definite improvements of the crystal quality in purity and crystalline perfection has been attained. A new era, i.e., SPACE AGE, was launched a decade ago. We have reached the point now to seriously consider the industrial usage of the "space". This conference on space processing is a step in this direction; to seek and establish a true dynamic equilibrium between man-space and also between technical utilization-fundamental research. A vast laboratory containing hard vacuum, radiation flux and near zero-gravitational body force is available to experiment. It seems possible that under space environment, large size

single crystals of higher perfection can be grown. My talk will confine itself to the problems of melt crystal growth.

Growing single crystals in space ought to be viewed as a unit step towards understanding many complex space processing problems. A single crystal grown from the melt is a result of controlled solidification as contrasted to casting, which is purposely uncontrolled. Proper understanding of the dynamics of solid/liquid interface in near 0-g will not only assist in growing dislocation-free, optical quality laser and maser materials, but will also present insight into whether a perfect ball bearing can be manufactured. I plan to discuss the following topics. Their relevance to space processing will be pointed out at the proper places.

A. Why 0-g crystal growth from the melt?
B. Which technique is most suited for space experiment and why?
C. What is the influence of growth parameters on crystal perfection?
D. What is the effect of electromagnetic body force and radiation on crystal growth?
E. How does the interface shape affect crystal perfection?
F. Does high-g affect crystal size and perfection?
G. How to study 0-g effects on earth (the crucial experiment)?
H. What materials are suitable for space processing?

A. Fig. 1 compares the magnitude of the interatomic forces of the solid matter, liquid matter, surface tension force and the 1-g gravitational body force (mg, m = 1 gm). The g-force will have negligible effect on the solid state processes since the cohesive force of the solid matter, and also the energy required for most solid state reactions (self-diffusion, phase-change, precipitation), are 10^8-10^9 times greater than g itself. However, the solid/liquid interfacial tension and the cohesive force of the liquid matter fall within the magnitude regime of g and, therefore, considerable interaction is possible.[1] To grow single crystals from the melt or liquid state in a near 0-g environment is, thus, an interesting proposition.

B. Some of the common techniques of single crystal growth from melt are: (a) Czochralski (1918), (b) zone-melting (1952), (c) Bridgeman, (d) Verneuil (1890), (e) flux, (f) hydrothermal, and (g) solution growth. Although the last of the three techniques can yield good optical quality single crystals, the crystal size is generally very small. In addition, they require an extensive knowledge of the phase equilibrium in the multi-component system.[2] The first four, a to d, are the most commercially used techniques. Details of these techniques are given in recent monograph[3] and in a review paper.[4]

(a) The Czochralski Technique

This technique of pulling from the melt is the preferred method for obtaining large

single crystals. A seed crystal is dipped into the melt and gradually withdrawn. Before growth can start, the thermal equilibrium at the melt/solid interface needs to be established and the provision has to be made so that the latent heat of fusion is removed from the interface. Some advantages of this technique are: (1) The crystal need never be touched; (2) control of orientation is easy; (3) the diameter of the crystal can be easily varied; (4) the crystal is cooled without external mechanical restraints. Dislocation-free single crystals of Ge, Si and such metals as Al have been grown. Nassau and Broyer[5] have discussed the criteria for the Czochralski technique. The ideal materials suitable for growth by this technique would have the following properties: (1) congruent melting point, (2) no destructive phase change, (3) low vapor pressure, (4) low viscosity, (5) suitable growth habit, and (6) suitable crucible must be available.

(b) The Floating Zone Technique:

In this technique, a thin molten layer of the material traverses through the body of the solid matter.[6] The technique is suited for high melting point materials (above 2000°C). Since no crucible is used, the problem of crucible contamination is eliminated. The strains due to differential expansion of the crucible and the crystal is absent. One shortcoming of the technique is the limitation on zone length,

$$Lm \simeq 2.8\sqrt{\frac{\gamma}{\rho g}} \quad \text{——— (Heywang's relation).}^{7}$$

Where Lm is the limiting maximum zone height, ρ denotes density, γ, the surface tension, and g, the gravity. Under near 0-g, Lm will be quite large, a decisive advantage of space processing. It is also difficult to obtain a proper temperature distribution. A large radial gradient usually encountered in the system gives rise to high dislocation densities.[3]

(c) The Bridgeman Technique :

The melt in a container is moved relative to a fixed temperature gradient.[4] The technique is suitable for low melting point materials. Generally, the dislocation density of the grown crystal is high.

(d) The Verneuil Technique (1890):

Large single crystals of saphire and ruby have been grown by the Verneuil or flame fusion technique. The technique may be considered to be an inverted arrangement of the Czochralski method,[8] where a liquid layer is continuously replenished. The crystal quality is moderate due to severe temperature gradient and highly localized heat source at the interface. The numerous disadvantages of this technique are: (1) highly strained single crystals, (2) chemical inhomogeneity--a serious problem

for laser materials, (3) high dislocation density and subgrain structure, and (4) contain index of refraction variation which affect the optical path of the crystal. For laser and maser applications, these inhomogeneity and imperfections lead to high optical losses, broad emission line widths and warping of the amplified light wavefronts. The advantage of the technique, however, is fast growth of large size crystals. At this stage, the Czochralski technique appears most suited for 0-g crystal growth. The crystal puller essentially consists of a crucible to hold the melt, a seed with known crystallographic orientation, a means of heating the melt, a mechanism for producing relative motion of the seed and melt and, if needed, provision for special atmosphere (see Fig. 2).

C. The crystal perfection depends on the critical control of the growth parameters, viz., the melt temperature, growth rate, diameter of the crystal and on the thermal gradient at the interface. Usually a compromise between the crystal quality and the ultimate size of the crystal, which depends on the growth rate and the thermal gradient, has to be made. Figures 3 to 5 illustrate this point. Higher growth rate, increased axial temperature gradient and larger diameter result in higher density of grown-in dislocations.[9,10] Since these line defects do not exist in thermodynamic equilibrium, they are difficult to eliminate by post-annealing treatments. Maximum diameter of dislocation-free Al single crystal grown is 0.3mm only.[9] Existing techniques have not lent themselves to grow a larger diameter metallic single crystal. The near 0-g crystal growth might be the answer.

The melt in the crucible experiences free thermal convection induced by gravity. Turbulent flow or overstability results if Rayleigh number Ra, which is a dimensionless parameter, exceeds a certain critical value ($\simeq 1700$). The Rayleigh number, Ra, is a product of the Grashof Gr and Prandtl Pr number.[11]

$$Ra = \left[\frac{g\beta \Delta T L^3}{\nu^2}\right] \left(\frac{Cp\mu}{k}\right) = Gr.\ Pr\ .$$

Where β = volume coefficient of thermal expansion
g = acceleration of gravity
ΔT = temperature difference across L
L = characteristic dimension of the system (length, height, diameter)
ν = kinematic fluid viscosity
μ = absolute fluid viscosity
Cp = specific heat at constant pressure
k = thermal conductivity.

In the case of metals, for reasonable choice of L and ΔT, Ra exceeds 10^5. It is certain from the above relation that under near 0-g, Ra will be greatly reduced and, thus, a large size, perfect single crystal of metals can be grown. A good sized dislocation-free single crystal of elemental and compound semiconductors has been

prepared on earth. It is thought that either they have a large Peirl's stress[12] or the intrinsic strength of the crystal exceeds the thermal and chemical stress close to the melting point.[13]

Seed Rotation:

This is provided to overcome the thermal asymmetry of the melt. An optimum rotation rate is desired for best results.

Chemical Inhomogeneity--Banding:

These are observed in the melt-grown alloy or compound single crystals. Generally, the solutes or impurities have different solubilities in the solid and in the liquid. Fig. 6 illustrates this fact schematically. The equilibrium distribution coefficient K_o is defined as the ratio C_s/C_L and is <1 or >1, depending on the binary phase diagram; but in most practical cases it is <1.

During crystal growth, as solidification proceeds, the solute is rejected at the interface and builds up an enriched diffusion layer.[14] Fig. 7 describes this situation on a composition distance plot. The thickness of the diffusion boundary layer is equal to D/V (diffusion distance, δ) where D is the solute diffusion in the liquid and V is the growth rate. Superimposed to this boundary layer, if a thermal convection exists (g-induced), then solute banding parallel to the interface is observed. These are two dimensional imperfections perpendicular to the growth axis which appear as striations. In laser crystals, they cause scattering of a laser beam and seriously impair the usefulness of crystals. Solute banding can be reduced by decreasing the thickness of the diffusion boundary layer or by eliminating thermal fluctuation on the interface. The second will be easier to achieve in the absence of gravity. The enhanced impurity concentration at the growing interface can also cause the interface shape to change from planar to a cellular form. Fig. 8 illustrates how to suppress constitutional supercooling which results in cellular structures and preferred growth directions in the crystals. High growth rates and sharp temperature gradient are required to avoid constitutional superconducting, which are in direct conflict to grow dislocation-free single crystals.[4]

D. Johnson and Tiller[15] have experimentally studied the effect of electromagnetic body force on δ and have shown the functional relationship,

$$\frac{\delta}{D_L} = B \exp(-mH^2) .$$

Where H = magnetic field, B, m = constant for the system. Higher H reduces the thickness, δ. Further work of Harvey and Utech[16] and M. Schieber[17] indicates that the solute banding is suppressed and also the thermal fluctuations damps out by the application of magnetic field.

Radiation:

G. D. Botsaris, et al[18], studied the effect of gamma-radiation on growth of KCL single crystals grown from aqueous solution. The dislocation density was reduced when the growth took place in a radiation field. The changes in equilibrium surface structure of crystals (KDP) grown under gamma-irradiation was investigated by C. Motoc.[19] It was concluded that the presence of irradiation is equivalent to growth in the presence of impurities. The factor of irradiation must be considered in any space processing.

E. Shape of the solid/liquid interface is an important parameter which determines the uniformity in thermal gradient and the pulling rate.[20] A planar interface is sought in order to grow a perfect crystal. A shape convex to the melt is the most common and is acceptable. The recent use of afterheaters,which are placed directly above the melt and surround the growing crystal, have resulted in production of low dislocation density compounds. The equilibrium shape of the interface in the absence of gravity will be dictated by surface tension force and will assume a hemispherical shape. This can be shown by the treatment of Beliustin.[21] The height-to-width ratio (h/w) of an interface is given by,

$$\frac{h}{w} = \frac{Bw}{w + Av} \quad .$$

Where $$B \simeq \frac{1}{2} \; ; \; A = \frac{g(\rho_1 - \rho_2)}{4\sigma_{12}} \quad ,$$

σ_{12} = surface energy per unit area at the crystal-solution interface,
ρ_1, ρ_2 = density of the crystal and the solution,
v = volume of the crystal.
Therefore, at g = 0, h/w = 1/2 = hemisphere. There might arise the problem of seed wetting, which, however, can be achieved either by changing the equilibrium interface shape by the use of afterheaters or by intentional impurities.

F. Effect of High-g on Crystal Perfection:

The preliminary results on the influence of high-g on solution crystal growth has been published by Schlichta and Knox.[22] The solution was rotated in a centrifuge. Higher g caused super saturation and, hence, crystal growth. The crystal size became smaller at higher g ($\simeq$ 40,000 g) and showed extensive strain damage due to high force fields. A brief review of the practical aspect of growing perfect single crystals was presented.

Let me discuss now the crucial experiments that we are planning to undertake, which should demonstrate the feasibility and practicality of 0-g crystal growth. Planned, is a single crystal growth of a ferro- or a ferri-magnetic compound under

an electromagnetic body force. On earth, the 0-g environment cannot be achieved over an extended period by the drop tower, or the airplane trajectory technique. The magnetic method, on the other hand, can provide a range of gravities including near 0-g for longer duration. Two possibilities exist. In one, the melt is placed in a magnetic gradient and the magnetic force is adjusted to counteract all or part of the g-body force. The second technique has been adequately described by Kirk.[11,23]

G. The experiment will consist of the crucible containing the melt with two electrodes on two sides so that a current is passed horizontally. The magnetic field line will superimpose also horizontally but normal to the current flux. The electric current density will interact with a component of the magnetic field transverse to it and yield a body force normal to the current-magnetic field plane. Fig. 9 illustrates the proposed experiment. The attention, however, has to be paid to the sources of error and the interferring effects of the impressed magnetic and electric field, for example, joule heating, galvanomagnetic and thermomagnetic effects. The equivalent gravities, according to Kirk, is given by a simple expression,

$$\frac{g^*}{g_c} = \sigma_e \frac{(\bar{J} \times \bar{B})}{\alpha \rho_o g_c} \quad .$$

Where g^* = equivalent gravitational acceleration produced by the imposed electromagnetic body force, $\frac{\text{meters}}{\text{sec}^2}$,

g_c = the earth's sea level acceleration, $\frac{\text{meter}}{\text{sec}^2}$,

$\bar{J}$ = electric current density, $\frac{\text{amperes}}{\text{meter}^2}$,

$\bar{B}$ = magnetic flux density, $\frac{\text{webers}}{\text{meter}^2}$,

$\sigma_e = \frac{\delta \sigma}{\sigma_o \delta T}$ = temperature coefficient for electrical conductivity charge, $^oK^{-1}$,

α = coefficient of volume expansion $= \frac{\delta \rho}{\rho_o \delta T}$, $^oK^{-1}$,

ρ_o = mass density, $\frac{kg}{\text{meter}^3}$.

Although conceptually the problem is straightforward, experimentally it is quite complex. Magnets with pole-gaps larger than 2 3/4 inches are not available to us. The crystal growth assembly including all essential parts has to be fitted in this small gap.

H. Finally, I would like to make some general comments regarding the materials to be suitable for space crystal growth. The fundamental research and the technological utilization should be considered jointly. Also, the basic attributes of space environment must be understood. For example, the selection of a congruently melting material which has a low vapor pressure takes into account the hard vacuum of

space. Table 1 lists some of the candidate materials. The listing is by no means complete. GaAs and $LiNbO_3$ single crystals are already available in large quantities. They will serve a good example to learn and acquaint oneself with the preparation of perfect single crystals. The near 0-g environment might also affect the preparation of the organic superconductors proposed by Little[24] about five years ago. Vast sums of money and effort have gone into the synthesis of this one-dimensional, room-temperature superconducting material without success. Space processing may be the answer.

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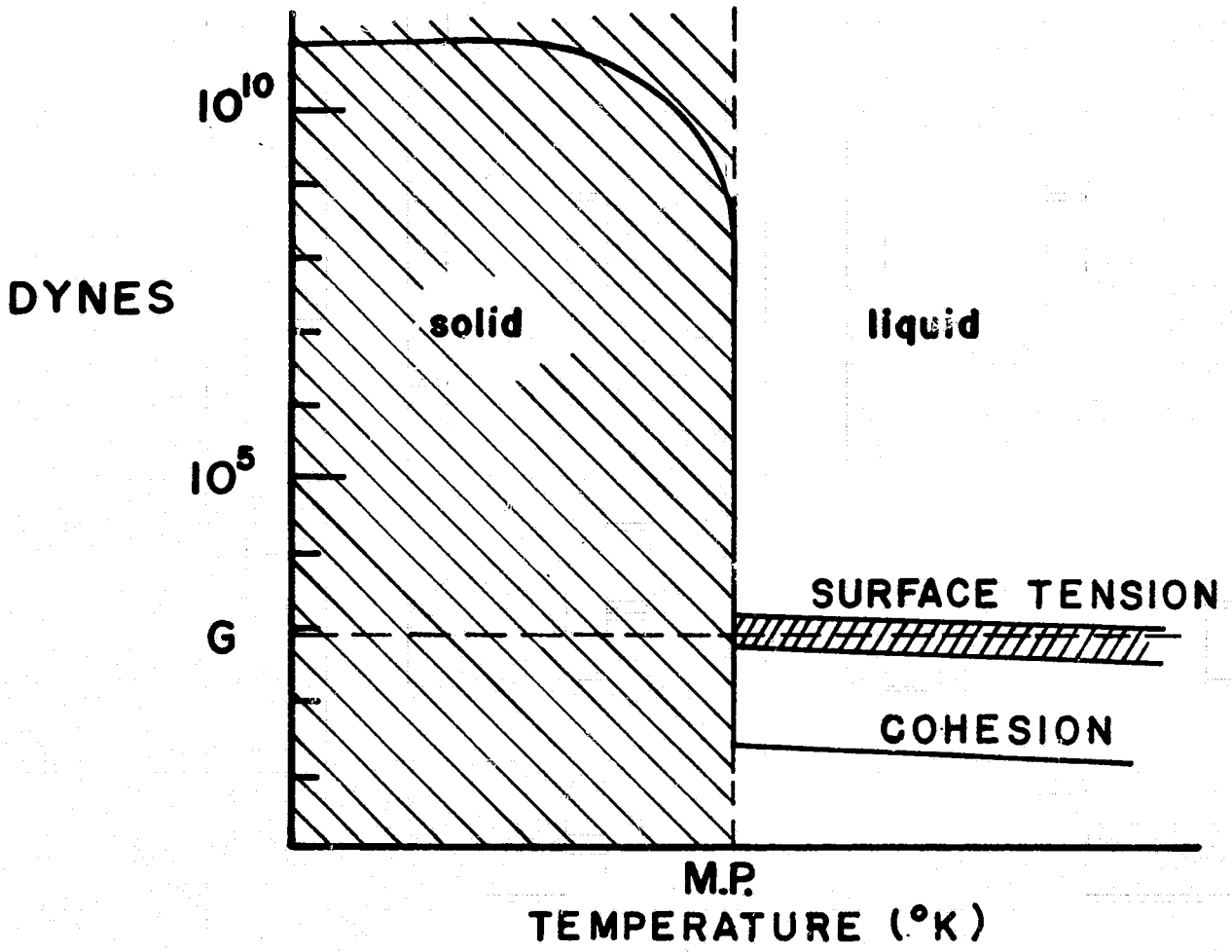


fig. 1. INTERATOMIC FORCES OF MATTER

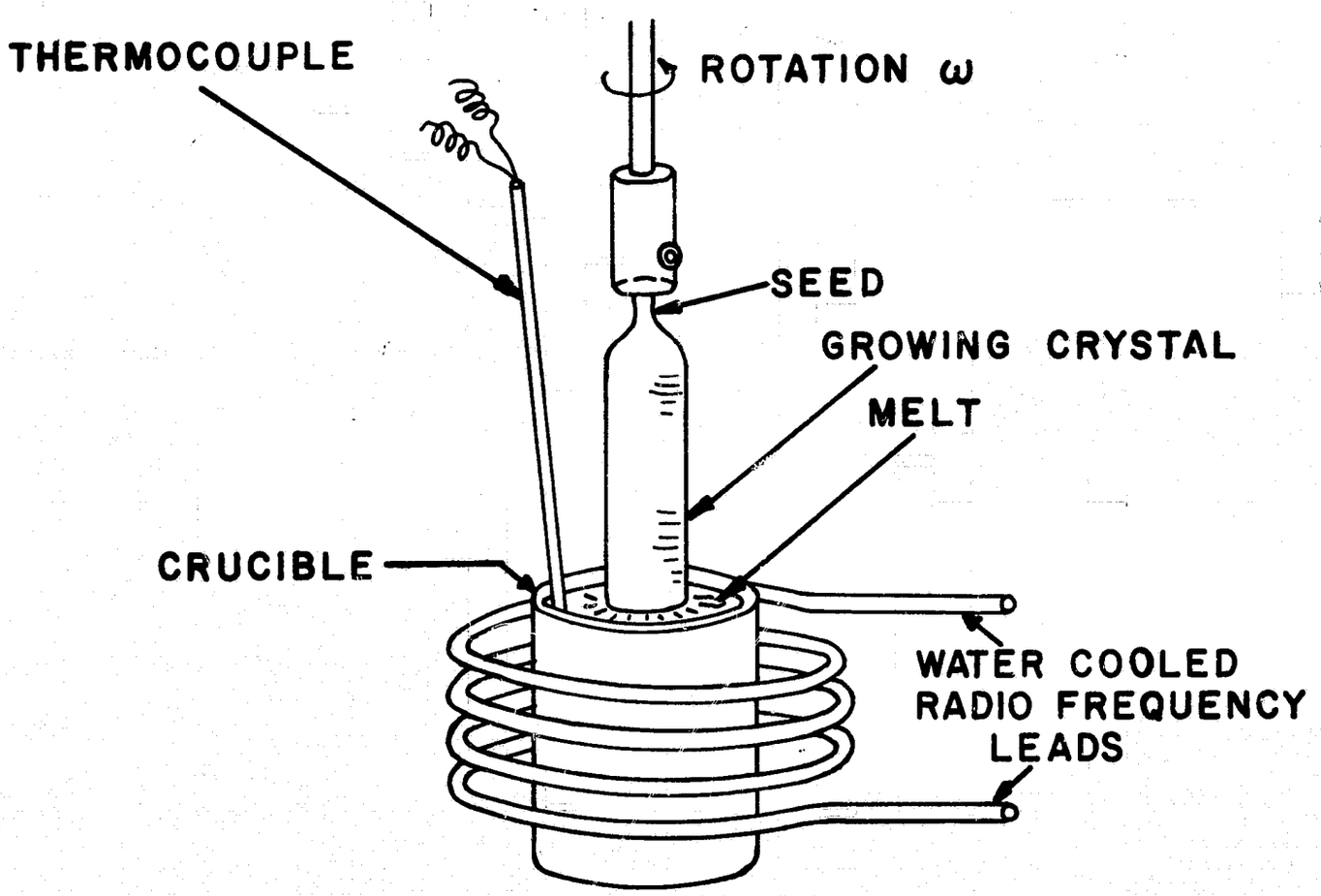


fig. 2 CZOCHRALSKI GROWTH
(schematic)

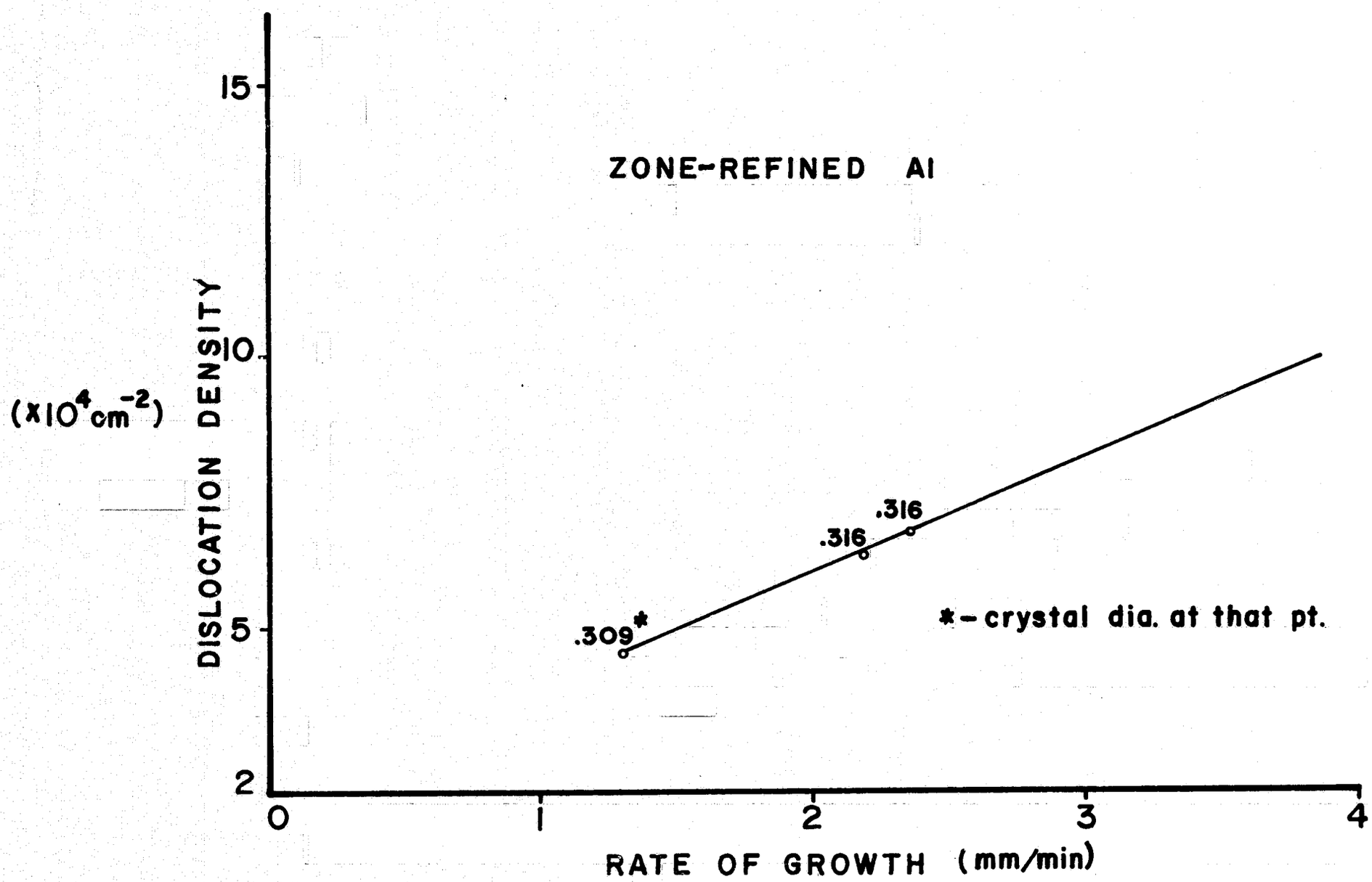


fig. 3. DISLOCATION DENSITY vs. GROWTH RATE

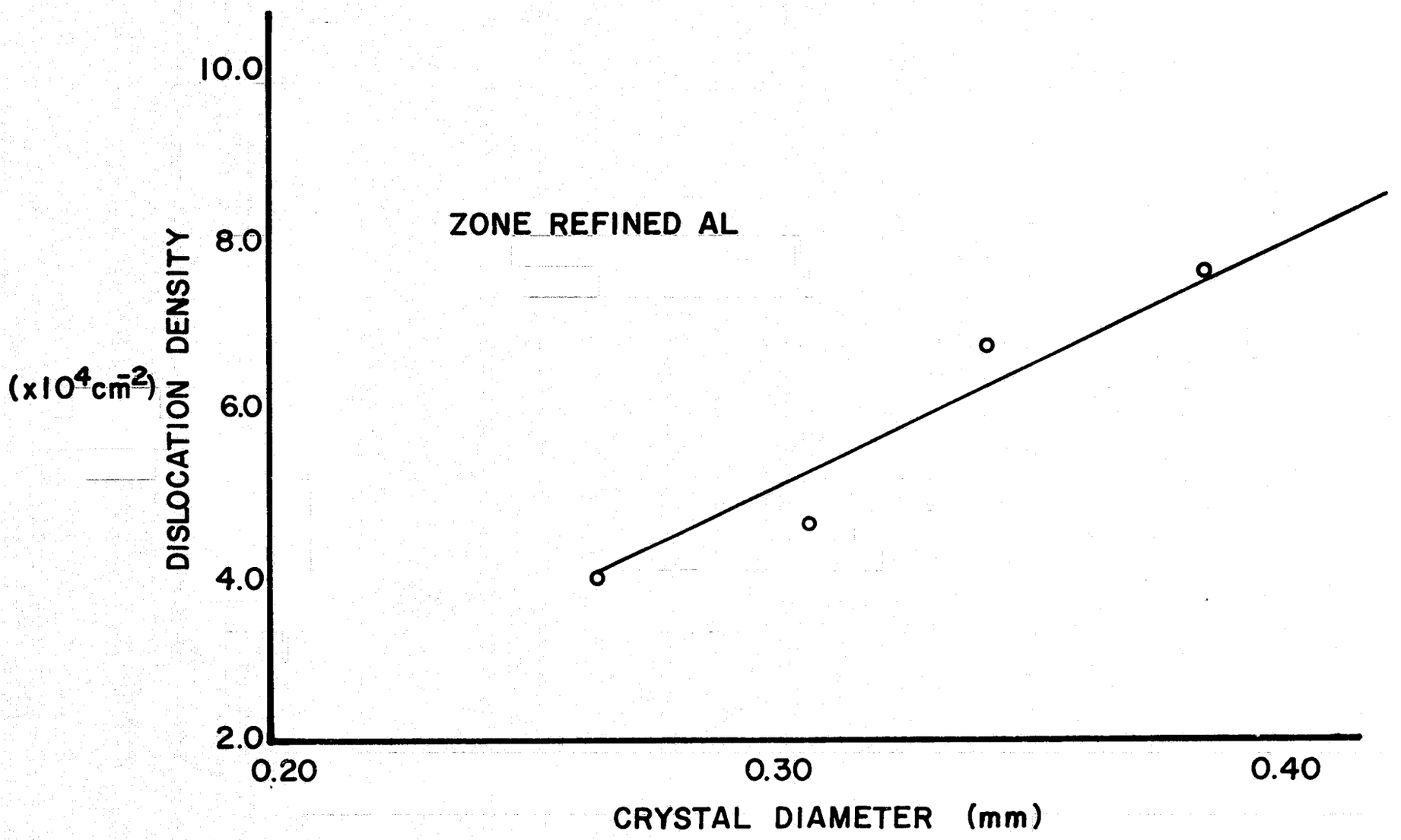


fig. 4 DISLOCATION DENSITY vs. CRYSTAL DIAMETER

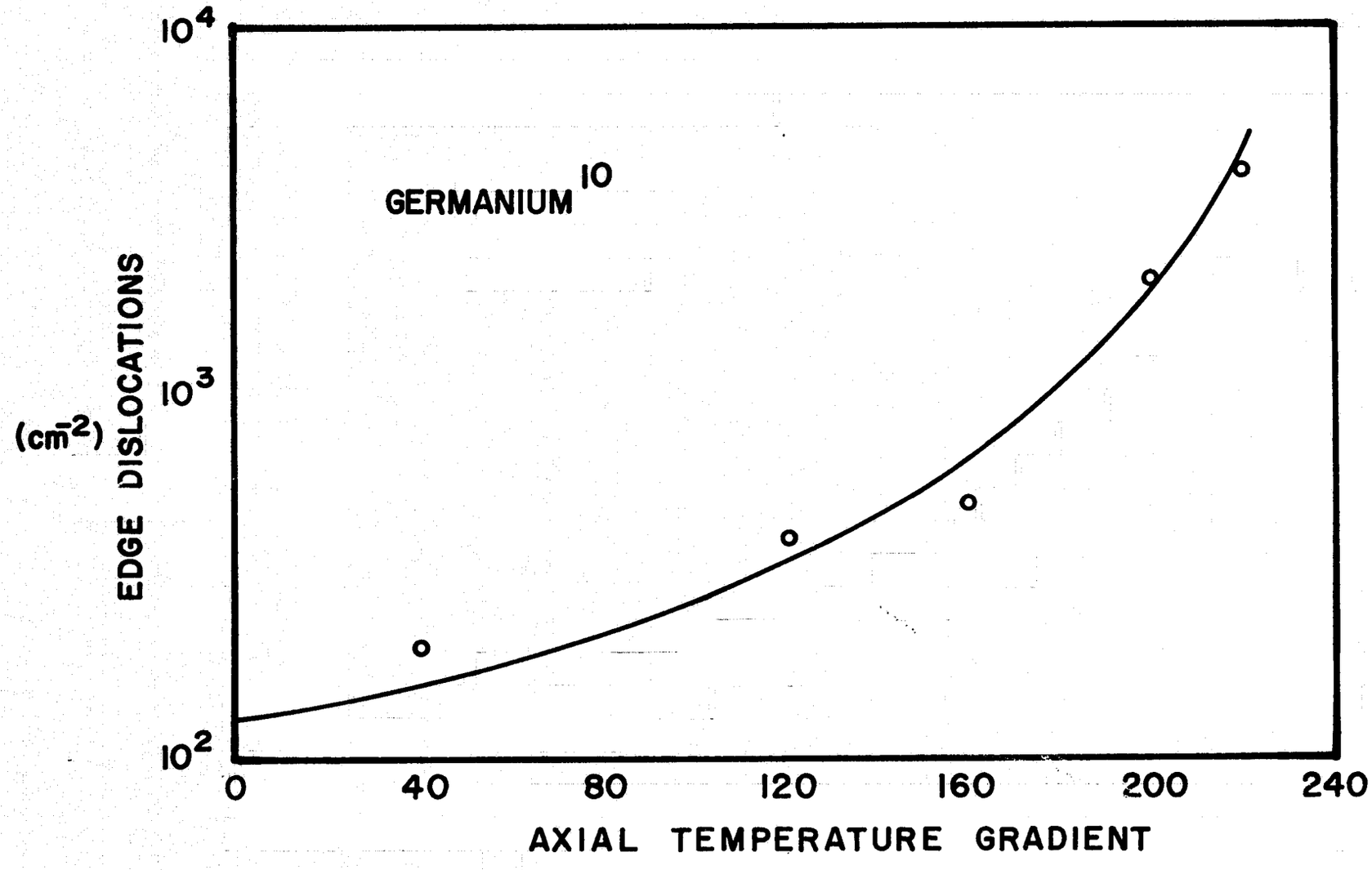


fig. 5 DISLOCATION DENSITY vs. AXIAL TEMPERATURE GRADIENT

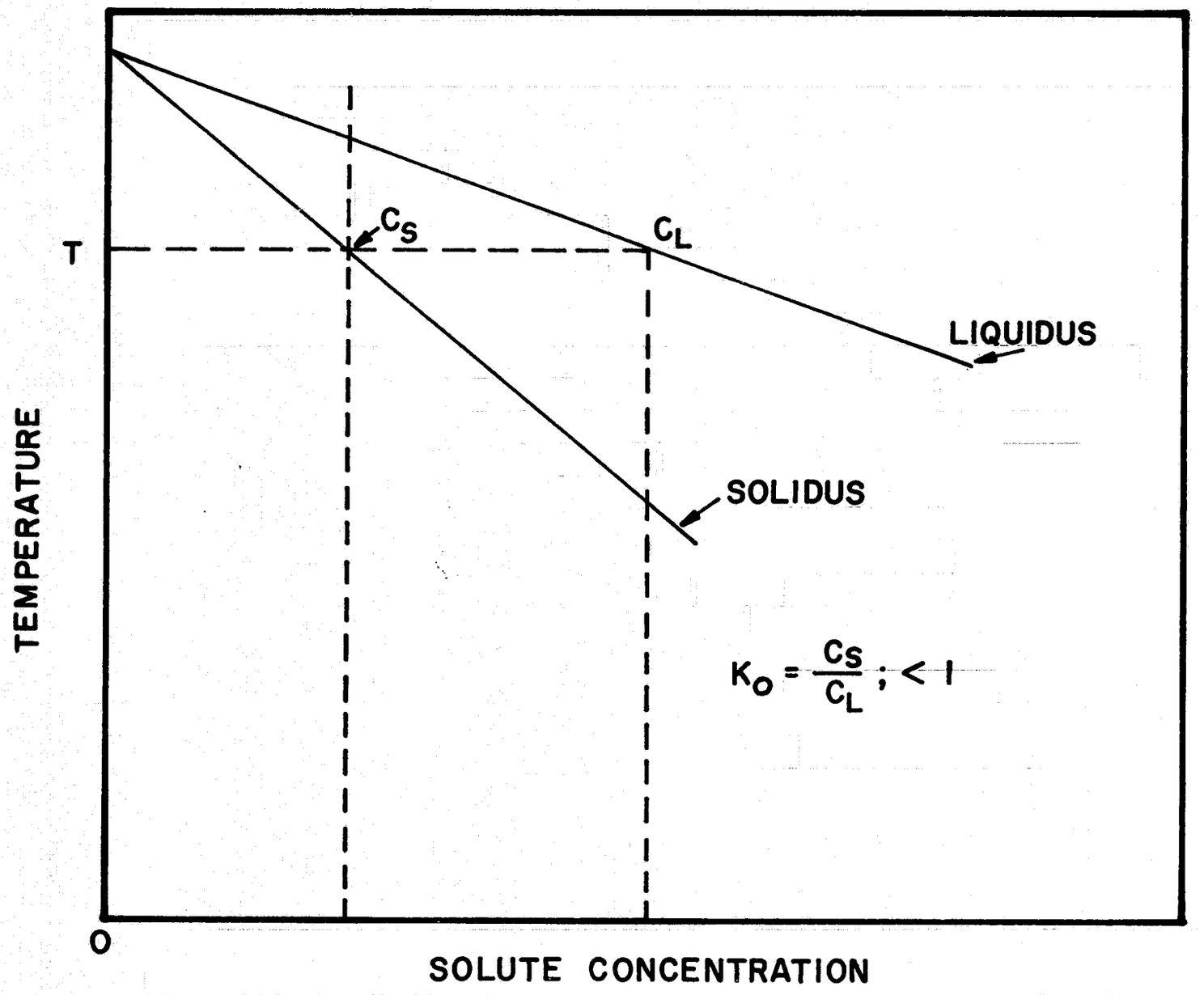


fig. 6 A SCHEMATIC TEMPERATURE - CONCENTRATION DIAGRAM

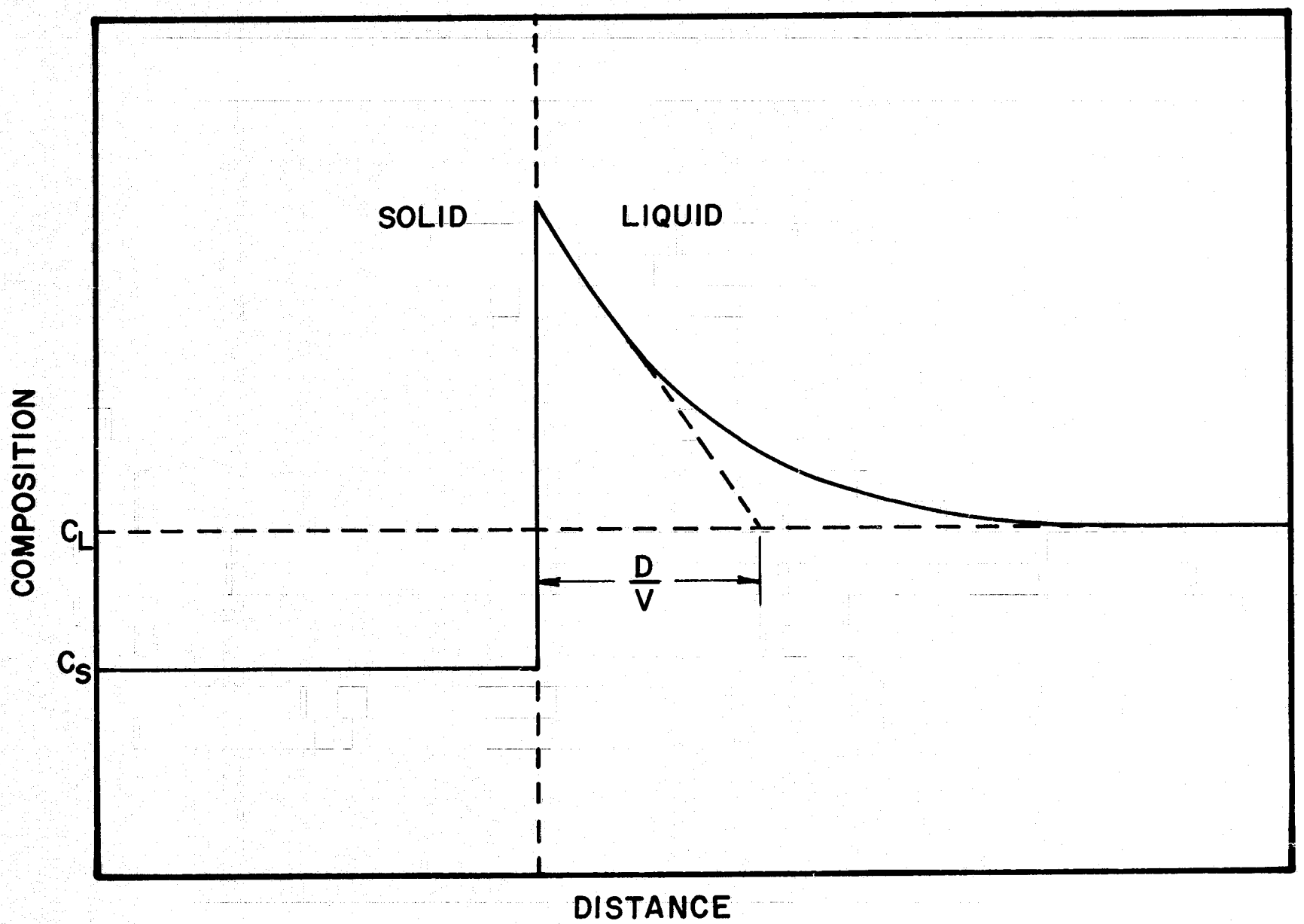


fig. 7 THE DIFFUSION BOUNDARY LAYER AHEAD OF A GROWTH FRONT

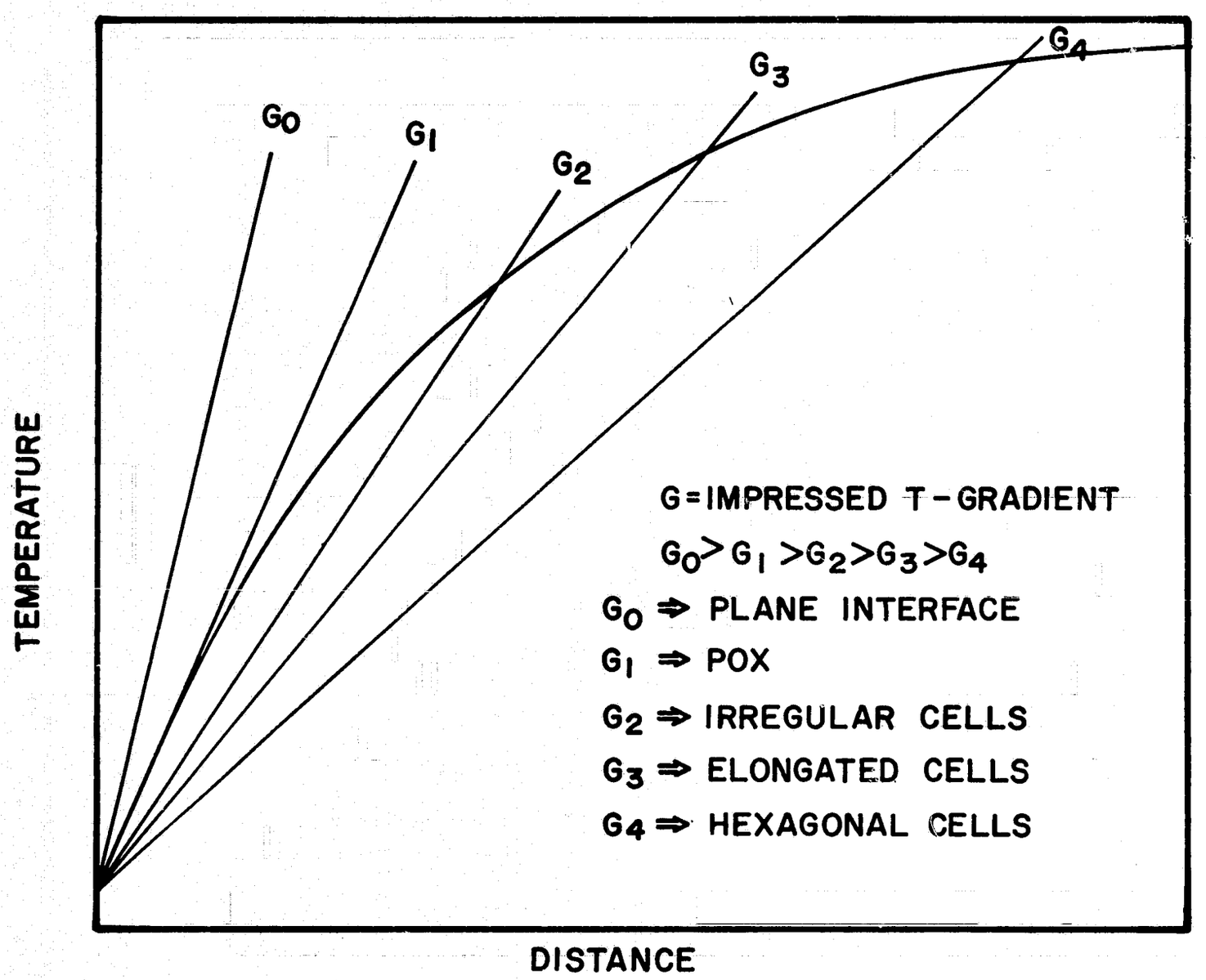


fig. 8 CONSTITUTIONAL SUPERCOOLING

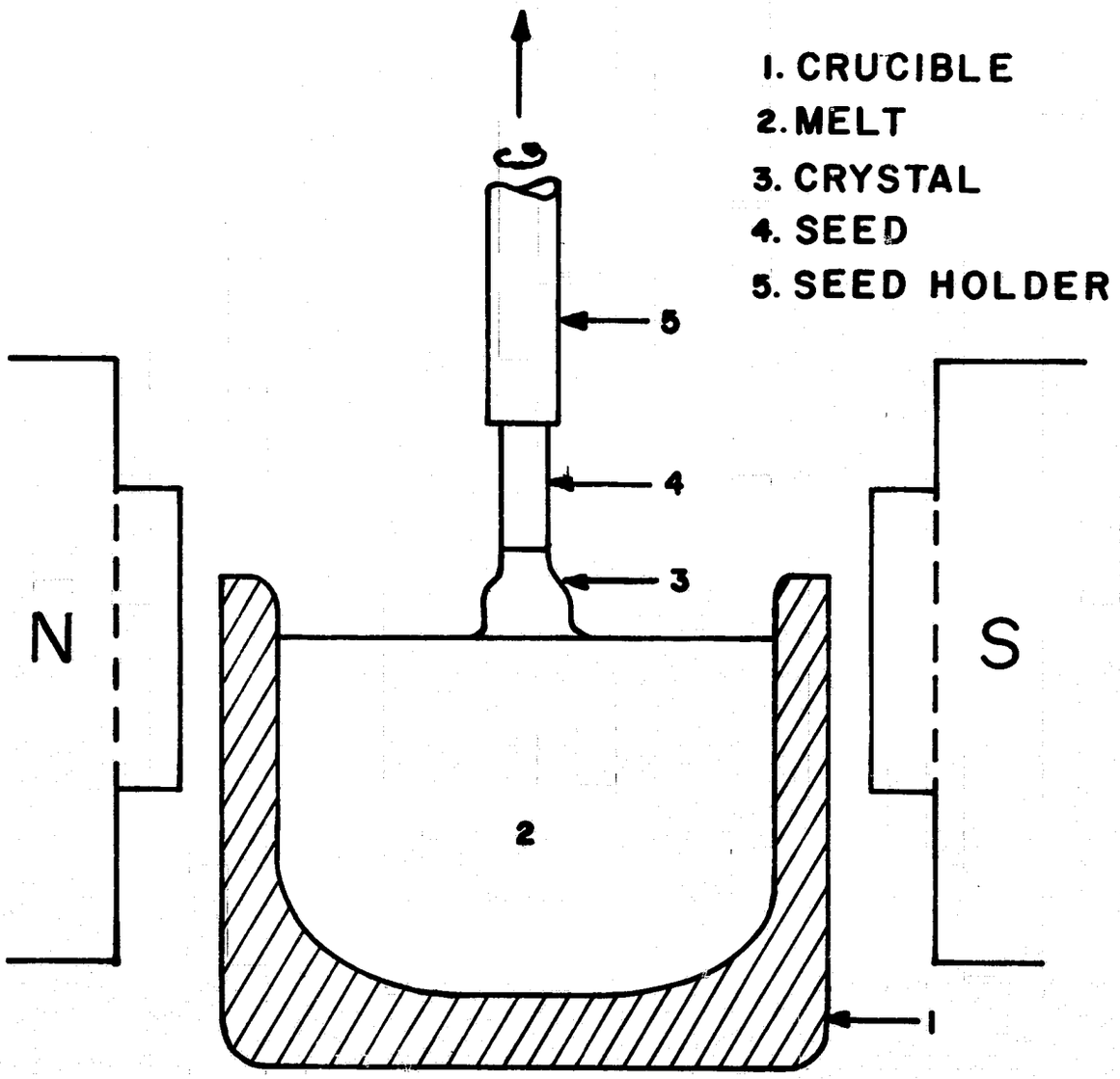


fig. 9. CRYSTAL GROWTH UNDER VARIOUS G-FIELDS

TABLE I. CANDIDATE SPACE PROCESSING MATERIALS

MATERIAL	MELTING POINT	CRYSTAL GROWTH TECHNIQUE	APPLICATIONS
Orthoferrite $TbFeO_3$	850°C	Flux Growth Hydrothermal	Memory Cores
Barium Sodium Niobate $Ba_2NaNb_5O_{15}$	~1500°C	Czochralski	SHG, Pyroelectric, and Memory
Linobate $LiNbO_3$	1260 ± 10°C Congruent Melting	Czochralski, Bridgeman, LiF—Flux	Electro-optic material, Piezoelectrics, acousto-optic modulators, transducers
Gallium Arsenide	1238°C (High as Vapor)	Czochralski, Bridgeman Horizontal Boat	Semiconductor devices, Laser, microwave devices
YIG $Y_3Fe_5O_{12}$	1560°C Incongruent Melting	Czochralski, Flux	Transducers, Laser Components
V_3Si	1950°C Congruent	Float Zone Melting	High Tc Superconductors
Organic Superconductors	------	------	Possibility of Room Temperature Superconductivity
Chlorpromazine	57°C	Zone-Refining	Tranquilizer

AN ANALYTICAL EXPERIMENTAL STUDY OF POSSIBLE EFFECTS OF GRAVITY ON CRYSTAL WHISKERS

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N70-20543

ABSTRACT

This paper reports on the progress of analytical and experimental efforts to determine if a 1-g environment has any effect on whisker growth. It is found analytically that the best quality whiskers are the ones most likely to be destroyed by gravity. A centrifuge experiment is set up to check this idea experimentally. The centrifuge is also being used to measure directly the effect of increased gravity on crystal growth by vapor deposition where convection is important.

I. INTRODUCTION AND BACKGROUND

The purpose of this investigation is to determine whether or not whisker growth is significantly improved in an earth orbit. This is part of a larger effort to study manufacturing in space. The scope is limited to whiskers to assure a complete and intensive investigation.

Whiskers are high strength, filamentary single crystals. They are of interest mainly because of their high tensile strength which approaches the theoretical limiting strength of a material as shown in Figure 1. Bulk crystal tensile strength is from two to three orders of magnitude below the predicted theoretical value. As the crystals cross section area becomes smaller in the neighborhood of 1 micron^2, the tensile strength increases by about a factor of 100. The smaller the area the greater the tensile strength with the tensile strength being roughly inversely proportional to the diameter.

So far, technology has been unable to fully utilize the high strength potential of whiskers. See Figure 2. This is partly because no rapid mass production method of growing good quality whiskers is available in an earth environment. Whiskers now available are either too short, have multiple branches, or are too scarce to be used in the reinforcement of high strength composites. In a zero-gravity space environment whiskers should grow longer, thinner, and stronger.

Whiskers used to strengthen composits should have a high aspect ratio. The aspect ratio is the ratio of whisker length to the thickness (or diameter). The long thin whiskers have more surface area per unit whisker tension, thus they do not pull free from the plastic matrix when the composite is under tension.

II. WHISKER DESTRUCTION DUE TO GRAVITY

Whiskers may be destroyed by a gravity-field as they grow. In this section we are not interested in the atomic growth process, but in preserving the whisker from mechanical destruction as it grows.

The thinnest whiskers have the highest aspect ratios and tensile strengths. However, the full potential of these small fibers has not been realized because they are not rigid enough to support their own weight so they fall due to gravity to a nearby surface where they adhere. This surface force is quite strong, and using a microscope, the whiskers may be seen sticking to the surface like adhesive tape as it is pealed from the surface. This adhesion stops the growth process. Just how long and thin must a whisker be before it bends under a lg force and is captured by an even stronger adhesive force.

The gravitational effect on a long thin whisker may be analyzed using the

equation for the deflection of a horizontal cantilever beam as shown in Figure 3.

$$d = \frac{WL^4}{8EJ} \qquad (1)$$

W is the weight per unit length of the whisker, L is the length, E is Young's modules and J is the area movement about the neutral axis. $J = \frac{bh^3}{12}$ for a rectangular cross section of thickness h, and width b.

For tin the following equations:

$$d = 2.3 \times 10^{-8} \frac{L^4}{h^2}$$

or

$$\frac{d}{L} = 2.3 \times 10^{-10} \frac{L^3}{h^2} \qquad (2)$$

result from using $E = 4.5 \times 10^{11}$ dynes/cm^2
$= 7.1$ gr/cm^3
$g = 980 \frac{cm}{sec^2}$

Lets say that if a whisker deflects 20% of its length that it is endangered. Letting $d/L = 0.2$ in the above equation, we have:

$$L_{max} = 216\, h^{2/3} \qquad (3)$$

L max represents the maximum length that a horizontal tin whisker of thickness h may have without being deflected by more than 20% of its length.

Figure 4 shows L max as a function of h. Whiskers having L and h coordinates falling in region 3 are not affected by gravity. If the L and h coordinates fall in region 1, the aspect ratio is greater than 1000; and the whisker has good bonding properties in a matrix. However, there are no coordinates common to both regions 1 and 3 indicating that all whiskers having desirable aspect ratios are endangered by gravity.

In compression induced whisker growth, experimentors have found that thick whiskers have a terminal length which is much less than the terminal length of thin whiskers. Just how far does this tendency go? We have pointed out that the thinner whiskers are usually destroyed by a gravity-field so we really do not know. Possibly the length would increase several

orders of magnitude as the diameter decreases. That is, 1μ thick whiskers which now are limited to a length of 1 mm may become as long as 100 mm if their thickness is reduced to 0.1μ.

Are there any flaws in this cantilever beam model used here? First the g-field might not be perpendicular to the whisker and the deflection-length ratio of 0.2 is rather arbitrary. However, the whiskers always break off at the base indicating that the base is the weakest point. This suggests that gravity is even more important than predicted by the uniform beam model.

The whisker base is most important in supporting the whisker. In a recent article Gabor and Blocher[1] show a picture of iron whiskers growing using an electron microscope which we show in Figure 5. Note that the base of the whisker is several times thinner than the rest of the whisker. This could easily reduce the rigidity of the whisker by a factor of 100 since the deflection of the cantilever beam in Equation 1 is inversely proportional to h^3.

Has anyone ever seen a whisker fall under the influence of gravity? Hock and Neumann[2] reported in 1954 that whiskers often disappear suddenly presumably having broken off at the root. This may have been due to gravity.

In our lab, whiskers of Ca and Tl have been observed lying flat on the substrate surface, probably due to gravity or vibration since they were sealed under vacuum away from air currents.

Experiments are underway in our lab to systematically increase the effective value of g and note its effect on whiskers of various lengths.

III. THE EFFECT OF ZERO-G ON WHISKERS GROWN BY VAPOR DEPOSITION

Conceivably a gravitational field could affect the atomic whisker growth mechanism. This would be much more likely in the vapor deposition growths which involve the gaseous states. In the vapor deposition process, a source material is slowly vaporized in the hot portion of the furnace and as the vapor moves to the cool region it becomes supersaturated and condenses metal atoms to make a solid which often grows in whisker form. This is done in an inert atmosphere as shown in Figure 6. The diffusion should be very slow; however, in a temperature gradient, convection currents are set up which add to the diffusion in transporting the atoms to the lattice. These circulating currents (due to gravity) are probably

unstable, thus they have an adverse effect on whisker growth. That is, an excess of supercooling could result in massive nucleation which produces polycrystals instead of a single crystal. The convection is due to warm and cool gas having a different density in the presence of a gravitational field. So at zero-gravity, convection is removed and diffusion will produce a more uniform vapor for better crystal growth.

An experiment is underway to test indirectly the above hypothesis. If 1-g produces an adverse effect on whisker growth, then 2-g should produce an even more adverse effect, etc. By applying several g's of acceleration to the whiskers during the growth by vapor deposition and by comparing this growth to 1-g growth, one would then predict the effects of 0-g.

Vapor deposition growth is suited to materials having a high vapor pressure at their melting point. Cadmium with a m.p. = 321°C and a vapor pressure .1 mm (at m.p.) could be used.

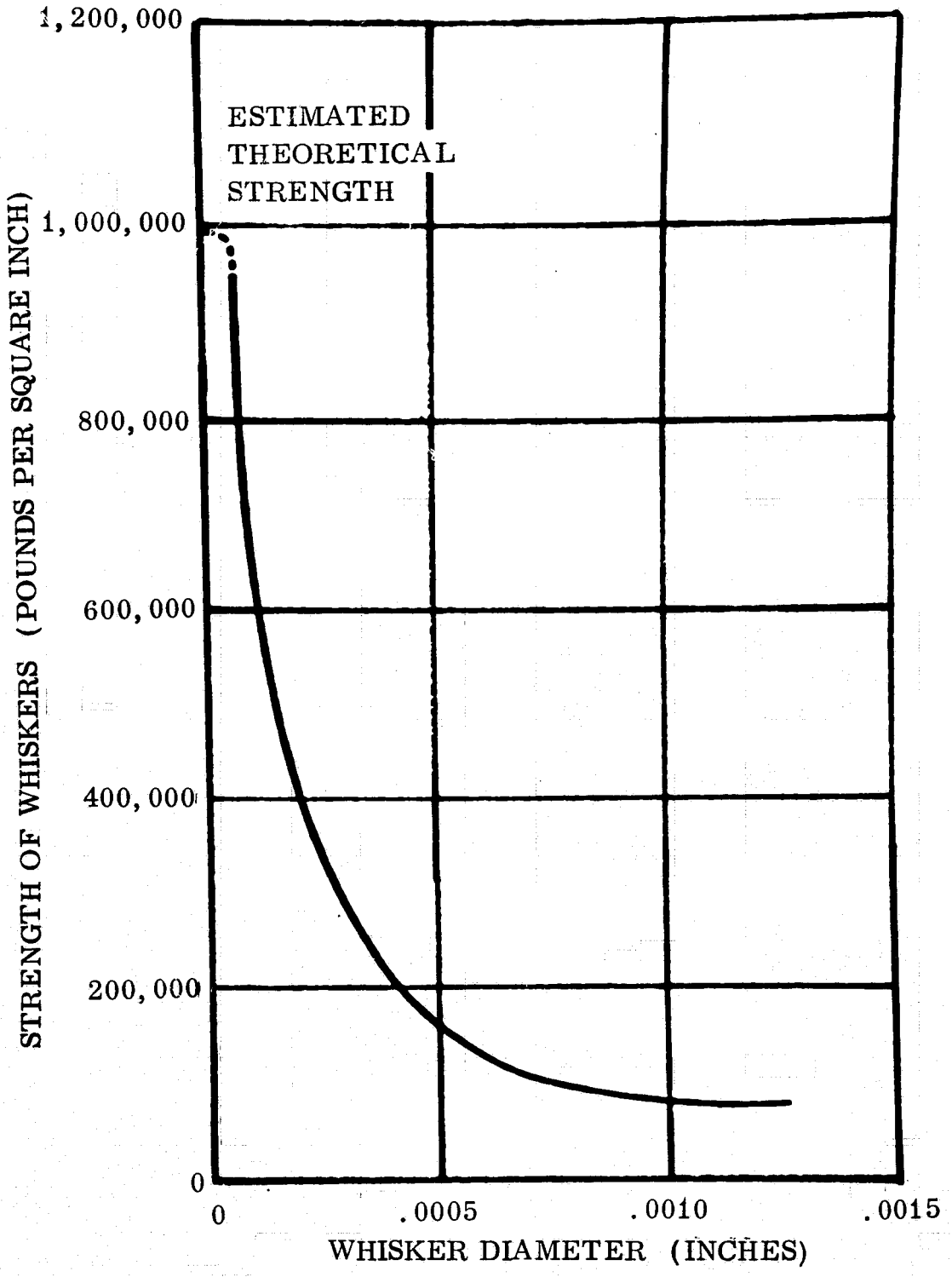
A source material cadmium is placed in the warmest portion of a furnace as shown in Figure 6. The Cd. slowly vaporizes and condenses in the cooler regions of the furnace. If the temperature gradient along the furnace is carefully controlled, the vapor will condense in the form of single crystal whiskers.

The experimental arrangement is shown in Figure 7. The gradient furnace is placed on a 1 m arm in the 0-75 G centrifuge. The centrifuge is equipped with an optics system, slip rings and gas lines, to monitor and control the furnace during crystal growth. A growth requires about 12 hours.

REFERENCES

1. Thomas Gabor and John M. Blocher, Jr., Journal of Applied Physics vol. 40, No. 7, p. 2696, 1969.

2. F. Hock and K. Neumann, Zeits f. Phy. Chem., 2, p. 241 (1954).



Whisker strength is a function of whisker diameter and drops sharply within the first .0005 inch, slowly decreasing with further increases in diameter. The curve shown represents the relationship of strength to diameter in one type of iron whisker. From S. S. Brenner. Scientific American, Vol. 203, No. 7, p. 65.

FIGURE 1

Reason for Whisker Study

1. Whiskers are the strongest materials known to man

2. Whiskers are the most nearly perfect crystals

Present Problems With Whiskers

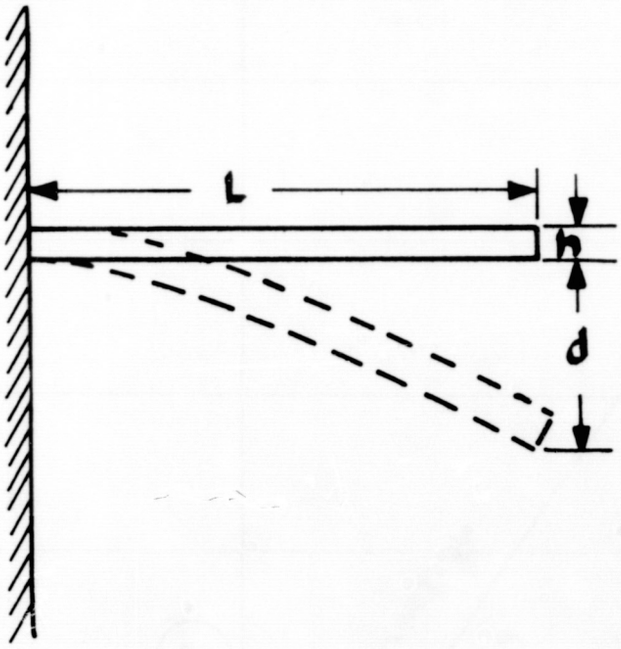
1. Too Short

2. Growth too slow

3. Technology has thus far been unable to build strong structures from whisker fibers.

FIGURE 2

CANTILEVER WHISKER
BEAM BENDING DUE TO GRAVITY



$$d = \frac{wL^4}{8EJ} \qquad J = \frac{bh^3}{12}$$

Where

W = Weight per unit length

L = Length

h = Vertical thickness

E = Young's Modulus = 4.5×10^{11} dynes/cm^2

J = Area Moment about neutral axis

b = Whisker thickness

$$.2 = \frac{d}{L} = \frac{wL^2}{8EJ} = 2.3 \times 10^{-10} \frac{L^3}{h^2}$$

$$L_{MAX} = 216\, h^{2/3}$$

Good Aspect Ratio is L/h = 1000

FIGURE 3

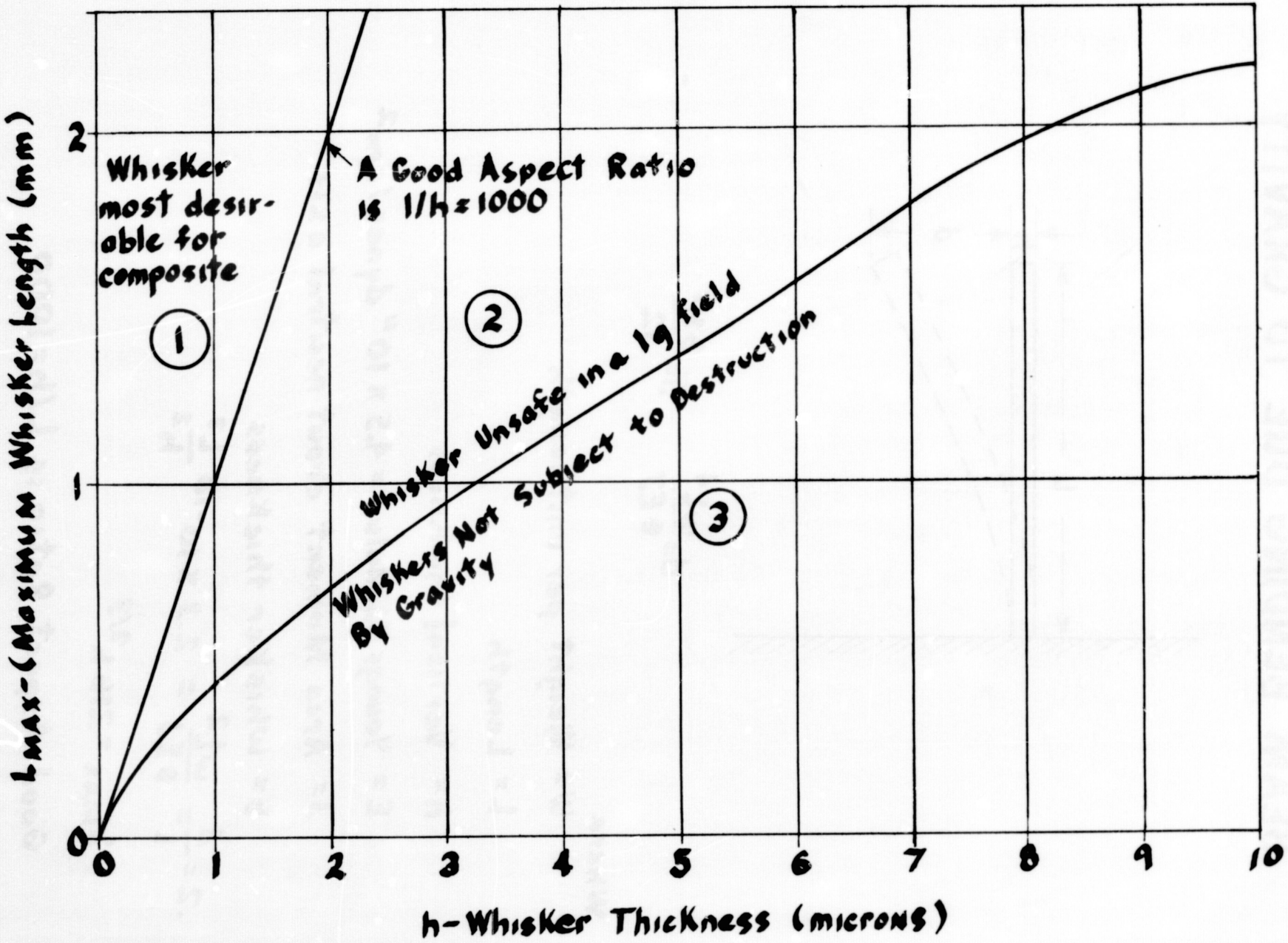
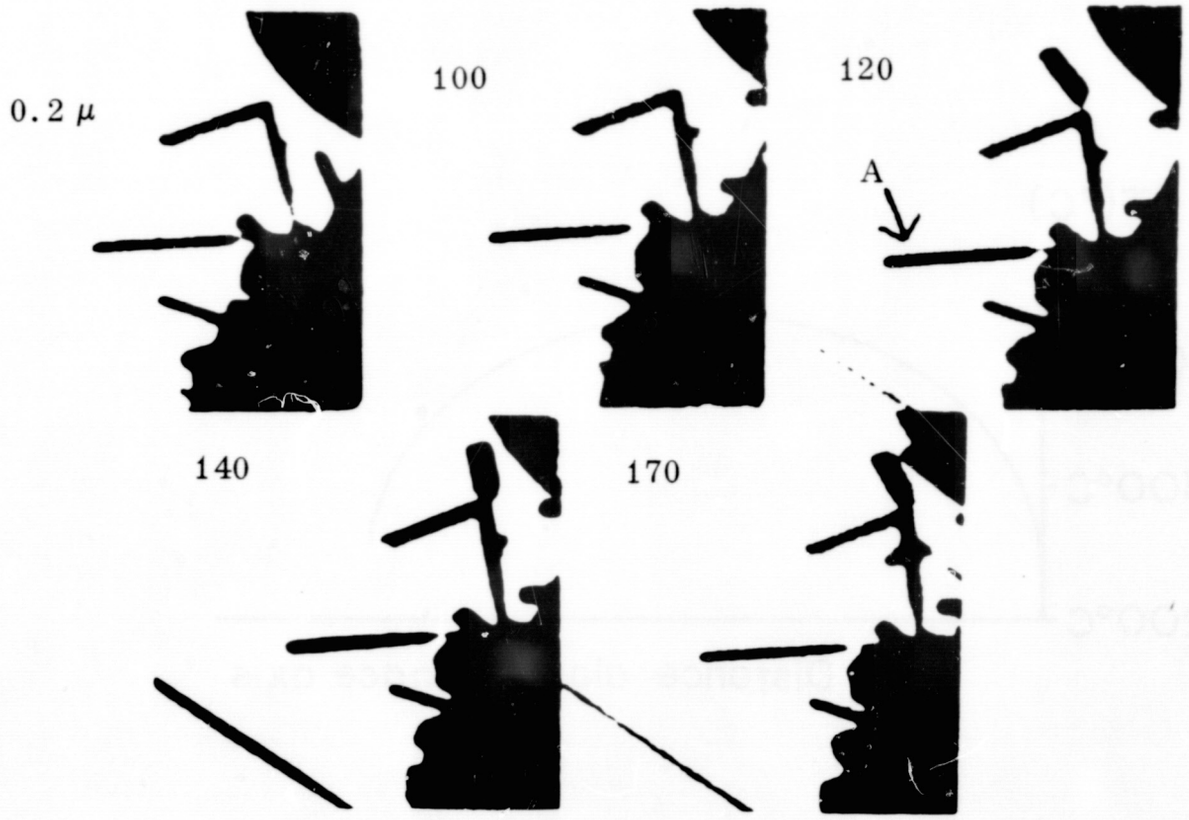

Lmax-(Maximum Whisker Length (mm)
h-Whisker Thickness (microns)
Whisker most desirable for composite
A Good Aspect Ratio is l/h = 1000
Whisker Unsafe in a 1g field
Whiskers Not Subject to Destruction By Gravity
1
2
3
0
1
2
3
4
5
6
7
8
9
10

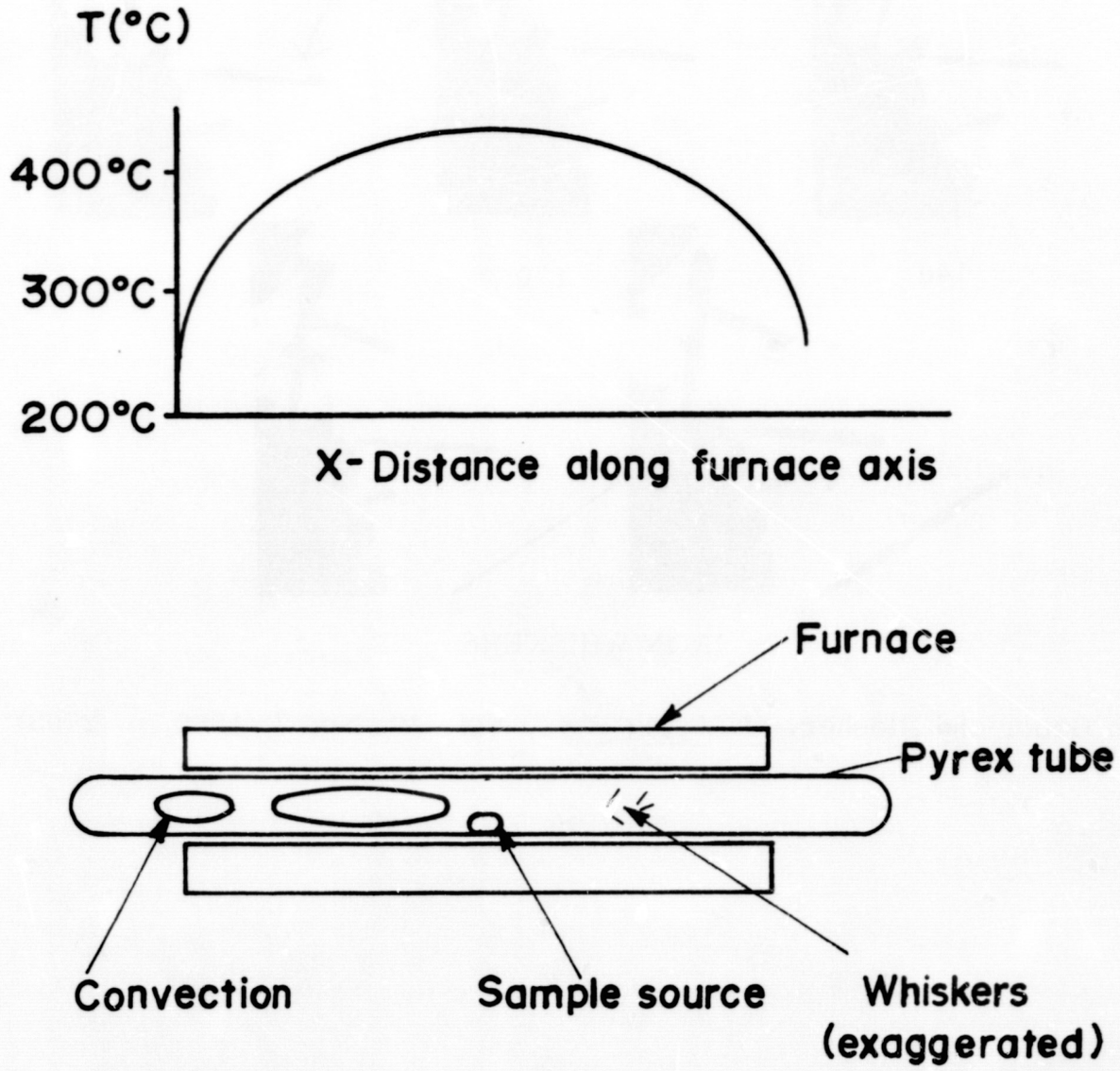
FIGURE 4



IRON WHISKERS

From Gabor and Blocher. J. Appl. Phy., Vol. 40, No. 7, 1969, p. 2703.

FIGURE 5



THE VAPOR DEPOSITION METHOD OF WHISKER GROWTH.

FIGURE 6

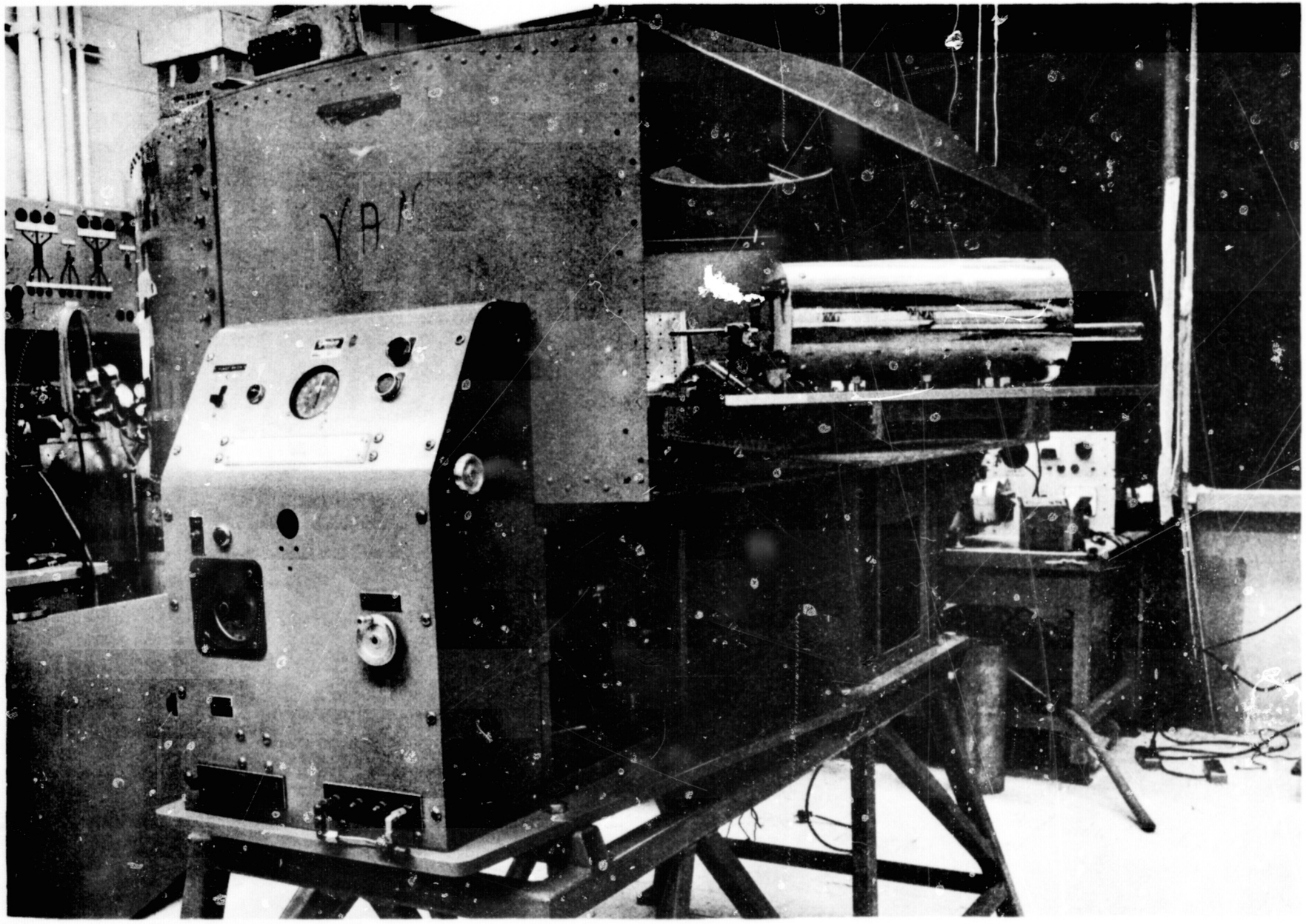


FIGURE 7

N70-30244

GRAVITY-DRIVEN AND SURFACE TENSION-DRIVEN CONVECTION IN SINGLE CRYSTAL GROWTH

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ABSTRACT

Analytical and mathematical studies of the floating-zone and the Czochralski techniques of growing single crystals are being conducted. The objective of these studies is to elucidate the role of convection in single crystal growth. Gravity-driven and surface tension-driven convection and possible couplings between these two convective modes will eventually be incorporated into the analyses. The analyses are expected to provide a basis for predicting the effects of a zero-gravity environment on crystal growth.

INTRODUCTION

The possibility has been suggested that single crystals of unprecedented perfection can be grown in a zero-g environment. One of the main advantages of a zero-g environment foreseen for achieving such a result is that gravity-driven convection is eliminated (Ref. 1). Gravity, however, is not the only driving force for the transfer of mass. Liquid-vapor surface tension (and, possibly, solid-liquid interfacial tensions) also is a potential driving force for fluid motion. A definite conclusion regarding the benefits of eliminating gravity-driven convection, therefore, requires that two questions be considered further:

- In what manner does convection affect crystal growth and thereby influence crystal perfection?
- What extent of convection is likely to be encountered under various g conditions?

Before these questions are explored further, the crystal-growing techniques to which the present study is limited should be defined; i.e., the floating-zone and the Czochralski technique. The floating-zone technique or some variant of it is foreseen as being the technique most directly adaptable to zero-g environment and was therefore chosen for study. The Czochralski technique is also being studied because high quality semiconductors are now routinely produced by this technique. Crystals produced by the technique are thus readily available to check theoretical predictions and to provide standards with which crystals produced by other techniques can be compared. Also, in common with the floating-zone technique, the Czochralski technique involves no mechanical restraint on the periphery of the growing crystal. Some features of crystals produced by either of these two methods, therefore, will be comparable.

The salient features of the floating-zone technique are illustrated in Fig. 1. A molten band or zone is produced in a rod of polycrystalline material. The method of heating may be radiant, induction, or electron-beam bombardment, depending upon the physical characteristics of the particular material being processed. The molten zone is caused to pass along the rod, by moving the heat source, with melting occurring at one interface and freezing at the other. By introducing a properly oriented seed at the freezing interface and controlling the rate of zone travel, single crystal growth can be accomplished. The main advantage of the technique is that crucible-melt contact is avoided thereby eliminating a potential source of contamination. Under 1-g condition, however, the size of the molten zone is limited by the need for surface tension to balance the hydrostatic pressure of the liquid. Also, a limiting factor is the tendency of surface tension to reduce the liquid surface area. A long thin molten zone would show a tendency to separate.

The essential features of the Czochralski technique are shown in Fig. 2. Material melt is contained in a heated crucible. A seed crystal is brought into contact with the melt surface. After wetting is completed, the seed is slowly withdrawn. The diameter of the pulled crystal is controlled by controlling the temperature of the melt and the rate of crystal pulling. Also, the crystal is rotated as it is withdrawn to eliminate thermal asymmetry. The melt may also be rotated for greater control of the thermal conditions.

CONVECTION AND CRYSTAL PERFECTION

Consider again the question of the relationship between convection and crystalline perfection. Convection may affect crystal growth processes indirectly by altering the temperature and concentration field throughout the fluid phase. Because both convection and solidification mechanisms, however, depend directly on local temperature and concentration conditions, convection and solidification are seen to be dependent processes. In fact, they may be said to be coupled processes. Each is a response

to imposed variations of a variety of possible independent parameters among which gravity must be numbered. The degree and manner of occurrence of either or both processes is thus interrelated. For example, the occurrence of compositional cells which have their origin in constitutional supercooling depends on the temperature gradient in the liquid phase (Ref. 2). The steeper the gradient, the less likely the occurrence of compositional cells. The steeper the external temperature gradient, however, the more likely that convection will result. The internal temperature gradient near the solid-liquid interface therefore may be reduced. The presence of a moving solid-liquid interface which is liberating heat, in turn influences the convective field.

Incidentally, the appearance of the various interface morphologies as a function of the liquid temperature gradient near the solid-liquid interface is shown in Fig. 3. The morphology changes from a planar to a cellular configuration as the temperature gradient decreases and the degree of constitutional supercooling increases (Ref. 3). The appearance of the cells attributed to constitutional supercooling is quite similar to the appearance of convection cells produced in thin layers of liquids. This is discussed later.

Another consideration in connection with the influence of convection on crystal perfection is the scale of fluid motion. This may be classified as macroscopic or microscopic. Both can affect crystal growth processes. To illustrate how macroscopic flows exert an influence on subsequent crystal perfection: the solid-liquid interface shape of a growing crystal is an important parameter of dislocation densities. This is because of the relationship between the shape of the interface to the thermal conditions of growth and the associated thermal stresses.

Figure 4 shows the temperature isotherms associated with a concave (to the liquid) interface shape. Near the solid-liquid interface, the temperature at the outer surface of the solid is lower than the temperature near the center. Thermal contraction, therefore, causes the outer surface to exert a compressive stress on the core of the crystal while the surface itself is in a state of tension (Ref. 4). If the solid-liquid interface is convex to the melt, the inner core will be in tension and the outer in compression. When the stress σ exceeds the yield stress σ_y, plastic flow will occur which will relieve itself into dislocations. Convection can be expected to exert a significant effect on the macroscopic interface shape profiles. Figure 5 indicates the result of convection on the macroscopic interface shape during a horizontal zone melting of an organic compound.

On a microscopic scale, convection is probably the cause of many puzzling crystalline imperfections. For example, temperature fluctuations having their origin in turbulent convection can result in fluctuations of crystal growth rate. Because the concentration of solute incorporated

into a solid is a function of the growth rate, the result of growth rate fluctuations is banding of solute in the solid (Ref. 6). Local segregation of solute on a microscopic scale can also lead to the introduction of dislocation lines at the bounding surfaces of the segregate (Ref. 7).

Although convection is recognized as being a possible cause of microscopic crystalline imperfections, the type or mode and scale of convection leading to these imperfections is just beginning to be investigated. The preceding discussion is a brief general indication of how convection can affect the perfection of single crystal growth from melt. Some possible modes and the extent of convection under varying gravity fields are now discussed.

GRAVITY AND SURFACE TENSION-DRIVEN CONVECTION

As indicated in the opening paragraphs, gravity is not the only possible motive force for fluid motion. Surface tension (and possibly solid-liquid interfacial tension) and the volume change which occurs on crystallization are also possibilities. In the present study the latter type of convection is not being considered. For the case of crystal growth by the floating-zone technique in which large temperature and concentration gradients at a free liquid surface are certainly present, considerable convection, which has surface tension as its driving force, can be expected. Fluid flow caused by surface tension gradients is called the Marangoni effect. (Several excellent general reviews of surface tension flows are given in Ref. 8.) If a free liquid surface experiences a temperature or concentration gradient, a surface tension gradient will result because surface tension is a function of temperature and concentration. Along the surface the liquid will flow from the region of low surface tension to one of high surface tension. Usually this will be from hot regions to colder regions because surface tension generally decreases with increase of temperature. The liquid moves the fastest near the surface, the depth of the disturbance depending on a variety of hydrodynamic parameters.

The occurrence of "tear drops" in a wine glass is a common illustration of the Marangoni effect. In this case evaporation of alcohol leaves the layer of liquid on the wetted glass wall with a higher surface tension than in the bulk of the liquid. As a result, liquid on the glass walls continuously draws up more liquid from the bulk until a "tear" is formed. When the "tear" becomes large enough it falls back into the liquid. Another less commonly observed fluid motion which may be classified as microscopic convection also has its origin in surface tension gradient. A cellular motion results if a thin layer of fluid is heated from below and cooled from above. This type of convection flow was first investigated by Bénard in 1900.

Lord Rayleigh developed a theory for cellular convection on the basis of an unstable density gradient. Rayleigh's theory, however, did not

agree with all experimental observation. For example, cellular convection was found in shallow pools cooled from below; a stable situation according to Rayleigh's theory. Also the flow patterns observed in some instances were opposite to those predicted by Rayleigh's theory. Hot liquid was observed rising below centers of depression, whereas hot liquid would be expected to coincide with elevated regions if the flow were gravity driven (see Fig. 6). The discrepancies were resolved when both gravity and surface tension were recognized as possible motive forces for fluid flow. Couplings between surface tension and buoyancy were also recognized as a possibility.

In one analysis of cellular convection (Ref. 9) a stability criterion for surface tension-driven flows based on a dimensionless number B is given. This number known as the Marangoni number expresses the ratio of surface tension to viscous forces and is defined as

$$B = \frac{-\frac{d\sigma}{dT}\frac{dT}{dy}d^2}{\rho \nu \alpha}$$

where dT/dy, ν, α, ρ, and d are vertical temperature gradient, kinematic viscosity, thermal diffusivity, density and thickness of the fluid layer, respectively. The term $d\sigma/dT$ represents the rate of change of surface tension with temperature.

For gravity-driven cellular convection the stability criterion is based on the Rayleigh number, which is given by

$$R = \frac{g\beta\frac{dT}{dy}d^4}{\nu \alpha}$$

where g is the acceleration due to gravity and β the coefficient of expansion.

In both cases, the onset of convection occurs when a certain critical value of the dimensionless number occurs. A criterion of instability when the coupling, under maximum reinforcement, between the two agencies is taken into account is given by

$$\frac{R}{R_c} + \frac{B}{B_c} \geq 1$$

where R_c and B_c represent the critical values. In general, R and B reinforce each other in such a manner that cellular convection may occur at a Rayleigh number R and a Marangoni number B smaller than their corresponding critical values, R_c and B_c.

The similarity between the appearance of Bénard cells and the hexagonal cells attributed to constitutional supercooling (see Fig. 7) is considered in a recent paper (Ref. 10). In this paper certain impurity patterns found in thin alkali halide crystals grown from the melt is attributed to segregation induced by microscale cellular convection.

Mention of various less familiar types of convection is found in the literature. Among these are flows caused by liquid-liquid interfacial tension gradients. Interestingly, a cellular interfacial convection structure was found to accompany the extraction of acetic acid out of ethylene glycol with ethyl acetate (Ref. 11). The suggestion is forwarded that interfacial tension-driven flows may also be important at solid-liquid interfaces (Ref. 12). Thermosolutal convection results in certain situations. In this type of convection the solute concentration varies vertically in a gravity field. The result is a layering of convection regions. The origin for this type of convection lies in the differing rates at which heat and solute diffuse (Ref. 13). Also of pertinence to the present study are the kinds of convective instabilities that occur. These include an oscillatory regime called overstability and a stationary regime called convective instability (Ref. 8b).

PRESENT INVESTIGATION OF CONVECTION

The present investigation is a natural outgrowth of an investigation of solid-liquid phase change for spacecraft thermal control (Refs. 14 and 15). Both studies contain common problem areas. For example, in both studies a means is needed to predict quantitatively the solidification velocities under zero-g conditions. In the present study, the zero-g condition will be first assumed to be approximated by considering conduction as the only mode of heat transfer. With this assumption, a zone crystal growth of a pure, one-component material is being mathematically modeled. The model being developed will predict melted zone length and solid-liquid interface shapes as a function of rod diameter, material, heater travel rate, and heater power output. The development of a model for a two-component melt will also be undertaken. The models will be experimentally checked with materials whose melts are transparent. The length of the melted zone and interface shapes will thus be readily viewed. The experiments will also investigate the effect of gravity by conducting the zone crystallizations both from the top and from the bottom. That is, the heater will be moved both up and down.

Results of these initial studies are expected to provide a basis for identifying the predominant convective modes as a function of the operating parameters. After this identification is made, the means of describing the convection mathematically will be investigated.

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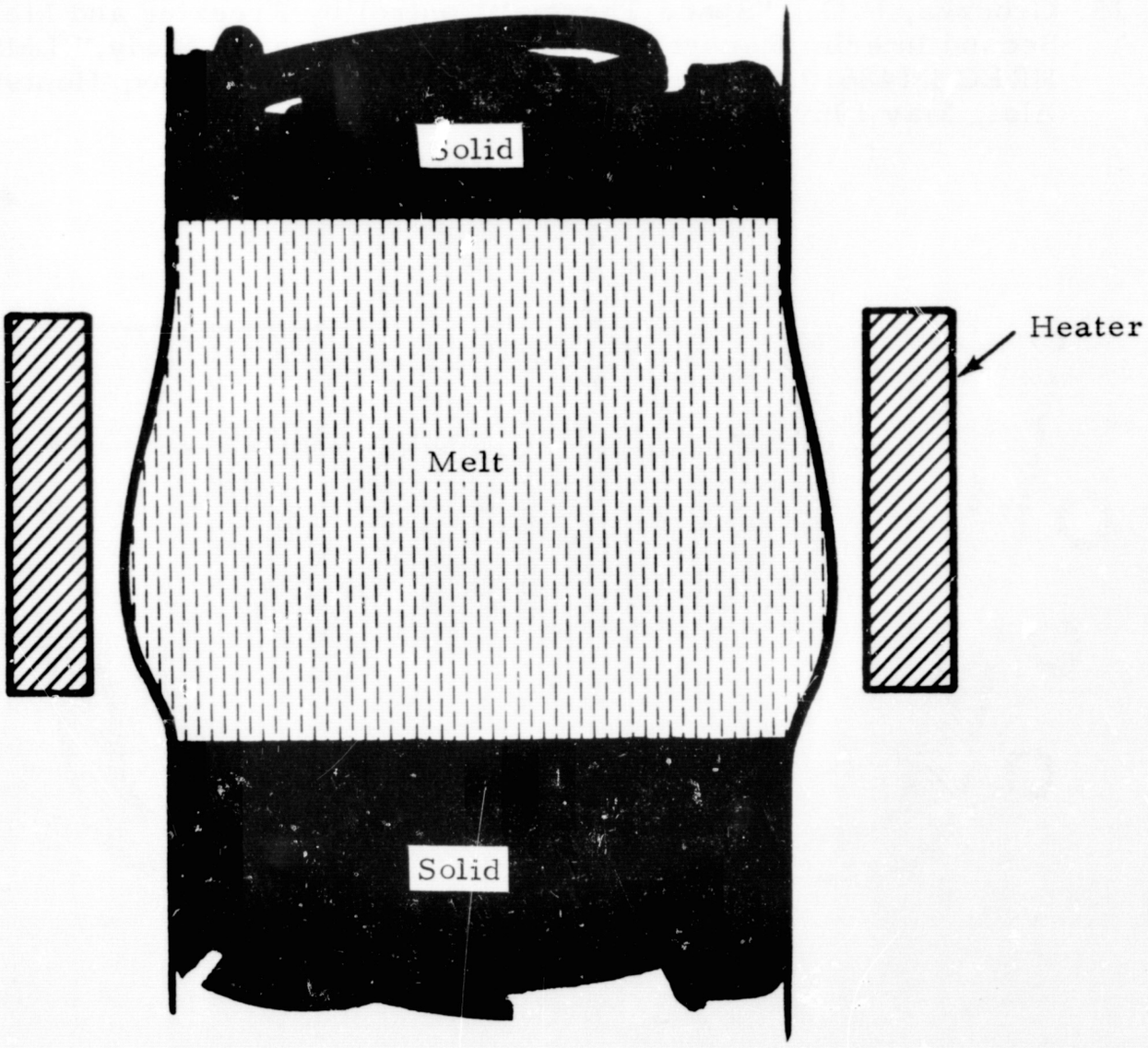


Fig. 1 - Salient Features of a Floating-Zone Crystal Growing Arrangement

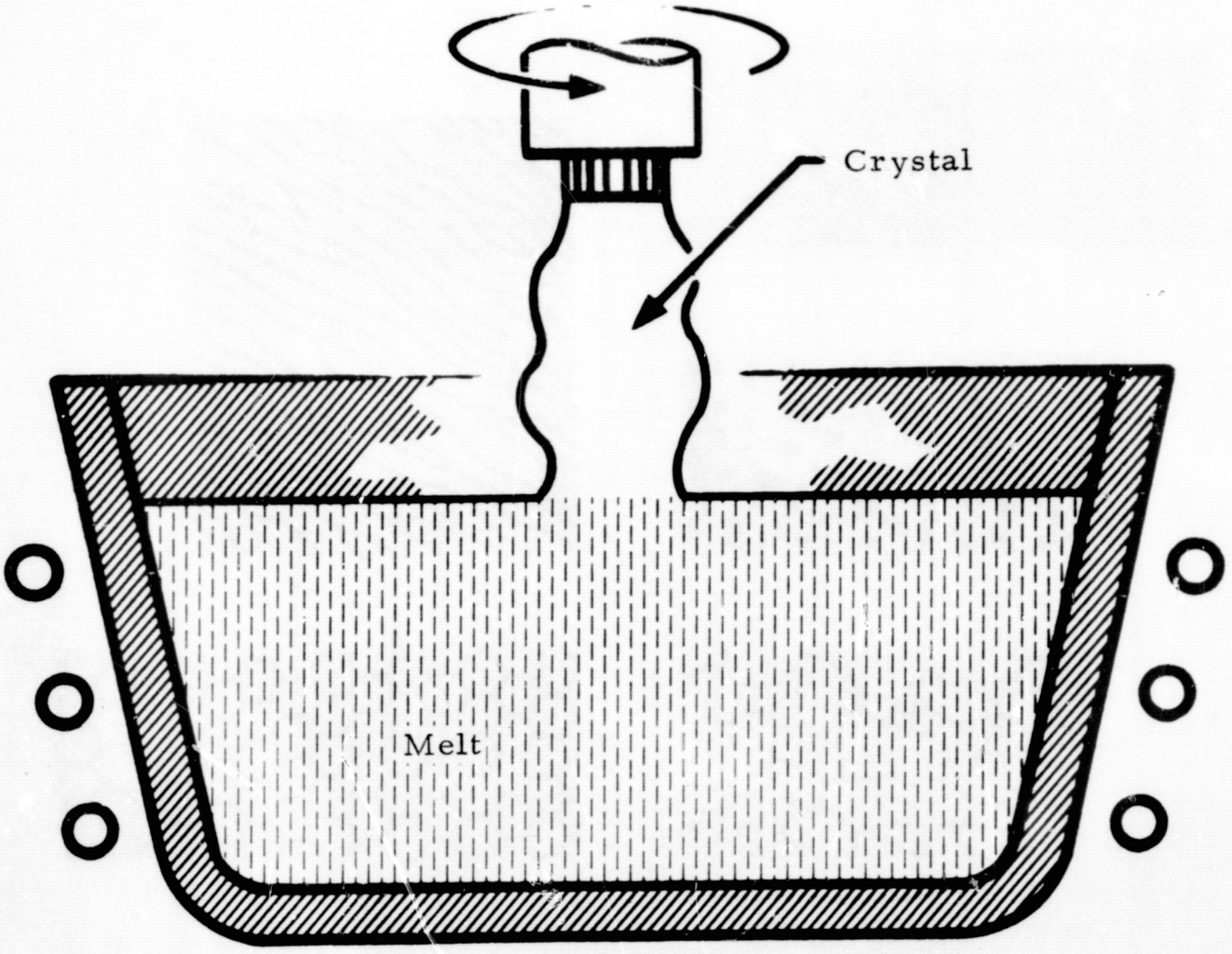


Fig. 2 - Czochralski Crystal-Growing Arrangement

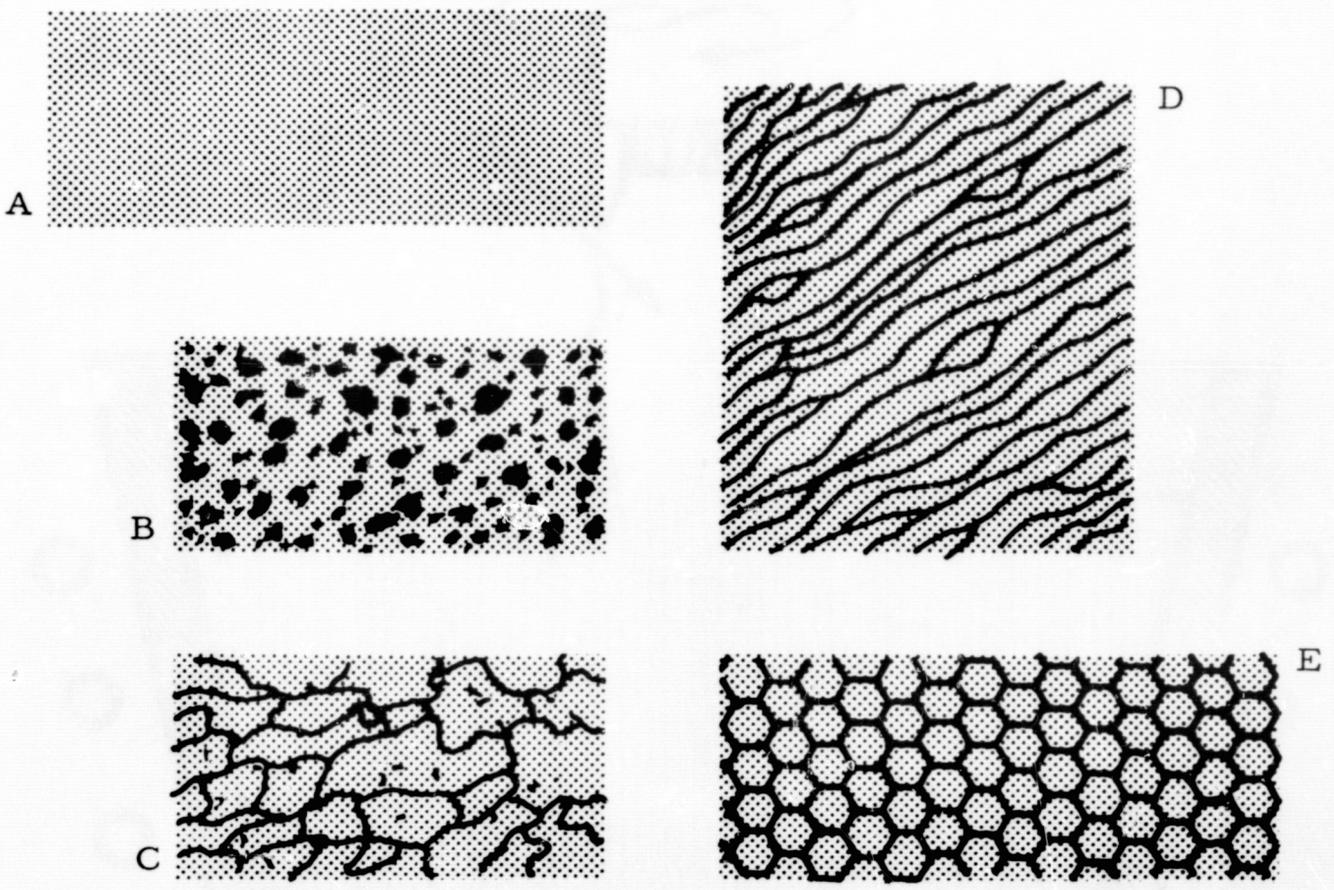


Fig. 3 - Illustration of the Various Morphologies as a Function of Constitutional Supercooling. Supercooling Increases from (A) to (E) (Ref. 3)

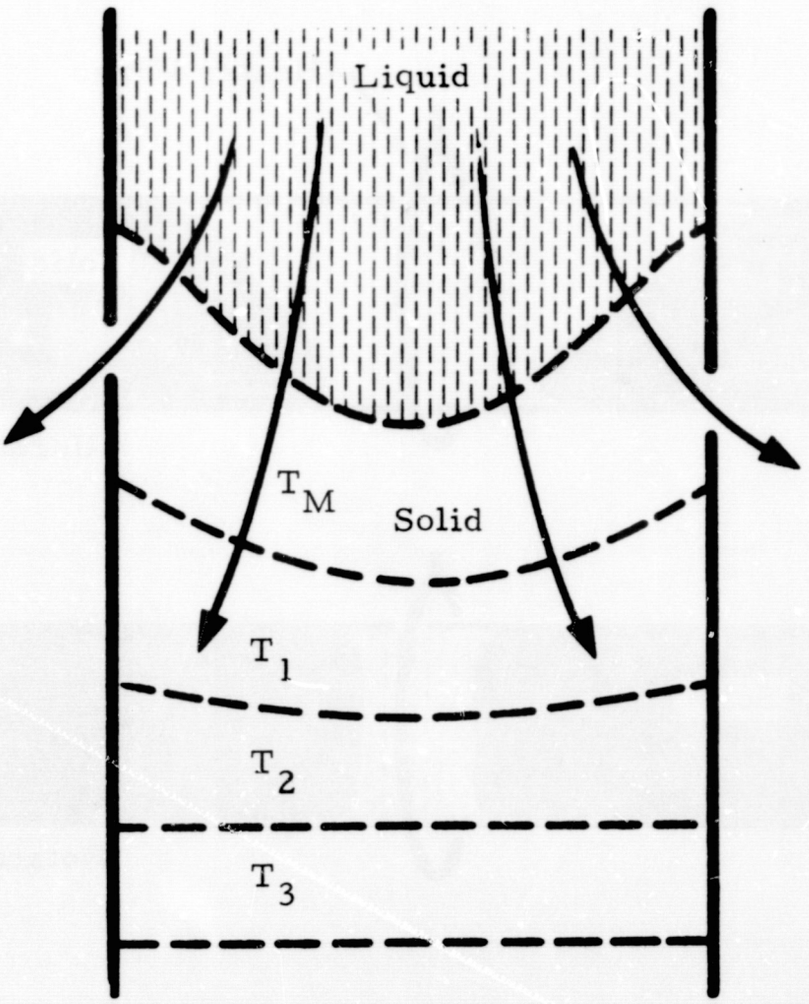


Fig. 4 - Possible Temperature Isotherms in a Crystal During Freezing (Ref. 4)

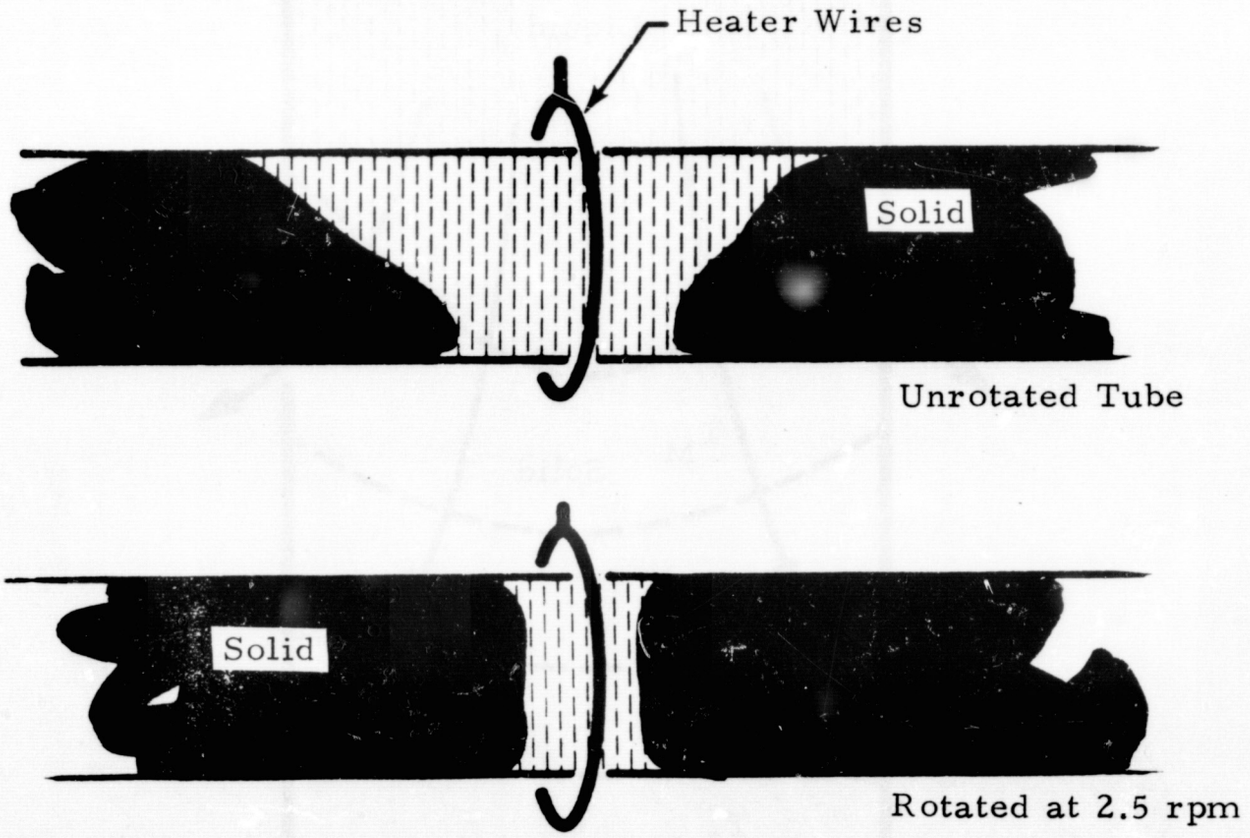


Fig. 5 - Effect of Convection on Solid-Liquid Interface Shapes in Zone-Melting (Ref. 5)



Surface Tension-Driven Cells

Gravity-Driven Cells

Fig. 6 - Fluid Flow Patterns in Bénard and Rayleigh Convection Cells



Hexagonal Cells

Worm-Shape Cells

Fig. 7 - Typical Cell Patterns Caused by Convection (Ref. 10)

N70-20545

THEORETICAL CONSIDERATIONS FOR LIQUID PHASE SINTERING AND SOLIDIFICATION IN THE SPACE ENVIRONMENT

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ABSTRACT

Many types of materials processing experiments planned for operation in the space environment involve crystal growth, metals joining, solidification or sintering. Complete characterization of the liquid-solid interface is essential for analysis of these experiments. The necessary interface condition of wetting is effected by both zero gravity and the composition of the environment. Wetting is achieved by decreasing the solid-liquid interface energy through preferential adsorption of one of the constituents in the liquid on the solid surface and/or by diffusion fluxes. Adsorption of the environmental gases on the solid surface prior to exposure to the liquid phase will decrease the solid-vapor interfacial energy and inhibit the wetting process. Sintering and joining processes involve two steps: First a solid-solid phase and then a liquid-solid phase. Analysis of these processes shows that the first step is dependent on diffusion coefficients, vacancy concentrations in the bulk, surface energy and contact geometry, in addition to time and temperature. The second step is dependent on surface adsorption controlled by crystal faceting, grain boundary grooving, and thermal etching. Knowledge of these specific material properties from laboratory experiments will help to define the specific effects of gravity separated from the effects of the gaseous environment in space.

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I. INTRODUCTION

The zero or negligible gravity condition achieved in a space station (SS) can be used in material processes which simultaneously involve liquid and solid phases. The two phases may tend to separate due to density differences under the influence of gravity but will not tend to separate in space. This fact has been discussed previously in several proposals to do crystal growth, metals joining, casting solidification, or sintering in space. One such process, liquid phase sintering, is discussed in detail here but much of the analysis is applicable to the other processes mentioned above. Liquid phase sintering occurs when a mass of small particles of different compositions is heated above the melting temperature of one of the compositions so that all the particles become bonded into a solid mass on cooling.

Liquid-phase sintering of powder compacts is common not only to metal composites such as iron-copper, but to cermets and ceramic porcelains. In many cases involving the more refractory materials such as carbides and borides, it is only in the presence of a liquid phase that the desired properties can be obtained. The most successful cermets developed to date are undoubtedly the cemented tungsten carbides. Although these possess poor oxidation resistance and high densities, properties which reduce their utility as structural components at elevated temperature, their wide application as cutting tools attests their unique properties of high hardness, strength, and toughness.

As an example some physical properties of selected liquid metals are shown in Table I. The solubility of carbon in these metals is shown because we are planning to demonstrate the effects of density in experiments using spherical carbon particles as the dispersed solid in the liquid metal. For the liquid phases the metal has been chosen. The composites Al-C and Ag-C would be studied to determine the effect of density difference between the liquid and solid phases. It can be seen that liquid Al has a density of 2.37 gm/cm^2 which is very close to that of carbon (2.22 gm/cm^3) while Ag has a density of 10.5 gm/cm^3 in the liquid state which is very much higher than that of carbon. On the other hand liquid Al has a surface energy of 920 $ergs/cm^2$ and liquid Ag of 923 $ergs/cm^2$. Use of these two material systems would demonstrate the effect of density on "liquid phase forming" at constant surface energy.

Before considering the parameters important to the sintering behavior of liquid-solid systems, it should be pointed out that for any sintering to take place, it is first of all necessary for the liquid to be retained within the compact. That is, adequate wetting is a necessary condition for liquid-phase sintering. It is, therefore, necessary

that consideration be given to the wetting phenomena and its relation to liquid-phase sintering under those conditions existing in a space station. In this case, a consideration of zero gravity as the only environment is erroneous. The total environment of SS includes (i) zero gravity, (ii) vacuum of 10^{-5} mmHg and (iii) residual gases. It is apparent that to fully understand the effects of zero gravity in the sintering process, or any other metallurgical process, one must separate those effects due to the inherent vacuum and residual gases since these may affect the degree of wetting obtained. In so doing it may be possible to ascertain the possible approaches for changing a system from a state of nonwetting to wetting. As discussed, density and surface wetting are the important variables in experiments leading to space materials processing. However it is vital that we define the environmental effects which cause variations in the surface wetting. The remainder of this discussion will emphasize the importance of our surface studies.

II. WETTING

Wetting may be discussed by analyzing the behavior of a liquid drop in contact with a solid surface as in Figure 1. The degree of wetting is measured by the contact angle θ . For $\theta > 90°$ a nonwetting condition exists while a wetting condition is described by $\theta < 90°$. The extent of wetting attained in any liquid-solid system is determined by the surface forces that act on the system to give a configuration having the lowest total surface free energy and thus minimizing the total free energy of the system. A vectorial analysis of the horizontal components of the surface forces gives the following expression for the contact angle:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (1)$$

where γ_{SV}, γ_{SL} and γ_{LV} are the surface energies of the solid-vapor interface, solid-liquid interface and liquid-vapor interface, respectively.

Consideration of this equation leads to several relationships between the contact angle and the various surface energies. Table II contains a summary of the effect of these relationships. It is noted that the only way to change a nonwetting system to a wetting system is by decreasing the solid-liquid surface energy. It is thus important to consider the ways in which the liquid-solid interface energy can be reduced for improved wetting.

One process which can change or reduce the solid-liquid surface energy is the preferential adsorption of atoms or ions at the interface.[1] The preferential adsorption of nickel from Cu-Ni alloys in TiC surfaces is

an example of this effect. A detailed description of the adsorption problem will not be attempted here; however, it will be mentioned that in the Gibbs equation relating adsorption and interfacial energy a term representing the thermodynamic activity of the surface active constituent in the liquid is included. Further, the adsorption of this constituent is dependent on the microscopic site it occupies on the surface. Dislocation cores intersecting the surface, vacancy cluster configurations, edges of ledges, etc. all promote favorable energy exchanges leading to preferential adsorption.

It is for this reason that a detailed knowledge of the surface conditions and the mechanisms promoting those conditions in a space station environment are important. Our surface studies are aimed at providing such knowledge. It should be pointed out that extensive evidence exists showing the effect of vacuum environments on surface faceting, thermal etching, and grain boundary grooving. Each of these phenomena will affect an adsorption process and surface energies, and they will be discussed in detail later.

Another process which may lead to a lower surface energy, and thus improve wetting, is that of diffusion. For instance, when a liquid comes in contact with a solid in which there is appreciable solubility of the solid in the liquid, a diffusion gradient exists across the interface, and the apparent surface energy changes.[2] Since the surface energy is related to the composition changes resulting from diffusion, it would appear desirable to decrease the rate of diffusion and hence, increase the time required for equilibrium to be reached. This can be accomplished by having diffusion take place from the liquid into the solid. In practice this condition is realized in the Ni + Mo alloy - TiC system when the addition of molybdenum to nickel enhances the wettability of titanium carbide and lowers the liquid alloy - carbide surface energy. Studies have shown that molybdenum diffuses from the liquid phase into the titanium carbide. In a system such as this, the controlling process or mechanism would be diffusion in the solid i.e. molybdenum diffusion in the carbide. This diffusion is in turn related to vacancy concentration, dislocation densities, and other defect structures in the solid phase. The possibility of controlling this process by controlling the defect structure of the solid phase at and near the liquid-solid interface is one of the reasons for doing our vacancy study which will be discussed in more detail later.

An example of some liquid metals and carbon selected for studying the effects of wetting or surface energy at constant density is shown in Table III. The composites Sn-C and Zn-C have liquid phases with very similar densities but dissimilar surface energies (575.9 ergs/cm^2 for Sn and 773 ergs/cm^2 for Zn) and could be expected to show the effect of different liquid surface energies on the process. These metals have

relatively low melting points and thus the power requirements in the space laboratory would be minimal for this kind of experimentation.

III. ENVIRONMENT

At this point it is necessary to inject a note about the composition of the environment. The gaseous environment in the experimental chamber of the space station must be duplicated in the experimental chambers on earth because it will effect the solid-vapor surface energy which in turn effects the process. It is not enough to duplicate the total pressure. Duplication of the partial pressures of molecular and atomic oxygen, for example, is necessary. It will be most convenient to use the vacuum of space to provide ejection of entrapped gases, reduction of surface reactivity, and separation of the experiment from the cabin environment. However, these subtle compositional differences in the residual gas must be considered.[4]

IV. ADSORPTION OF ACTIVE GASES

If there is any change in the fraction of atomic to molecular oxygen, consideration must be given to possible adsorption phenomena and any effects these may have on the sintering process. It is advantageous to consider the sintering process as passing through two stages, i.e. the heating up or "initial" stage when only solid and gas phases are present and the liquid-phase stage when one of the solid phases becomes a liquid. In the initial stage we can treat the problem of adsorption by considering the Gibbs adsorption equation in the form:

$$d\gamma = -SdT - \Sigma \Gamma_i d\mu_i \qquad (2)$$

where γ is the specific surface free energy, S the entropy, T the absolute temperature, Γ_i the surface density of the i th component and μ_i the chemical potential of the i th component.[5] If we consider a solid surface (component 1) in equilibrium with a gas (component 2), then as the gas pressure p_2 is varied at constant temperature we have:

$$d\gamma = -RT\Gamma_2 \frac{dP_2}{P_2} \qquad (3)$$

The procedure is to invoke some analytical expression relating Γ_2 and P_2 and integrate equation (3). For these analytical expressions we choose (1) the Langmuir isotherm for a gas of atoms or molecules which do not dissociate and (2) the modification of the Langmuir isotherm for diatomic molecules which dissociate on adsorption. These are

$$\Gamma_2 = \frac{K P_2}{P_2 + P_0} \tag{4}$$

$$\Gamma_2 = \frac{K P_2^{1/2}}{P_2^{1/2} + P_0^{1/2}} \tag{5}$$

where K is a constant of the order of the number of adsorption sites per unit area, and P_0 is a characteristic pressure at which saturation effects set in. For these two cases integration of (3) gives, respectively,

$$\gamma = \gamma_0 - KkT \ln\left(1 + \frac{P_2}{P_0}\right) \tag{6}$$

$$\gamma = \gamma_0 - 2KkT \ln\left[1 + \left(\frac{P_2}{P_0}\right)^{1/2}\right] \tag{7}$$

where γ_0 is the surface energy at gas pressure $p_2 = 0$.

Equations (6) and (7) illustrate that the surface energy γ can change considerably for any gas which is sufficiently strongly adsorbed and that this change is a decrease of the surface energy.

For the space vacuum we can now predict that the presence of atomic oxygen will lead to the adsorption of these atoms on the surface of solid materials and that this adsorption will most likely lead to a lowering of the specific surface free energy of the solid. If this solid phase is then to be exposed to a liquid phase (as in the second sintering stage) we can predict, based on the decreased surface energy of the solid at the vapor-solid interface, that an increase in the contact angle of wetting will result. An increased contact angle means, in turn, that wetting during the space sintering operation would be decreased.

It thus becomes apparent that a knowledge of the complete environment of the zero gravity experiment is important if the true effects of a zero gravity are to be accurately ascertained from experiments involving liquid and solid phase combinations (as in liquid phase sintering). More specifically, the extent of the adsorption phenomena must be determined together with their quantitative effects on the wetting phenomena.

V. EFFECT OF HIGH TEMPERATURE AND VACUUM - THERMAL FACETING

One effect due to the combined action of vacuum and high temperature on a metal surface is thermal etching.[6] In this case one can observe two distinct phenomena (i) the formation of grooves at grain boundaries (a result of surface energy forces) and (ii) the surfaces of the grains show thermal faceting, which when fully developed is a simple surface structure consisting of facets usually of only two types of planes. One of the planes is of low Miller indices while the other is more complex and is of the orientation necessary to keep the average surface orientation parallel to that of the original surface. Thermal faceting can take place with metals or nonmetals, and close control of temperature and residual gas in the surrounding vacuum is required if consistent (reproducible) effects are to be observed.[7,8]

Thermal faceting is related to surface free energy in that the specific surface free energy of a crystal will vary with crystalline orientation. If orientations exist where the surface free energy is markedly low, smooth surfaces of intermediate orientations may reduce their total surface energy by breaking up into facets of the low-energy orientations. However, as the average surface orientations remains parallel to the original surface, the formation of facets is limited. At the point of minimum energy, a certain fraction of the surface will be covered with facets, and the surface between facets will be tilted with respect to the original surface and will not in general be of a low-energy orientation. However, the final faceted surface will have a lower energy than the initial smooth one.

The change in surface energy due to faceting will affect wetting. Therefore, this effect must be completely categorized if the response of sintering in zero gravity is to be understood. Also it is evident from the above that the usual assumption, i.e. "the solid surface energy remains constant" made in interpreting the wetting phenomena during liquid phase sintering cannot be applied in the case of sintering in a space environment.

VI. MASS TRANSPORT AND DIFFUSION IN INITIAL SINTERING STAGE

Thus far it has been pointed out (Section II) that adsorption and diffusion phenomena occuring at the solid-liquid interface during liquid phase sintering can influence the degree of wetting and thereby control the sintering process. It has been further pointed out, Section IV, that in the initial stages of the sintering process, when only solid and gaseous phases are present, adsorption of the gases on the solid surface can effect surface energies and thereby effect the wetting phenomena. Still another phenomenon must be considered with regard to this initial stage. It is the mass transport and diffusion

that results in some degree of sintering in the solid state. It is important to consider this phenomenon because it results in a bonding of similar and dissimilar components and ultimately affects the distribution of components or phases in the final sintered compact.

The degree to which diffusion occurs and mass transport results in the initial sintering stage is dependent on a number of factors, i.e.:

(1) Surface energy of phases
(2) Plastic flow which has, or is, occurring. This gives rise to pipe diffusion along dislocation cores.
(3) The degree to which the various diffusion paths operate under the experimental conditions.
(4) The geometry of the contact area between pairs of spheres being sintered.
(5) The diffusion coefficients of phases present.

In the consideration of diffusion sintering models it is customary to consider the geometry of the system as either "pairs of contacting spheres" or "contacting spheres and plates". In our case the "pairs of contacting spheres" is applicable and will be considered.[9,10,11,12]

In general, material transport is expressed in terms of the reverse flux of lattice vacancies. Various possible sites for vacancy creation and annihilation and several types of diffusion paths are possible, as shown in Figure 2, with arrows showing the direction of vacancy diffusion. Mass transport will, therefore, be in the reverse direction.

From Figure 2 we see that at least five possible paths exist for material transfer when initial (solid state) sintering occurs between pairs of spheres. Of these, the first four paths are generally considered to be most effective during the initial stage of sintering. The geometric changes which occur between pairs of spheres for the first four cases are given in Figure 3. These are not the only possible changes which can occur since the limitation to the number of processes in a system is that a free energy decrease accompany the configuration change.

The nomenclature used for the sintering models in Figure 3 is as follows. A pair of spheres of radius R sinter to form a neck of radius x, such that the contact area between spheres is πx^2. The outer surface of this neck is of axial length ρ. The spherical surface is approximated by $x^2/2R = Y$.

The standard approach to the description of a sintering model is to express the volume change $(\frac{dV}{dt})$ in terms of the geometric change which

is fixed by assuming which vacancy sinks and sources are operating.[13,14] This in turn fixes the vacancy path, and therefore, the material transport direction. As an example, only the configuration change in cases I and II (Figure 3) utilize the grain boundary as a vacancy sink. In the first case (I) two vacancy paths (a) and (b) are possible. Path (a) represents bulk diffusion in that vacancies from the neck surface migrate into the bulk of the sphere and then into the grain boundary being formed. Also, vacancy motion occurs via path (b) which consists of vacancy migration from the neck surface via boundary and surface diffusion to the newly formed grain boundary between the two spheres. The net transport of material will be in the reverse direction, i.e. from the region of the grain boundary formed to the neck surface, resulting in the neck growth as shown.

In Case II one vacancy path is assumed operative from the grain interior (acting as a source) to the grain boundary (acting as a sink), i.e. bulk diffusion. The result here is that neck surface growth will not occur but grain boundary growth will, as shown.

For the four transport models considered applicable during the initial stage of sintering there is an implicit assumption that all vacancy sources and sinks are not simultaneously operative. This results in the ability to interpret quantitatively the observed effects. However, the limitations of this approach should be recognized. In particular the ability of any one source or sink to change its character and subsequent operation as a function of thermal cycling must be considered. Table IV lists the relations assumed in each model.

The rate of volume diffusion (dV / dt) for case I is expressed at the formed grain boundary. The boundary area is x^2 and dV / dt = x^2 dy/dt Next, the continuity equation, $y = x^2/4R$ is determined by equating the inner and outer volume of the shaded axes. For the other three cases the continuity equation expressed the relation between neck growth and shrinkage (case II) or between neck growth and surface curvature (case III and IV).

For a single component system the vacancy diffusion flux is driven by the gradient of the chemical potential which results from change in surface curvature. The highest vacancy concentration is then found at the surface of the neck, i.e. the nonspherical segment which connects the two spheres. The shape of the neck surface is important since the excess vacancy concentration under a curved surface is expressed by:

$$\Delta C = C_o \frac{\gamma \delta^3}{kT\rho} \qquad (8)$$

where

ΔC = change in vacancy concentration

C_o = vacancy concentration under a flat surface (in bulk)

γ = surface energy

δ^3 = vacancy volume

k = Boltzmann's constant

T = absolute temperature

$\rho = \frac{1}{1/R_1 + 1/R_2}$ where R_1 + R_2 are maximum and minimum possible radii of curvature. This is the effective axial length from vacancy source (neck) to center of boundary formed.

Once the excess vacancy concentration (ΔC) is known, the vacancy flux (J) per unit length can be computed from:

$$J = 4\pi D_v \Delta C \quad \text{vacancies/sec - cm} \qquad (9)$$

where D_V = vacancy diffusion coefficient

The length over which vacancy diffusion must occur is from source to sink and this is, in effect, equal to ρ in Equation (8). Then if the volume of each vacancy diffused is δ^3 the total volume of vacancies diffused will be:

$$J\rho\delta^3 = 4\pi D_v \Delta C \rho \delta^3 \qquad (10)$$

Equation (10) above represents the volume of vacancies diffused per unit time and, therefore, the volume of material transfer per unit time. This amount of material transfer per unit time is equal to the rate of volume diffusion (d V /dt), i.e. volume change.

Therefore, for case I $y = x^2/4R$

$$\frac{dV}{dt} = \pi x^2 \frac{dy}{dt}$$

$$dy = 2x\frac{dx}{4R} = \frac{x\,dx}{2R}$$

$$\frac{dV}{dt} = \frac{\pi x^2}{2R}\frac{x\,dx}{dt} = J\rho\delta^3 = 4\pi D_v \Delta C \delta^3 \rho$$

$$x^3 dx = 8R D_v \Delta C \delta^3 \rho\, dt$$

substituting $\Delta C = C_o \gamma \delta^3 / kT$

$$x^3 dx = 8R D_v \frac{C_o \gamma \delta^3 \rho}{kT\rho} \delta^3 dt$$

$$\int x^3 dx = \int 8R D_v C_o \gamma (\delta^3)^2 dt / kT$$

$$x^4 = 32\, R D_v C_o \gamma (\delta^3)^2 t / kT \qquad (11)$$

Again: x = radius of neck which results during initial sintering

R = initial radius of sintered spheres

t = time of sintering

T = temperature of sintering

δ^3 = vacancy volume

k = Boltzmann's constant

D_v = diffusion coefficient for vacancies

γ = surface energy

C_o = vacancy concentration under a flat surface

We have expressed in Equation (11) the neck radius which forms due to material transport during sintering at temperature (T) for a time (t). As shown, three parameters D_V, γ, and C_o must be determined for the

conditions under which sintering occurs if a rigorous analysis of initial sintering effects is to be made. It is toward a determination of these constants that the point defect studies of contract NAS8-24952 are aimed.

VII. SURFACE ENERGY (γ)

From the discussion in Sections IV and V it is apparent that the surface energy (γ) will not be a constant for the entire sintering process but will, due to thermal faceting and adsorption, tend to some lower energy value. This is due to the fact that we will be heating in vacuum in the presence of active residual gases (O). It is also expected that the presence of residual gases will affect the faceting process. Therefore, only via experimental determination under actual and simulated vacuum and residual gas environments can we expect to obtain an unambiguous quantitative value for (γ).

VIII. VACANCY CONCENTRATION UNDER A FLAT SURFACE (C_o)

The C_o of interest in most sintering procedures will simply be the bulk vacancy concentration. This value could be determined from a knowledge of the energy of formation of a vacancy (E_v^F) and the temperature T of sintering, i.e.:[16]

If we assume that our system consists of N atoms at some temperature T then we let E_v^F equal the energy required to remove an atom from a normal site in the system and place it in the surface. Also let n equal the number of such vacancies formed. The total increase in internal energy (E) due to vacancy formation will be nE_v^F.

The entropy of mixing of N atoms and n vacancies in a system of N + n sites is given by:

$$S = k \ln [(N+n)!/N!n!] \tag{12}$$

where k = Boltzmann's constant

The free energy, F, of the system with n defects (vacancies), relative to the free energy of a perfect (defect free) system is:

$$F = E - TS \tag{13}$$

or

$$F = nE_v^F - Tk \ln [(N+n)!/N!n!]$$

$$F = nE_v^F - Tk [\ln(N+n)! - \ln N! - \ln n!]$$

or

using Sterling's approximation $\ln X! = X \ln X - X$

we obtain $$F = nE_V^F - kT[(N+n)\ln(N+n) - n\ln n - N\ln N] \quad (14)$$

The equlilbrium value of n is that for which d F / d n = 0

or $$\frac{dF}{dn} = 0 = E_V^F - kT[\ln(N+n) + 1 - \ln n - 1]$$

$$-\frac{E_V^F}{kT} = \ln n - \ln(N+n)$$

$$e^{-E_V^F/kT} = \frac{n}{N+n} \qquad \text{for } N >> n$$

$$\frac{n}{N} = e^{-E_V^F/kT} = C_o \quad (15)$$

Equation (15) represents the concentration of vacancies in a one component system, and can be substituted in the expression for the change in vacancy concentration (Δ C). For our experiments it is anticipated that two-component systems will be used. The existing condition will, therefore, be somewhat complicated in that two individual vacancy concentrations will be present and will have an effect on Δ C. Also, two energies of formation, i.e. E_V^{F1} and E_V^{F2} will be involved and for the temperature of sintering (T) two vacancy concentrations will be present C_o^1 and C_o^2. This condition will in turn complicate the vacancy source and sink considerations in that the component with the lower E_V^F, will, for a given temperature, possess a higher concentration of vacancies. This will result in a vacancy concentration gradient which exists across the specimen "neck". This gradient may, if large enough, override all other vacancy sink-source considerations. Therefore, a determination of the vacancy concentration as a function of temperature at or just below specimen surfaces must be determined for each component to be utilized in the sintering process. This can be determined via the series of experiments outlined in contract NAS8-24952.

IX. THE VACANCY DIFFUSION COEFFICIENT (D_V)

Most studies into the diffusion of vacancies in a solid have been conducted via high temperature quenching and resistivity experiments.[15] The quenching of a solid results in a supersaturation of vacancies and subsequent low-temperature annealing provides the energy for migration and annihilation at sinks. This process results in a change (decrease) in electrical resistivity which can then be used to determine the half life of vacancies and their diffusion coefficients. For the interpretation of effects expected in the initial stage of sintering an approach which utilizes a supersaturated vacancy situation in the individual components is not accurate.

Thermal equilibrium will be achieved throughout the solid-spherical particles of the two phases in our system. This equilibrium, reached after some time at the sintering temperature, will have the following characteristics:

(1) In the bulk of the solid spheres, a vacancy concentration (C_o) will be reached. The value of (C_o^1) in one phase (sphere) will not be equal to (C_o^2) that in the second. Although vacancy sinks and sources will be active in the bulk, the equilibrium condition dictates that the net number of vacancies will not change if temperature remains constant. This further dictates that a variable vacancy sink mechanism is not operative and, therefore, that vacancy sinks whose effectiveness changes with time can be ignored as inoperative, i.e. dislocation loops, tetrahedra, etc.

(2) Across the region of the neck (boundary) formed (or forming) between the two spheres, a definite vacancy gradient will exist, causing a net flow of vacancies from one sphere to the other. This flow will be present simply because of the concentration differences C_o^1 and C_o^2 and is not limited by the active action of sinks.

Under the conditions of thermal equilibrium the diffusion coefficient (D_V) may be given by:

$$D_v = A_v^M Z \nu b^2 \exp(E_v^M/kT) \qquad (16)$$

where A_v^M = the entropy of vacancy migration

Z = the coordination number (12 in fcc)

ν = the atomic frequency 10^{13} sec^{-1}

b = the atomic diameter

E_v^M = the activation energy for vacancy migration

The constants A_V^M and E_V^M have been determined for a large number of metals and can be obtained from the literature. However, this has been done under experimental conditions which assume either a fixed vacancy sink and/or a variable vacancy sink condition. Therefore, before a choice of constants can be made, the type of mechanisms involved in the system must be determined. This can be done via the annealing and heat treating studies by a determination of the process kinetics. That is, the fixed vacancy sink condition reflects itself as a 1st order reaction and the variable vacancy sink condition as a second or higher order reaction.

X. SUMMARY

It has been the intent of this paper to point out those areas of research that are important in the overall study of liquid phase sintering in space. From a consideration of the various research areas, several concepts relevant to materials experiments in space emerge. The first of these concepts is that materials processes that involve a liquid phase are most likely to be influenced by the details of gravitational fields. This is perhaps self-evident. Perhaps more important is a realization that most of the possible metallurgical processes proposed for space experiments will be influenced by the details of the gaseous environment. For instance, the high percentage of O and O_2 in the residual gases of the space vacuum will have significant effects on the results.

The close or direct connection between materials processes employing a liquid phase and the residual gases of the space vacuum occurs through a consideration of surface free energies. The behavior of a liquid phase in the absence of a gravitational field will be controlled by the surface energy terms. That is, surface energy terms will predominate and be responsible for driving any reactions or establishing the equilibrium states. However, surface energies are significantly affected by the gaseous environment through the process of adsorption and consequently the effect of the gaseous environment on such energy terms must be determined.

For the proposed experiments on sintering, it was pointed out that a two-step process is involved. In the initial stage, where only solid and gaseous phases are involved, a significant amount of material transport is expected to occur. In theoretically considering the mechanism involved, the conclusion is reached that the vacancy concentration is a function of the surface energy terms. Also, the phenomenon of thermal faceting is expected and is shown to be a function of surface energies. Specific relations between these mechanisms must be determined for the space environment. In the final stage of the sintering experiment, the liquid phase makes its appearance and the phenomenon of wetting is of crucial importance. Again, wetting is a function of

surface energies and the important relations must be determined.

Figure 4 is an attempt to show the connections between the various mechanisms involved in liquid phase sintering in the space environment. At best it is incomplete and represents a first attempt, on our part, of such a representation. We feel these inter-relationships to be crucial for the space experimental program.

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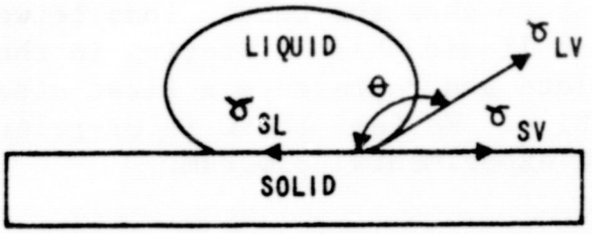


Figure 1 LIQUID DROP ON SOLID SUBSTANCE

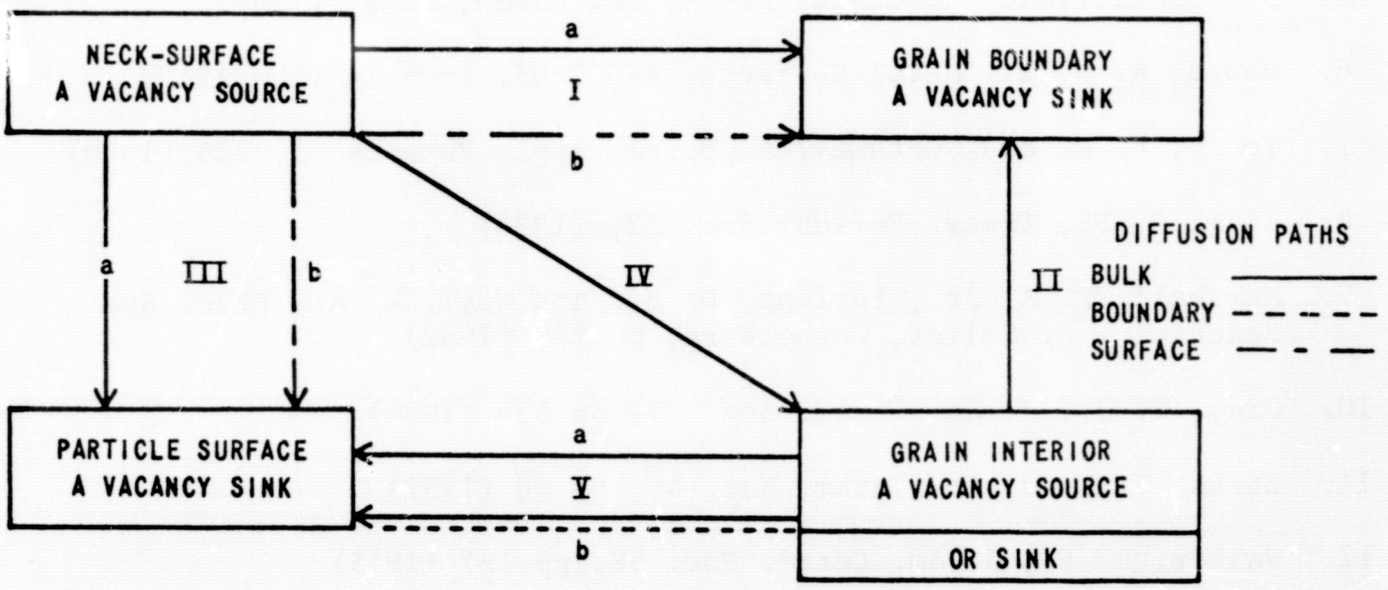


Figure 2 VACANCY SOURCES, SINKS AND PATHS FOR SINTERING BETWEEN PAIRS OF PARTICLES

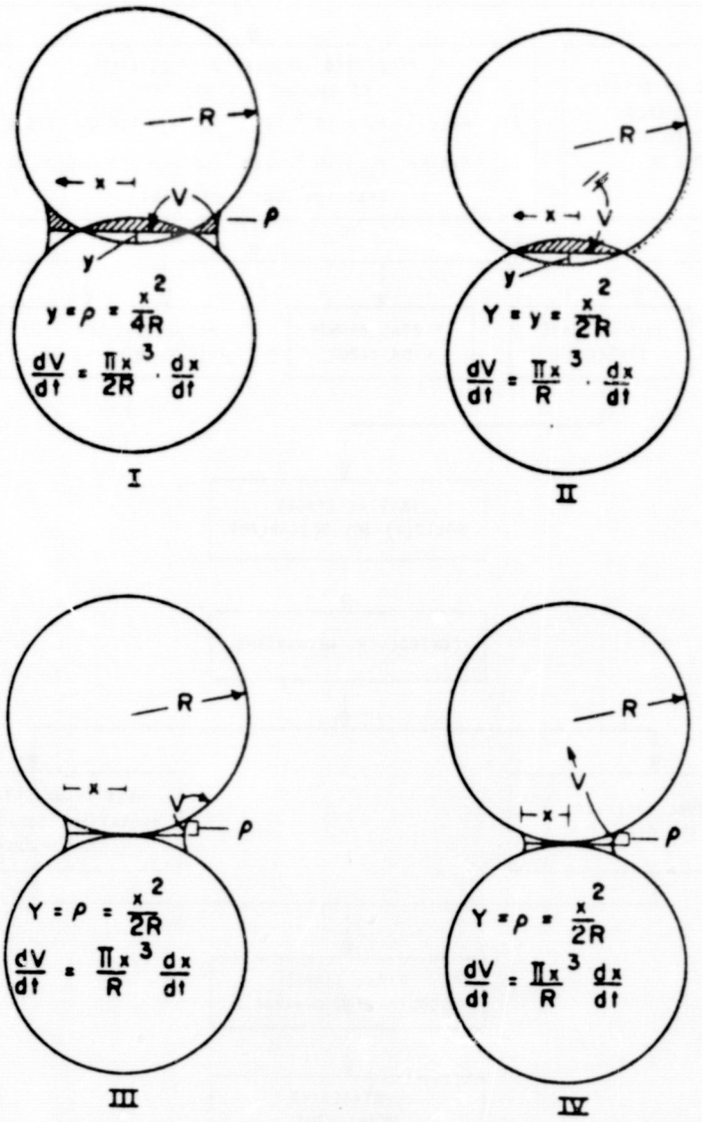


Figure 3 GEOMETRIC EXPRESSIONS FOR SINTERING BETWEEN PAIRS OF SPHERES

where: R = radius of spheres

X = radius of neck.

ρ = axial length of neck outer surface

Y = spherical surface

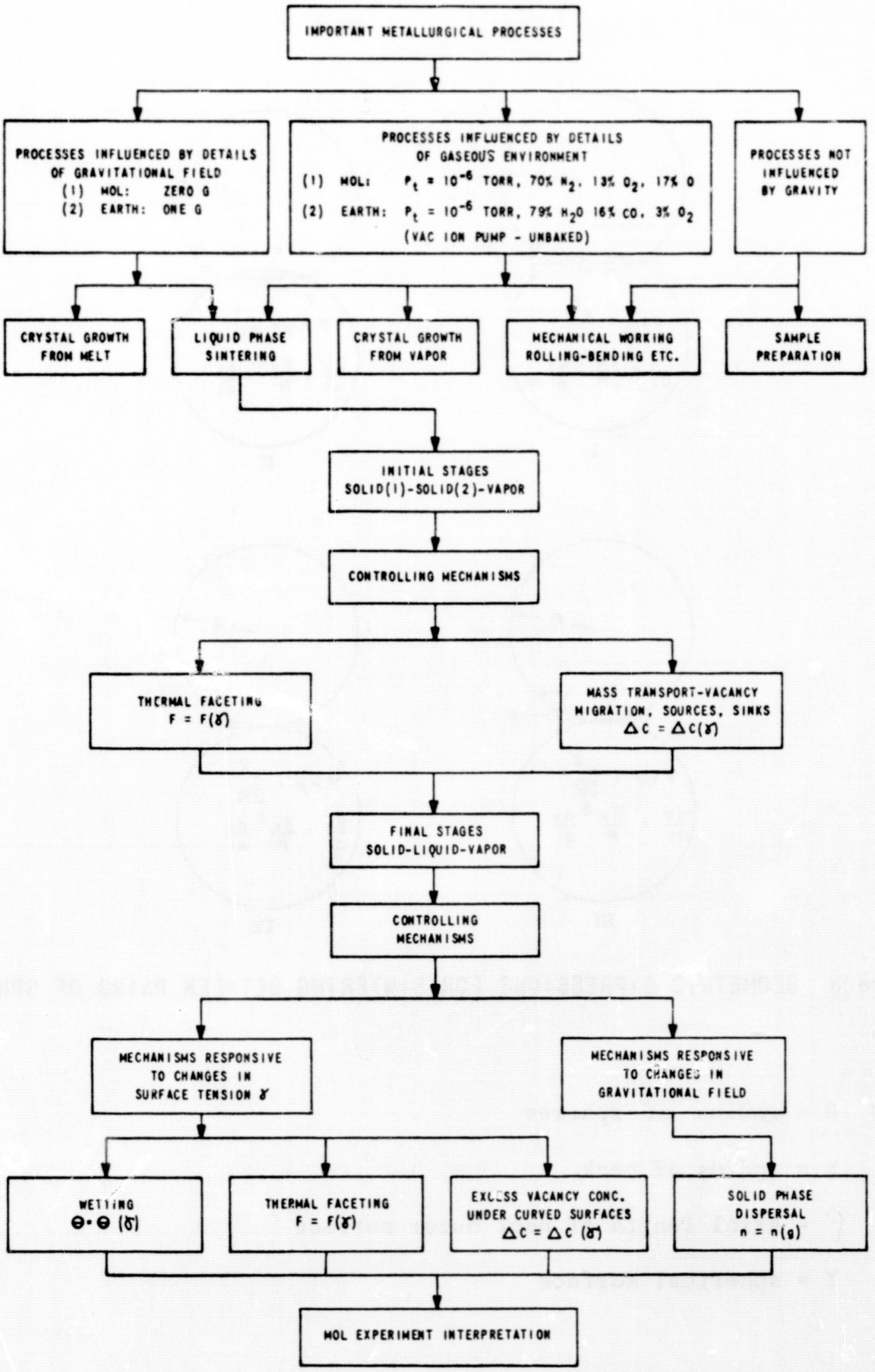


Figure 4 IMPORTANT METALLURGICAL PROCESSES

TABLE I

PROPERTIES OF LIQUID METALS AND CARBON SELECTED FOR EXPERIMENTS ON THE EFFECT OF DENSITY ON LIQUID PHASE SINTERING

	Melt Pt. °C °F	Density gm/cm^3 at °C	C Solubility W/O at °C	Surface Energy $ergs/cm^2$
Carbon	3727	2.22/-	--	-
Silver	960/1760	10.49/960	.0012/1600	923.0
Aluminum	660/1220	2.37/660	Trace	914.0

TABLE II

EFFECT OF DECREASING ONE SURFACE ENERGY ON CONTACT ANGLE, MAINTAINING OTHERS CONSTANT

Decreased Surface Energy	Change in Contact Angle	
	Initial Angle	Initial Angle
	$<90°$	$>90°$
Liquid-Vapor	Decrease	Increase
Solid-Vapor	Increase	Increase
Solid-LIQUID	Decrease	Decrease

TABLE III

PROPERTIES OF LIQUID METALS AND CARBON SELECTED FOR EXPERIMENTS ON THE EFFECT OF SURFACE ENERGY ON LIQUID PHASE SINTERING

	Melt Pt. °C °F	Density gm/cm^3 at °C	Carbon Solubility	Surface C. Energy ergs/cm^2
Carbon	3727	2.22/ -	--	--
Tin	232/449	6.83/409	Trace	579.5
Zinc	420/787	6.92/420	Trace	784.8

TABLE IV

Case	Vacancy Source	Vacancy Sink	dV/dt	Continuity Equation	Produces
I	Neck	Boundary	πx^2 dy/dt	$y = x^2/4R$	Neck growth and shrinkage
II	Dislocations	Boundary	πx^2 dy/dt	$y = x^2/2R$	Neck growth and shrinkage
III	Neck	Surface	$2\pi x\rho dx/dt$	$\rho = x^2/2R$	Neck growth
IV	Neck	Dislocation	$2\pi x\rho dx/dt$	$\rho = x^2/2R$	Neck growth

CHEMICAL REACTION IN LOW AND ZERO GRAVITY
A FEASIBILITY STUDY

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ABSTRACT

This paper presents the results of a theoretical study to determine the effect of low and zero-gravity on chemical reactions, specifically catalytic polymerization of ethylene using transition metal complexes. Fixed bed, slurry reactor, and fluidized bed polymerization processes are compared under earth gravity and low or zero gravity conditions. Fixed bed polymerization under low or zero gravity does not offer any particular advantages or disadvantages compared to normal gravity processing.

Polymerization in slurry reactors does not appear to be advantageous at this time because the introduction of gas in liquid under a zero gravity environment involves wholly new concepts of bubble formation, growth, and motion, and liquid-gas separation. Comparison of two-phase (gas-solid), stirred fluidized bed polymerization under normal and zero gravity conditions indicates that it would be possible to obtain longer contact times between gaseous monomers and solid catalysts, more rapid heat transfer, lower power requirements, and improved catalyst regeneration capability. A theoretical model of the chemical and physical interactions of the gas and solid phases under normal and reduced gravity is described. This model is used to evaluate the potential performance of slurry and fluidized bed reactors. Techniques are proposed to adapt fluidized bed polymerization for zero-gravity operation. An earth-based approximation of a low-gravity fluidized bed reaction is also described. The approach outlined in this paper might serve as a guide for future studies of space polymerization of other materials.

INTRODUCTION

Manufacturing in space is becoming an exciting and important aspect of our overall space effort. It is exciting because new freedoms are provided with the unique combination of low and zero-gravity forces, unlimited space, and high vacuum. We may be able to utilize these factors to make existing earthbound procedures more attractive and to create new processes and materials not now available to man. The significant aspect arises when determining man's role in space. As interesting as scientific research and experimentation is, the real impact will be made in performing productive tasks that will affect the industrial and economic elements of society.

In exploring the behavior of chemical reactions and processes in a low-gravity space environment, several interesting phenomena were noted. The most basic is the general independence of chemical reactions from gravity. This is primarily due to the small mass of the molecules and atoms involved in these reactions. It was also found that the radiation and vacuum available in space can be used to great advantage to initiate and assist chemical reactions. It is our intent to consider utilization of zero gravity because of its truly unique quality.

Gravity does play a role, however, in large-particle chemistry or polymerization. Many of the present polymerization processes use solid particles to catalyze various reactions. This paper examines the possible beneficial aspects of low and zero gravity for two-phase reaction processes involving a solid phase in a fluid medium. Specifically, the continuous production of polyethylene is investigated for solid catalyzed polymerization in which solid particles are conveyed by either liquid or gaseous phases. Polyethylene polymerization is selected for study because it is a widely used process having a minimum of unknown factors.

Post-reaction, low-gravity separation of two and sometimes three phases, and mixing and flow within a proposed reactor are examined and compared with similar processes on earth. The advantages and problems encountered in this type of processing are probably typical of the many commercial solid-fluid processes. Compared to the suspension and emulsion polymerization processes, the fluidized-bed process is the most attractive under zero-gravity conditions because the free-floating particles can be most efficiently utilized.

Solid particles may be suspended in a gas or liquid phase, forming a fluidized bed, a contacting system which has been successfully used in reaction processes such as the catalytic cracking and reforming of gasoline, and the production of iron from its ore. On earth the fluidized particles attain a suspended state when the gravitational (minus the buoyant) forces on the particles are counterbalanced by the drag forces of the continuous gas or liquid stream. In gas-solid systems in particular, the gas rises in two paths, one a smooth path through the solids and the other a series of bubbles. The bubbles are unlike those in a pure liquid and are associated with the vigorous mixing process of the bed, a process which accounts for its excellent heat transfer properties. The bubbles are disadvantageous for reaction in that a good portion of the gas may bypass the bulk of the solid particles. In reduced gravity flow, little excess gas is required to suspend the particles and longer contact times between gaseous reactants and the solid are possible. Some new process problems are anticipated but they are not expected to be particularly troublesome.

OLEFIN POLYMERIZATION UNDER NORMAL GRAVITY

The early catalytic polymerizations with transition metal complexes were brought to a profitable manufacturing stage with the work of K. Ziegler and coworkers (1, 2, 3), who used titanium tetrachloride reduced in situ with a metal alkyl, the cocatalyst. The most renowned of his systems is that composed of $TiCl_4$ and trialkylaluminum in which chloride ions are stripped from the tetrachlorides, and $TiCl_3$ precipitates from the solution. The initial procedure is still in use, and new catalysts having similar mechanistic features have been developed. This is represented schematically in Figure 1. The primary systems considered in this study are those in which a preformed solid catalyst is distributed in a liquid and/or gaseous phase. Because of an induction period for precipitation and catalysis, a long holdup time is required for continuous operation. Chlorobenzene has been effectively added to the hydrocarbon solvent in an effort to reduce the induction period.

Transition Metal Halides

In a number of investigations, Natta, et al. (4-9) developed a feasible mechanism for the stereoregular polymerizations. They found it would be possible to precrystallize $TiCl_3$ and that the use of a precipitation step with its induction period was unnecessary. A dry milling operation may be used (9) to produce a finely divided $TiCl_3$ powder.

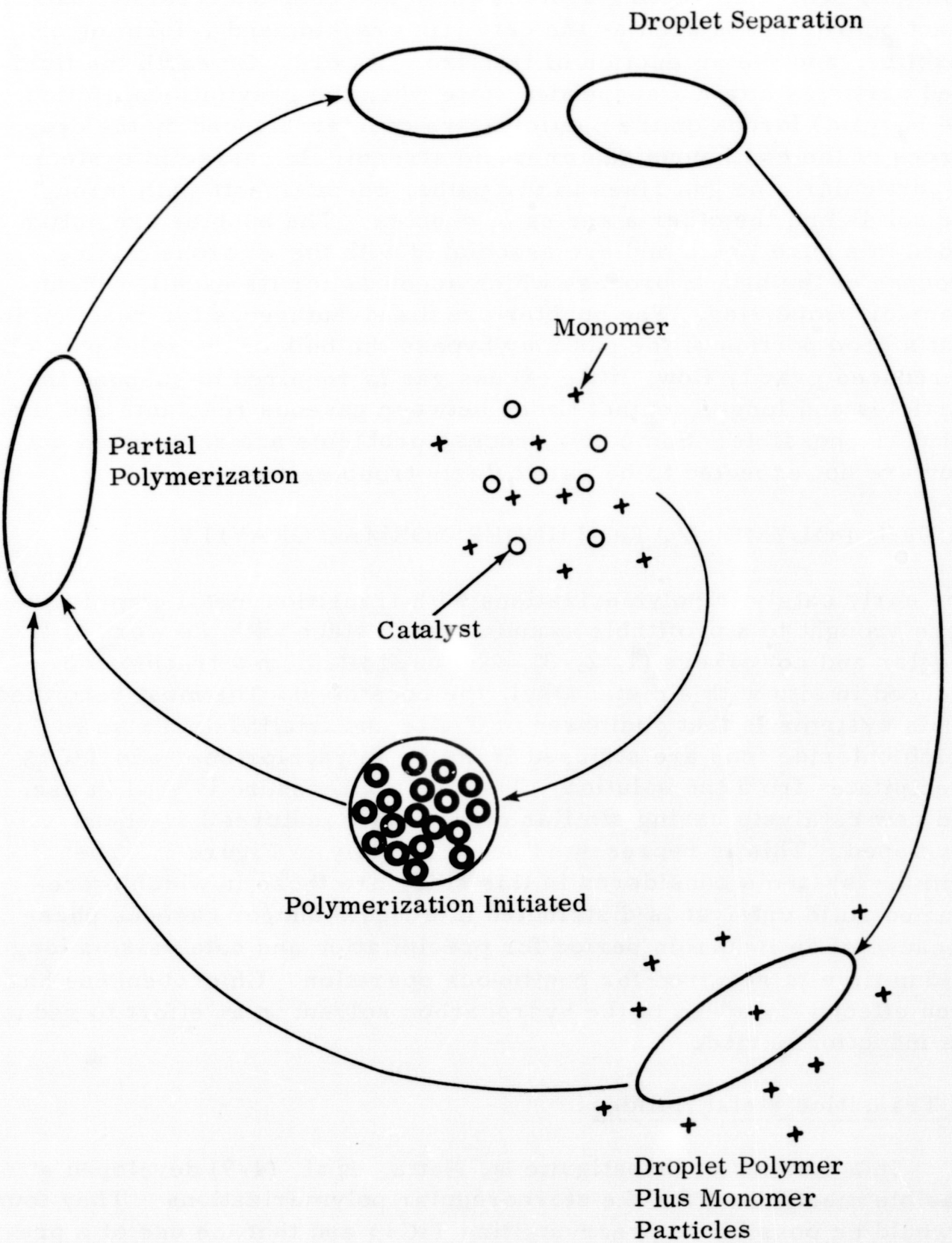


Figure 1. Typical Polymerization Reaction

The product is susceptible to degradation by both oxygen and moisture. In the purification process the catalyst may be deactivated by an alcohol wash. Other transition metal halides were also found to be sufficiently active catalysts (for example, the chlorides of vanadium, chromium, and zirconium). The molecular weight of polymers produced is related to the ratio of reducing agent to catalyst as well as to the total quantity of catalyst. Adding hydrogen gas decreases the molecular weight and adding diluting gas reduces the rate of reaction. Natta (10) and Schindler (11) have proposed the following mechanism for propagation:

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - (CH_2 - CH_2)_n - R} + CH_2 = CH_2 \xrightarrow{k_1}$$

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - (CH_2 - CH_2)_{n+1} - R}$$

The termination may be by a transfer reaction,

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - R} + CH_2 = CH_2 \xrightarrow{k_2} \overset{(+)\ (-)}{X\ CH_2 - CH_2} + CH_2 = CH - R$$

or by hydride formation,

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - R} \xrightarrow{k_3} \overset{(+)\ (-)}{X\ H} + CH_2 = CH - R$$

A side reaction which is also likely to occur is

$$\overset{(+)\ (-)}{X\ H} + CH_2 = CH_2 \xrightarrow{k_4} \overset{(+)\ (-)}{X\ CH_2 - CH_3}$$

The propagation rate, assuming steady state in all but the propagation reaction, is given by

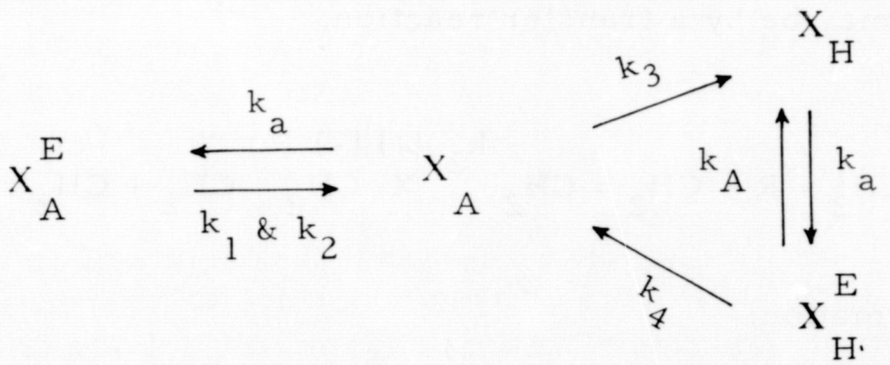
$$R_p = k_1 C_M C_E = (k_4/k_3)\, k_1 C_o C_E^{\,2} \Big/ \left[(k_4/k_3)\, C_E + 1 \right]$$

in which: C_M, C_H are the concentration of sites with metal-alkyl bonds (on which propagation occurs) and with hydrided or terminated bonds, respectively

$C_o = C_M + C_H$ = Total concentration of active sites

C_E = effective concentration of ethylene

Schindler (11) has shown that if the rate of adsorption controls the overall propagation rate a similar form of expression results. In this instance, let X represent catalyst sites as shown below:



Constants and superscripts are defined as follows:

k_a and k_d = adsorption and desorption rate constants for ethylene

superscript E = ethylene

subscripts A, H = active alkyl bond and latent hydride bond, respectively

In this case, $R_p = C_E^{\,2}/(B_o + A_o C_E)$

where $A_o = (k_1 + k_2)/k_a k_1 C_{xo}$, $B_o = k_3(k_1 + k_2)(k_4 + k_d)/k_4 k_a^{\,2} k_1 C_{xo}$

Although this mechanism confirms the often found result that the rate is proportional to either a first or second power of the ethylene concentration, some experimental evidence indicates that the rate becomes second order as C_E increases. This condition may be fit empirically by

$$R_p = kC_E (1 + KC_E)$$

where k and K are empirically derived constants. Rate expressions for ethylene and propylene are given in Appendix 1.

Transition Metal Oxides

Standard Oil (Indiana) Reaction. The preferred catalyst consists of a γ-alumina support impregnated with 8% MoO_3 activated by treatment with hydrogen, and then promoted by a reducing agent such as calcium hydride. The catalyst size varies from 4-6 mesh for fixed bed operation to 20-85 mesh for slurry operation (12). Polymerization temperatures range from 75 to 300°C and pressures from 500 to 1500 psig. The reaction may be carried out in either a solution or a suspension phase, depending on whether or not the polymer formed is soluble in the carrier solvent.

Phillips Petroleum Reaction. The catalyst consists of an SiO_2/Al_2O_3 = 9 support on which 3% chromium oxide is impregnated. Ethylene in solution is usually fed to the catalyst; the solvent is eventually used for extraction. The catalyst size is probably similar to that used in the Standard Oil Processes, except for the gas fluidized bed version with size range 40-100 mesh. Solution polymerization uses temperatures of 130-170°C with a pressure of about 400-600 psig. Suspension and fluidized beds operate at lower temperatures, (90-110°C). See Appendix 2 for additional details on Phillips catalyst and solvent.

OLEFIN POLYMERIZATION PROCESSES

Earthbound Processes

Fixed Bed. A 5-10 wt. % solution of ethylene is fed in the Standard Oil process (13-16) or 2-4% in the Phillips process, the latter at an hourly space velocity of 1.0-6.0 liquid phase (17). In the fixed bed

processes some major problems may occur. Because of the poor heat transfer through the bed, high localized temperatures may result causing increased polymer agglomeration, catalyst degradation, and loss of selectivity. If no heat were removed from the reaction, the total conversion of ethylene would leave the product 1000° hotter than the starting temperature (18). One of the reasons for feeding a low percent of ethylene at fairly high space velocity is to partially overcome this problem. Power losses due to pressure drop across the bed will increase as the extent of polymerization increases, thus increasing pumping costs. Operation at high temperature is required to keep polymer in solution. Also, in cases of severe channeling, some of the solution-containing monomer may bypass a good portion of the catalyst.

Slurry Reactor. The catalyst particles are stirred in an autoclave which may be operated in either a continuous or a batch fashion. The autoclave is baffled in such a manner that the lower portion of the vessel is stirred vigorously while the upper portion remains quiescent. The main problems with slurry operation are the fairly high costs of power consumption. The use of finer particles and higher liquid velocities partially reduce the necessary power requirements. Heat transfer problems are usually brought under control by cooling jackets.

Fluidized Bed. In one version of the Phillips process, a stream of gaseous ethylene is fed through a fluidized bed of particles. The reaction is initiated at 260 psig to coat the catalyst in order to prevent premature agglomeration and then is raised over 80 minutes to the operating level of 450 psig for the remainder of the reaction. An average reaction rate of 13 g/polymer/hr/gm-catalyst has been reported (19). A much finer particle size and the highest ethylene velocities are required in this process. This is represented schematically in Figure 2. Additional information on the process may be found in Appendix 3. Some reactant gas bypasses the catalyst as bubbles but the heat transfer is excellent in this process. Heat removal may be expedited by liquid film boiling as described in Appendix 4.

Low Gravity Processes

Fixed Bed. In order to maintain a fixed bed condition in low or zero gravity, either downflow or an additional screen will be required. No benefits or disadvantages of this type of operation is expected outside of earth's gravitational force.

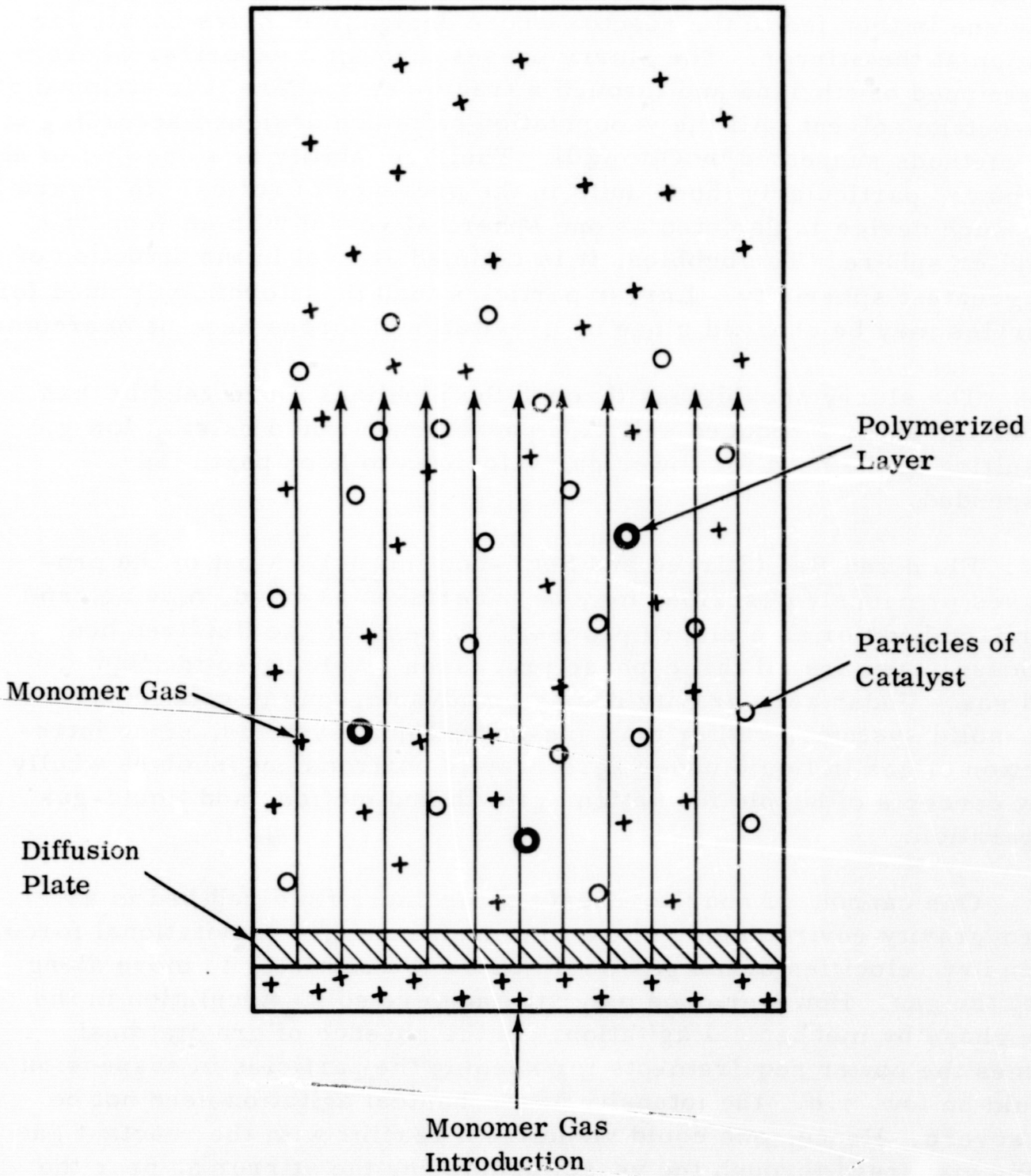


Figure 2. Fluidized Bed Polymerization

Slurry Reactor (Fluid-Solid Conveying). A diagram of the proposed slurry type reactor is presented in Figure 3. At start up, liquid iso-octane is fed to the stirred reactor with the stirrer on. Gaseous ethylene is then fed to the reactor whose design minimizes bubble formation at the stirrer. The slurry passes through a vaporizer where it is stripped of ethylene and through a fractionator where it is stripped of iso-octane solvent. All the vaporization units are designed according to the methods suggested by Otto (20). Their reliability is somewhat of an unknown, particularly those units in the presence of solids. In Figure 3, one such device is depicted as one spherical vessel with an eccentric smaller sphere. The bubbles, it is claimed, travel in the direction of its greatest sphericity. Larger particles than those ordinarily used for slurries may be charged since no gravitational forces need be overcome.

The slurry should pass through the pipelines more readily than under lg, since a reduced saltation phenomenon would exist at low g, resulting in the need for lower gas velocities to keep particles suspended.

Fluidized Bed (Stirred and Semi-continuous). Most of the processes previously described may be undertaken as fixed, moving, and fluidized beds or as a slurry process. Except for the fluidized bed process, they are all three-phase processes involving solid, liquid, and gas. Under zero gravity it may be advantageous to concentrate on gas-solid systems, rather than gas-solid-liquid systems, since introduction of gas in liquid under zero gravity environment involves wholly new concepts of bubble formation, growth and motion, and liquid-gas separation.

One cannot, of course, create an ordinary fluidized bed in a zero-gravity environment, since in the absence of a gravitational force, even low velocities of the gas would cause the particles to move along with the gas. However, one may still achieve solid circulation in the gas phase by mechanical agitation. In the absence of gravitational forces the power requirements for keeping the particles in suspension would be low, i.e., the intensity of mechanical agitation need not be as severe. Hence, one could visualize a reactor with the reactant gas being dispersed through the vessel and having the stirrer as near the exit as possible. Such a system would offer the basic advantage of a fluidized bed, i.e., improved heat transfer and low temperature gradients in the system with reduced power requirements. Another advantage is that regeneration of the catalyst can be undertaken in situ as compared with the slurry process where solid-liquid separation must be accomplished.

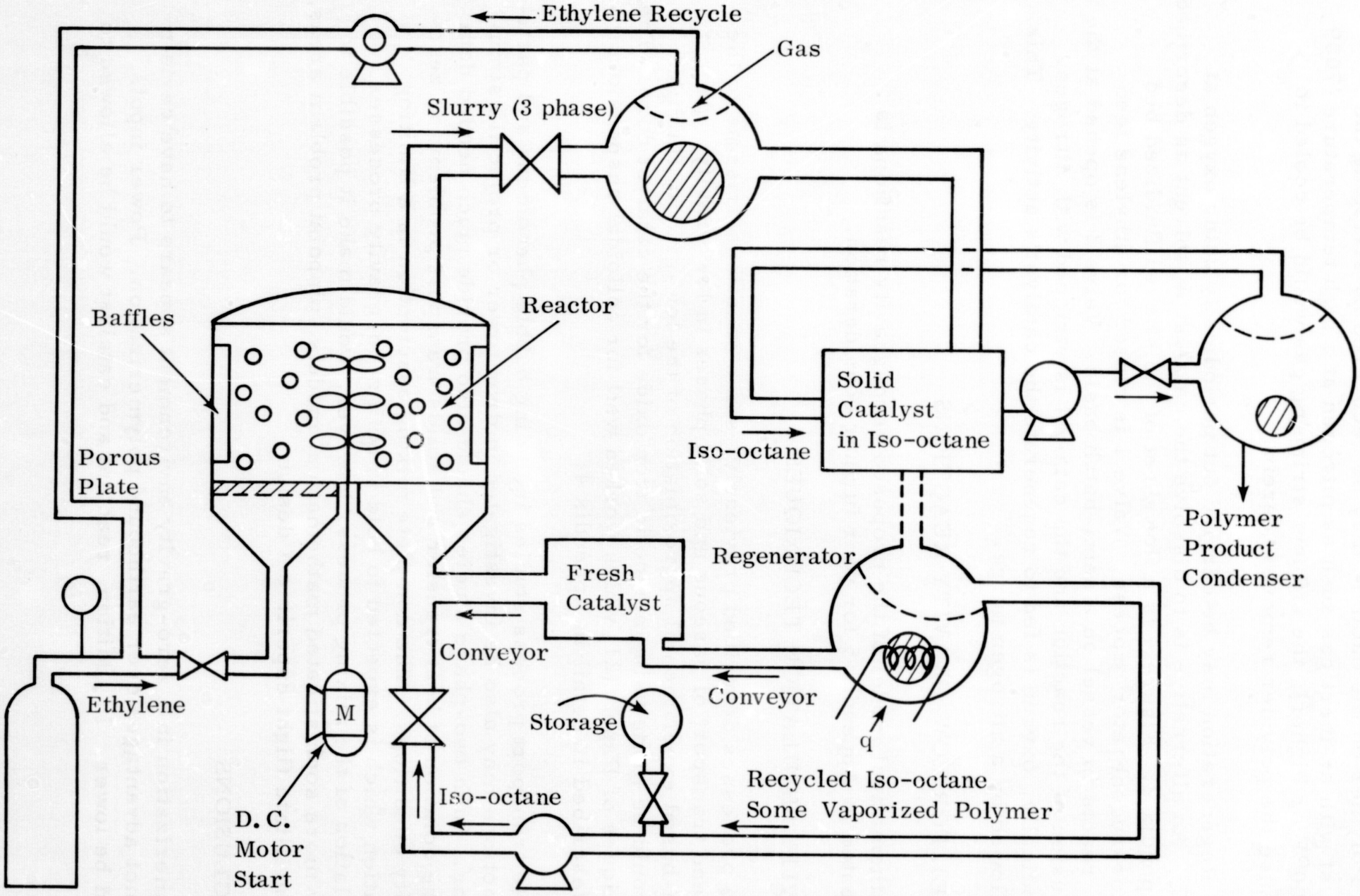


Figure 3. Zero Gravity Slurry Type Reactor

Polymer on the catalyst may be recovered by stripping the catalyst with an inert gas such as nitrogen at a high temperature (700° to 1100°F or higher); the effluent stripping gas would be cooled to condense the polymer removed therein.

Regeneration may be carried out periodically using oxygen at 540°C. An alternative is to dissolve the catalyst in solvent as described in Appendix 2. Figure 4 is a flowsheet of the stirred fluidized bed reactor-regenerator process. Valve 1 is closed for ethylene feed which reacts in vessel on a semi-batch basis. Valve 2 is opened at the conclusion of the reaction and the catalyst is stripped with nitrogen. Periodically, oxygen is fed to regenerate the catalyst's activity. This is followed by a nitrogen purge.

MODEL FOR LOW-GRAVITY REACTIONS

A mathematical model of the proposed zero-gravity reactions is presented in Appendix 5 for your further consideration.

GRAVITY SIMULATION TECHNIQUES

In the processes described previously, some questions arise as to the flow and transport of gaseous and solid phases in low gravity. An earth-based experimental approximation of the low-gravity fluidized bed could be made using magnetic iron oxide for the catalyst core. The techniques of Papell (21) which worked well for colloidal suspensions are described in detail in Appendix 4.

Simple transport process studies including bubble phenomena and particle motions may also be investigated in drop tower or projectile simulations. Such two-phase studies should also provide much needed data for the solution of heat transfer and solids transport problems in zero-gravity conditions. The complete mixing assumption is a limiting condition which is expected to hold in both zero-gravity processes. Simulation of the mixing process, however, would make it possible to apply more sophisticated mathematical models, pinpoint problem areas, and facilitate flight experiment design.

CONCLUSIONS

Polymerization in a zero-gravity environment appears to have certain distinct advantages over earthbound polymerization. Power inputs would be lower. In addition, reactant and catalyst would be allowed to

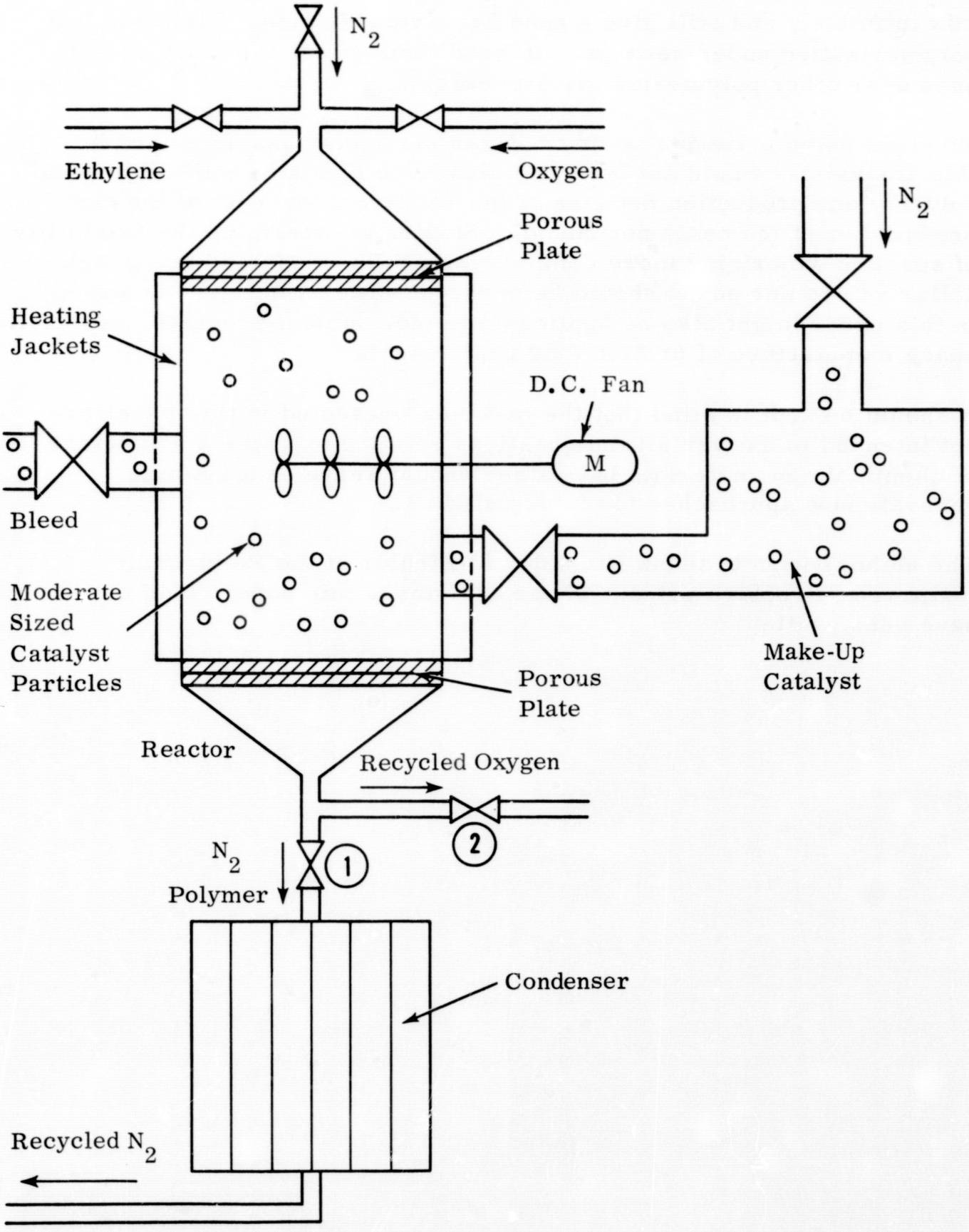


Figure 4. Stirred Fluidized Bed

mix intimately and still give a good heat transfer rate. Fluidized bed polymerization under zero-gravity conditions offers the most advantages over other polymerization processes.

Ethylene polymerization in space -- the particular example used in this analysis -- would not be economically competitive with earthbound polyethylene production because of the relatively low cost of the end product (about ten cents per pound). Studies to determine the feasibility of space polymerizing more complex molecular products having high dollar values per pound should be pursued. The principles discussed in this paper might also be applicable to biochemical products, especially space manufacture of protein food supplements.

It should be kept in mind that the concepts presented in this paper are not intended to answer all the questions relating to space manufacture of chemical raw materials but rather should serve as a guide to generate new approaches for future studies.

The authors wish to thank Dr. Edward Ziegler of the Polytechnic Institute of Brooklyn without whose assistance this paper could not have been written.

APPENDIX 1. RATE EXPRESSIONS

Ethylene.

Activation energies: $TiCl_4/Al(i\text{-}Bu)_3$, $\Delta E = 10.4$ k cal/g-mole

$Ti(OBu)_4/Al\ Et_3$, $\Delta E = 13$ k cal/g-mole

Propylene. From Natta (22),

$$R_p \text{ (gms } C_3 \text{ reacted/hr)} = k_o G_{TiCl_3} \text{ (grams) } P_{C_3H_6} \text{ (atm)} e^{-\Delta E/RT}$$

$$k_o = 2 - 3.4 \times 10^7 \text{ (hr-atm)}^{-1}$$

$$\Delta E = 10 \text{ k cal/g-mole}$$

APPENDIX 2. DETAILS ON PHILLIP'S CATALYST AND SOLVENTS

Solvent:

Inert liquid under reaction conditions which does not deactivate the catalyst should be used. Saturated aliphatic compounds are more suitable than aromatic compounds since they do not undergo alkylation reactions. Cyclohexane has a high boiling point and adequate solvent power for polyethylene. The solvent is used in slurry process or for removal of polymer from the catalyst.

Catalyst Preparation:

Commercially available silica-alumina is suitable as a support. The productivity of the catalyst does not increase with chromium content greater than three-to-one. The chromium is deposited on the support by impregnation with aqueous solutions of any chromium compound that can decompose to chromium oxide when exposed to dry air at 540°C. This activation treatment is required to dehydrate the catalyst to a sufficiently low level and to oxidize at least two-thirds of the chromium to the hexavalent state. The silica-alumina support used may be in the form of granules 14/28 mesh or 5/32-inch pellets. The preferred support has a large pore size and a low surface area to facilitate the dissolution of the coating of polymer that is subsequently formed. The active catalyst surface area/weight ratio is 400-600 m^2/g and pore diameter is 65-150 A^o, with a sulfate content less than two weight percent.

Catalyst Regeneration:

Catalyst recovered from a polymerization may be regenerated by oxidation with hot air at 540°C in the same way as for the original activation step. Too high an activation temperature (820°C) results in a marked decrease in catalyst activity. This can be attributed to a reduction of the proportion of chromium that is in the hexavalent state. Some poisons are water, oxygen, carbon monoxide, compounds of sulfur, oxygen, nitrogen and halogens. Oxygen at temperatures of 150°C or less acts as poison, apparently through a reversible adsorption.

Steam-aged silica-alumina covered with a 0.8 molar solution of aqueous chromium inoxider is allowed to stand several minutes, and the excess solution is filtered. Impregnated material is dried at 100-200°C and then activated by fluidizing with air at 540°C for 5 hours to give a catalyst containing 2-4 weight percent of chromium.

APPENDIX 3. ADDITIONAL INFORMATION ON EARTHBOUND FLUIDIZED BED POLYMERIZATION

Although the catalyst has a particle size in the range of 40 to 100 mesh, finer (e.g., microspheroidal) particles may be used. The reaction temperature is 200°F to 230°F, which is just below the polymer melting point of 240°F to 260°F. The preferred operating pressure range is 25 to 500 psig. A linear velocity of 0.5 to 1.0 feet/second may be used if dilute phase operation is desired. A particular technique is suggested to prevent agglomeration of catalyst particles by polymer. This involves initial operation of fresh catalysts for 30 minutes to 2 hours at a pressure from 25 to 80 percent of the full process operating pressure. This pre-conditioning step builds up a small amount of polymer which then prevents further agglomeration. This step may be carried out in a first fluidized reactor, delivering the conditioned catalyst to a second polymerization reactor.

APPENDIX 4. CONTROLLED GRAVITY (BASED ON REFERENCE 22).

The validity of the magnetic zero gravity simulation depends on the properties of the magnetic fluid and the characteristics of the field that supplies the magnetic forces.

A suspension was produced by dispersing submicron particles of magnetic iron oxide (Fe_3O_4) in a medium of normal heptane. An extremely stable, low-viscosity, magnetic colloid system containing a 6.83 weight percent particle concentration was prepared in this manner. The particles were essentially spherical in shape, uniformly distributed throughout the liquid, and approximately 0.1 μ in diameter. No significant changes were observed in the boiling point and apparent viscosity. The stability of the colloid system was also unaffected by the earth's gravity or applied magnetic forces in fields of 50 kilogauss, which yield magnetic gradients of 9.1 kilogauss per inch. Under these forces the particles remained dispersed throughout the liquid for extended periods of time.

The apparent stability of the colloid allows an assumption to be made concerning the equivalency between magnetic body forces and gravitational forces. Consider a microscopic volume consisting of a magnetic particle surrounded by a volume of liquid. The influence of the magnetic body force on the system is essentially limited to the solid particle. The particle experiences a force in the direction of the magnetic gradient and, in turn, influences a specific volume of the fluid by some adsorption mechanism, so that magnetic force is transmitted to the liquid. The apparent stability of the system suggests that the applied forces are smaller than the forces that hold the solid liquid systems together, even though calculations showed that the distance between particles is about five times the diameter of the particles themselves.

APPENDIX 5. DESCRIPTION AND MODEL DEVELOPMENT FOR LOW GRAVITY

Force and Displacement in Slurry and Fluidized Beds

Solid phase. Although the basic flow schemes will remain the same, each unit will present new design and operational problems because of the low gravity environment. Under a reduced-gravity condition, the forces required to suspend particles are as follows:

- Drag force on the particle. The gas or fluid stream flowing through the vessel will lose momentum to the particles. The net force on the particle will be parallel to the flow direction of the fluid.
- Particle impact at solid surface. The propeller blade transfers momentum to the particles and the particles in turn lose momentum at the walls.

- Surface tension and Marangani Flow. The surface tension forces between gas and solid are likely to be small relative to drag forces in systems with large circulatory or bulk flows.

- Buoyancy and gravity forces. These decrease to zero as the gravitational field disappears.

No attempt is made to establish mathematically the exact nature of the circulation currents in this study. The injection of gas should be toward the axis of the propeller blade to disperse as many particles as as possible.

Gas phase. Marangani forces on a gas bubble, because of either temperature or concentration gradients and hence surface tension, may influence the bubble motion (23). With pressure pulse, bubbles suspended in a liquid under conditions of weightlessness will approach one another if the natural frequencies of bubble oscillation are greater or smaller than the pulsation frequency, and vice versa. A bubble situated close to the wall of the vessel will move toward the wall during a pressure pulse (24). In non-pulsing flow, bubble formation is encouraged by the forces emanating from the mechanical agitator. In the presence of solid particles, it is difficult to estimate whether bubbles will form and if they do, to what extent they will grow.

Typical earth analysis. The gas velocity required for incipient fluidization (when particles first begin to rotate) has been shown by Davidson and Harrison (25) to be given by

$$U_o = 0.00114\, g\, d^2\, (\rho_s - \rho)/\mu$$

in which:

U_o = superficial velocity of fluidizing medium, cm/sec

g = gravitational acceleration

d, ρ_s = particle diameter and density, respectively

ρ, μ = fluid density and viscosity, respectively

Apparently as gravitational acceleration is reduced, the velocity of fluid necessary for fluidization is also reduced.

A gas bubble in a fluidized bed differs from that in a liquid in that particles and gas enter and leave it. Its rise velocity is given by

$$U_b = 0.71\, g^{1/2}\, V^{1/6} \left[(1-\epsilon_o) / \left(\frac{\rho_s}{\rho_s - \rho_f} - \epsilon_o \right) \right]^{1/2}$$

in which:

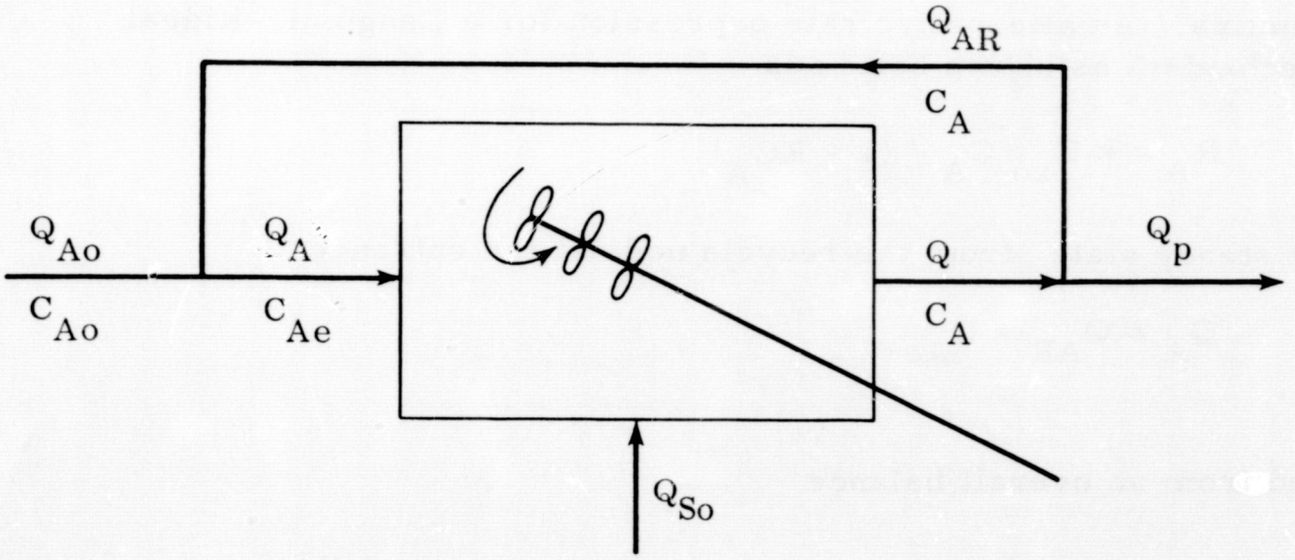
V = volume of the bubble

ϵ_o = void fraction at incipient fluidization

Here again, one would expect bubble velocities to be significantly reduced at low gravity. Whether a bubble will form or not at near zero gravity is in doubt, with only a slight understanding of fluidized bed bubble formation at unit gravity to act as guide. Some non-reactive simulated solid-gas mixing studies will be needed.

Conservation equations

As an example, the conservation equations are derived for a slurry reactor. The method, with some modifications, may be extended to a stirred fluidized bed.



Component balances across reactor. Assuming good mixing, the reactor may be schematically represented as above. The quantities

are defined as follows:

C_A, C_{Ae} = concentration of ethylene leaving reactor, and entering reactor, moles/vol.

C_p = concentration of polymer leaving system

Q = volumetric flow rate, vol/time

Accumulation = Net input + Generation rate

$$\frac{dC_A}{dt} = Q(C_{Ae} - C_A) + R_A V$$

The reaction in terms of ethylene consumption may be depicted as

$$n\, C_2H_4 \longrightarrow (C_2H_4)_n, \quad \text{where} \quad n \approx 1,400$$

with a rate expression for ethylene formation

$$R_A = -R_p = -kC_{xo}\, C_A\, (1 + KC_A)$$

in which: $k = k_o \exp(-E/RT)$, a temperature dependent quantity, and C_{xo} is initial catalyst concentration. The dependence on catalyst concentration was obtained from Friedlander's (26) work on molybdenum/alumina. An alternative rate expression for a Langmuir-Rideal mechanism as shown before is

$$R_A = k\, C_{xo}\, C_A^2 / (1 + KC_A)$$

At steady state, from the recycle node at the entrance

$$Q_A = Q_{AR} + Q_{Ao}$$

and from an overall balance

$$Q_p = Q_{Ao} + Q_{So}$$

The recycle rate may be maintained by controlling the overall residence time which in turn controls the desired conversion. There may very well be an optimum value of recycle rate.

Energy balance

$$\frac{dU'}{dt} = q - P\frac{dV'}{dt} - \Delta\left[W\left(u + PV + \frac{1}{2}\ \frac{\langle v^3 \rangle}{\langle v \rangle}\right)\right]$$

in which U', V' = Internal energy and volume of system, respectively
u, V = Intensive (unit mass basis) for these properties
q = Heat input
v = Velocity of fluid
W = Flow of mass into system = ρQ

At steady state, if kinetic energy is neglected

$$q = -\Delta\left[\rho Qh\right]$$

where h = enthalpy of fluid (mass basis) and h is primarily dependent on the heat of reaction

$$\Delta h_r = -.9 \text{ k cal/g } C_2H_4 \text{ reacted}$$

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N70-20547

INDUSTRIAL CHEMISTRY IN SPACE* ≠

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ABSTRACT

Chemical manufacture relates to a space environment as it relates to air-free chemical preparation. For example, oxygen-free copper would be a premium product.

I. INTRODUCTION

The usefulness of space ships as chemical factories rests on two points: (1) the elimination of the need for a container and the attendant possibilities of contamination and (2) the elimination of air.

Metallurgists are well aware of the contaminating effects of crucibles and it seems very likely that air has similar serious deleterious effects on the properties of many solid products. It seems likely also that the growth of crystals such as diamond from carbon vapor is seriously retarded by monolayer impurity films from these sources.

Therefore, we suggest that the possible merits of chemical manufacture in orbit outside the atmosphere be examined.

II. ORBITAL CHEMISTRY TECHNIQUES

A. DISTILLATION

Two heat sources--sunlight and radio frequency inductive heating--are

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available so distillation onto surrounding metallic collector baffles possessing blackened rear surfaces to facilitate radiative cooling appears to be possible. Since rf power carries a heavy weight penalty, every effort should be made to use sunlight.

At our distance from the sun 2 calories per minute fall on each square centimeter of surface normal to the solar direction so a parabolic mirror 100 meters in diameter might be able to deliver about eleven megawatts at its focal point perhaps a hot spot area of 100 square centimeters for a 110 kilowatt per square centimeter influx could be intersected. Such a heat source would evaporate a metal like copper at something approaching twenty five pounds per second! (Heat of vaporization taken as 60 kilocalories per mole.) For carbon (170 kcal/mole) the rates would be less but one sees that in principle tons of material could be processed per day.

Weightlessness makes both the deployment of the mirrored parabolic surface (presumably aluminized mylar similar to that used in the Echo satellites) and the feeding of material to the evaporator feasible. Figures 1a and 1b present schemes. Some problems exist in the design and deployment of the collector baffles but they appear to be manageable.

In the first design (Figure 1a) the two megawatts of sunlight is restricted to a 60° cone and thus can enter a rather narrow evaporator port possibly about as shown in Figure 2. The tungsten baffles constitute an open house with many spaces for gas escape but allowing no escape of the vapor to a slight extent through the light beam port.

Tungsten, with a melting point at 3410°C and a boiling point at 5927°C, should radiate the heat from the condensing vapor. Table I gives data for various candidate substances.

B. CRYSTAL GROWTH

The growth of crystals from a melt heated by the solar beam seems to be particularly straightforward. Due to the zero-gravity environment, perfectly homogeneous spherical single crystals of large size could be grown by seeding a slightly supercooled melt. By distilling away impurities which would serve as nucleating sites and making use of the high cooling rates possible in space, the manufacture of large amorphous spheres of normally crystalline materials also seems possible.

Also epitaxial growth on seed crystals from the vapor should result in near perfect superpure crystals.

C. PLASMA CLEANING OF SURFACES

Surfaces probably can be cleaned by alpha particle (helium ions) bombardment or by hydrogen plasma. Thus a 1 curie polonium source ($2.2 \cdot 10^{12}$/min.) should remove a monolayer of oxide from 1 cm^2 in about 1 hour exposure in the space vacuum. This technique probably would be more practical than supplying radio frequency power to generate beams of helium and/or hydrogen plasma.

D. DEAERATION BY BAKING IN SPACE

There is a distinct possibility that heating of a finely powdered solid or a liquid in the space vacuum, if accompanied by proper stirring, will accomplish a degassing of air adequate to essentially remove it.

E. WELDING AND JOINING

It would seem to be obvious that contact pressure welding should be infallibly effective in a spacecraft.

III. CONCLUSIONS

The possibilities of industrial chemical production of impurity sensitive materials is intriguing to say the least. At this time more actual evidence of the advantages of air-free and container-free production need demonstration.

We have some examples which are dramatic and convincing. Oxygen-free high conductivity copper in making vacuum circuit breakers practical serves as a good case. It has also been established that beryllium can be made ductile by vacuum distillation or zone refining.

It is our hope that crystal growth will be substantially facilitated by the removal of the inhibiting effects of air. Our main goal in this area is large sized diamond grown from carbon vapor.

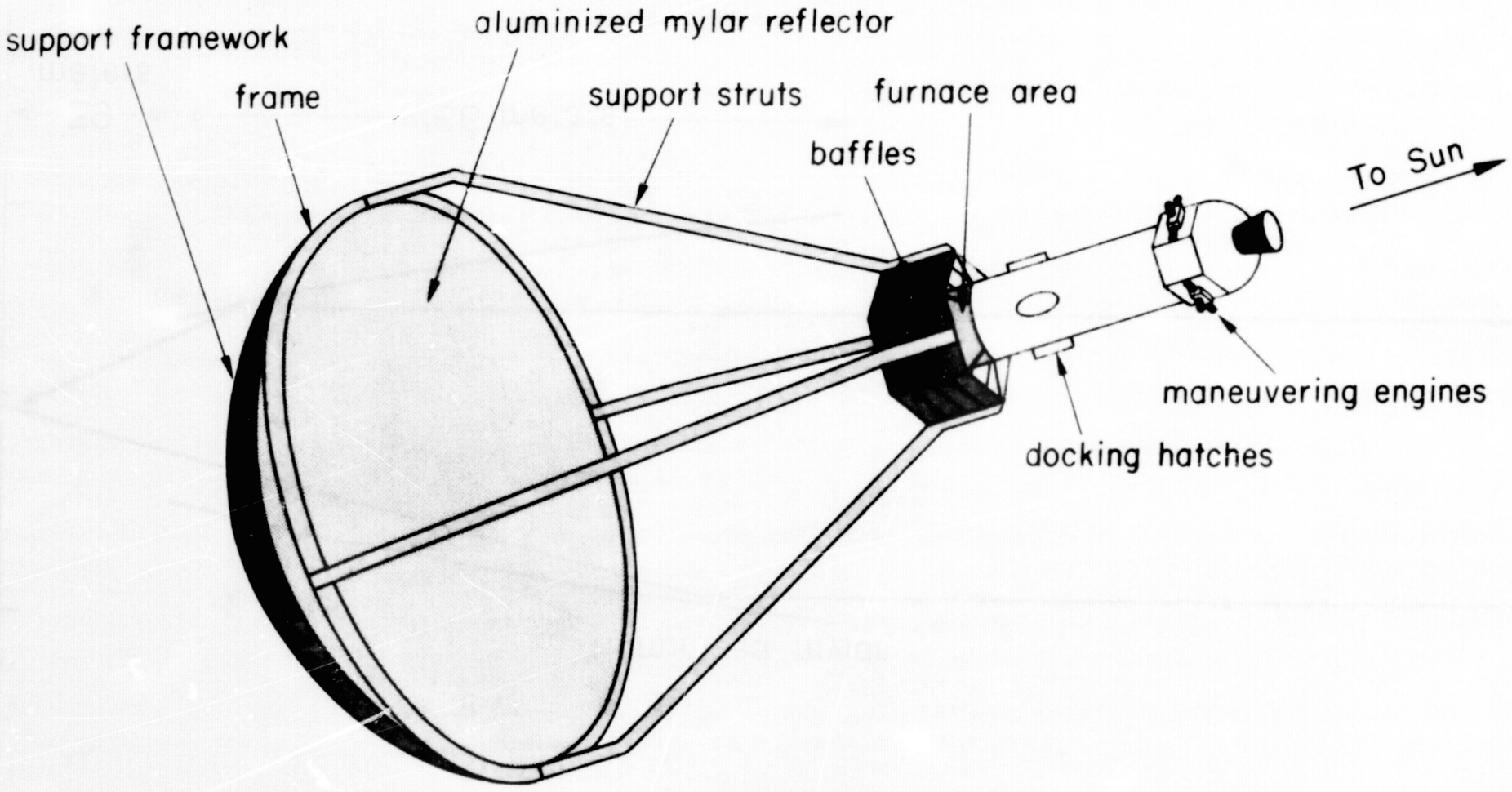


Figure 1(a). Orbiting Solar Furnace

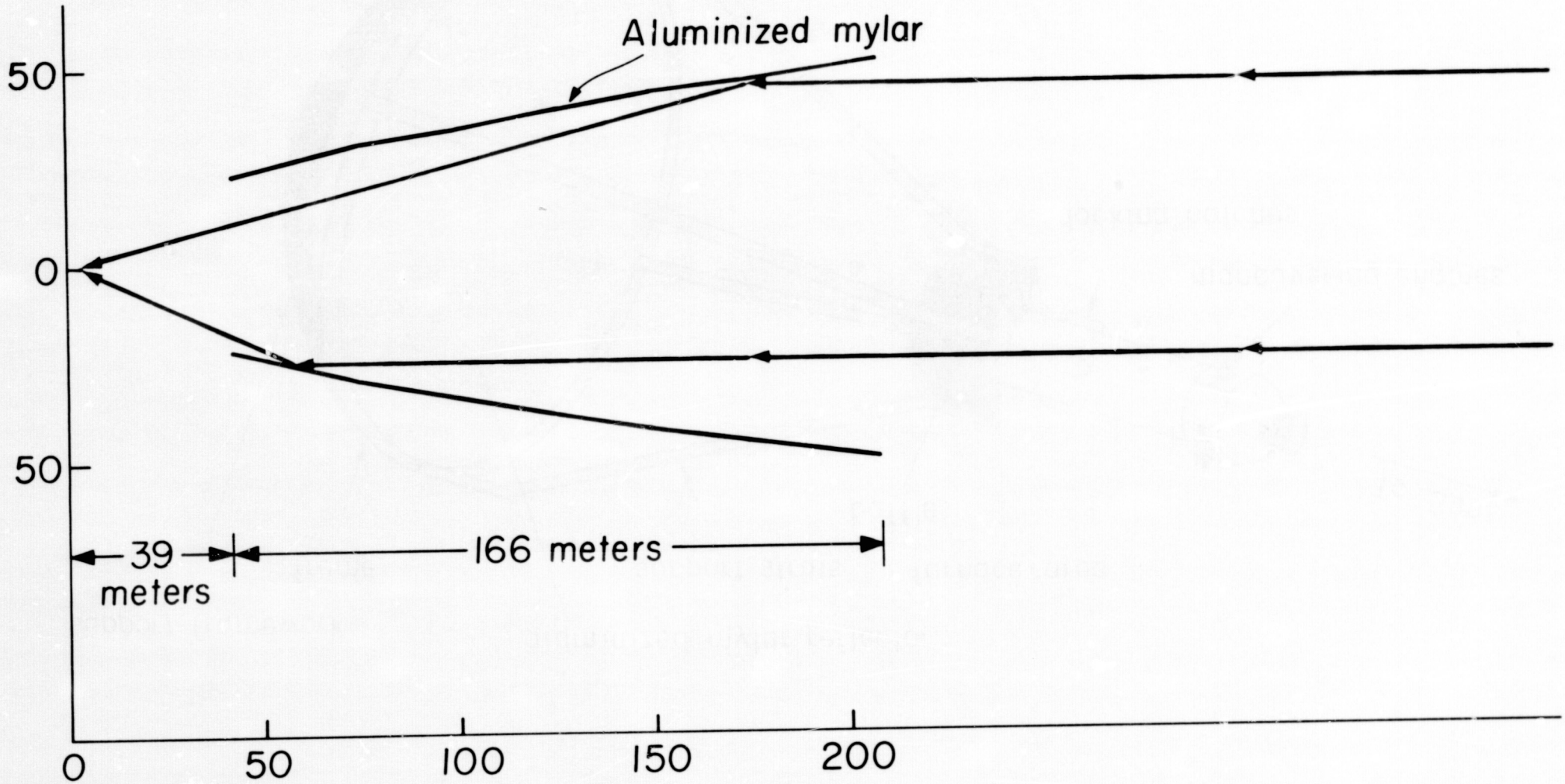


Figure 1(b). 2 Megawatt Soiar Furnace for Space Chemical Plant

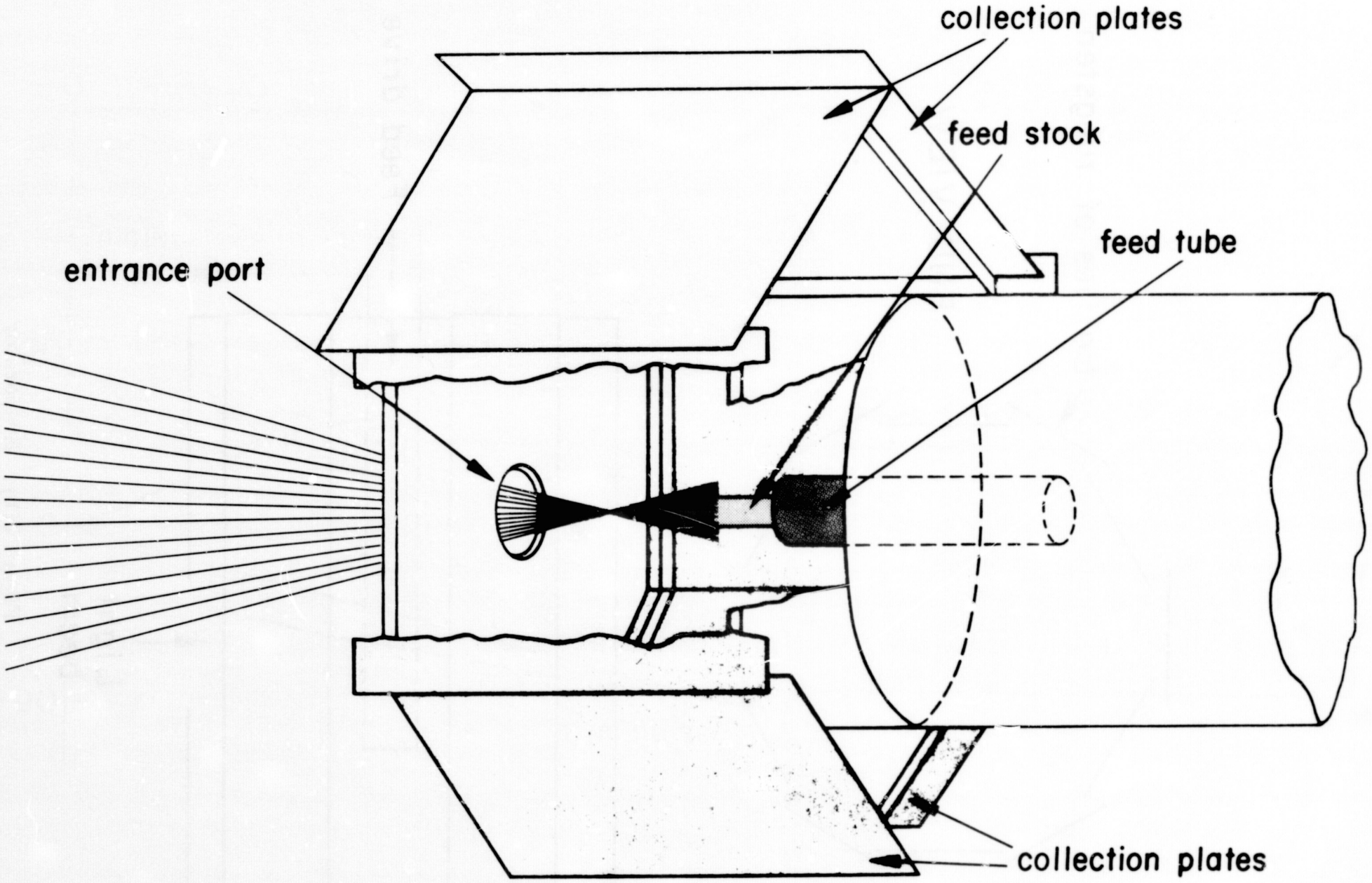


Figure 2(a). Evaporation Area of Solar Furnace (external support network not shown)

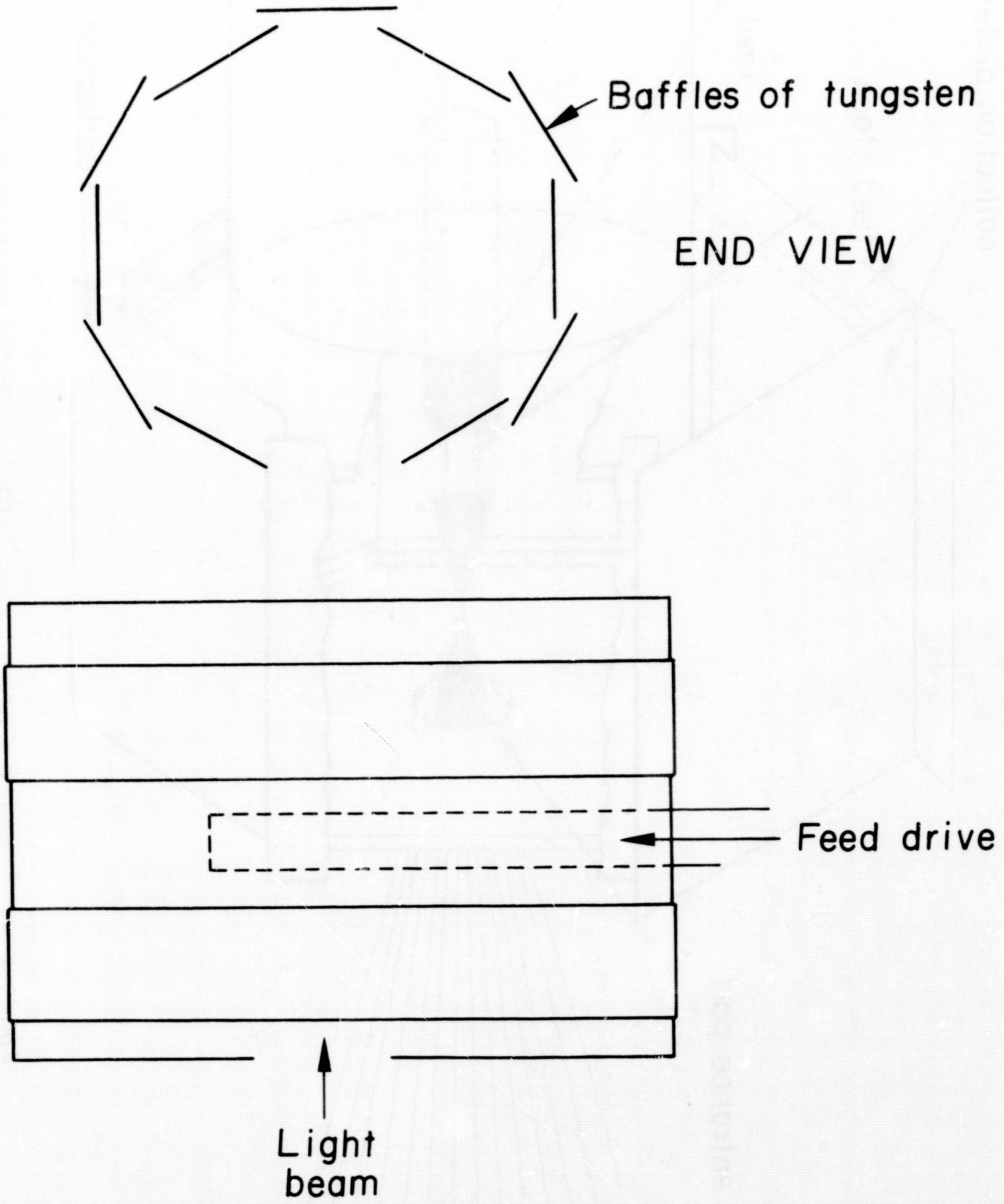


Figure 2(b). Evaporator

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ON THE PRODUCTION AND SEPARATION OF INDUSTRIALLY USEFUL ISOTOPES IN SPACE

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ABSTRACT

Preliminary work on a concept of an orbital facility for production and separation of industrially useful isotopes will be discussed. The production facility consists of a large solar powered electrical generator and a high current charged particle accelerator that produces isotopes by bombardment of a suitable target. Several possible methods for chemical or physical separation of the produced isotopes in space will be discussed. Emphasis will be placed on the production of plutonium or uranium-233 for use in terrestrial power reactors. Possible advantages of an orbital facility over a terrestrial one will be discussed.

Environments that are accessible in space and that have characteristics that are difficult or impossible to achieve on the earth can make possible new large-scale industrial processes that will directly benefit people living on earth. Among these characteristics are the following:

1. A state of weightlessness.
2. A vacuum that extends throughout an arbitrarily large volume.
3. The presence of the earth's magnetic field outside the earth's atmosphere.
4. Solar energy at intensities ranging from zero through 0.14 watts per square centimeter at the earth's orbit to approximately 7.0 kilowatts per square centimeter near the sun's surface.

5. Line-of-sight observational access to all of the earth's atmosphere and surface.

6. Access to raw materials, particularly on the moon and asteroids, the extraction of which will not affect the earth's natural environment.

7. Physical separation from the earth's biosphere.

For an industrial process in space to be worth developing, however, it should satisfy several conditions:

First, the total costs per unit mass of the product made in space, including all transportation costs to and from space, should be competitive with the cost of making the product by terrestrial means. In the case of products that are made from raw materials originally found on the earth, the value of the product must obviously be greater (in many cases, much greater) than the cost per unit mass of placing material in space and returning it to the earth at the time when large-scale production in space is anticipated.

Second, the expected market for the product should be large enough to justify the total anticipated costs of development and use of the space-based production facility.

Third, the "externalities" associated with the space production process should compare favorably with those associated with terrestrial production of the same product. Such externalities include the danger of major accidents, health hazards to the public and operating personnel, pollution of the earth's environment, aesthetically unpleasant (or pleasant) side effects, and spoilation (or conservation) of scarce raw materials.

Note that I have not insisted that the cost of a product be less if made in space than if made on earth, but only that the cost be "competitive." Insistence on lowest cost methods for production, such as have characterized much of modern industry, has often led, through pollution and other harmful side effects, to very high external costs to the general public. I am rapidly becoming convinced that perhaps the most important benefit to humanity to be found in large scale human activity in space will be through a gradual transfer of industrial processing and manufacturing, with all of their damaging effects on the earth's natural biological environment, to space. If, as now seems most likely, there is little or no biological activity on the moon or the asteroids, I would far rather have us do our massive scrapping, digging and boring for raw materials there, and throw our waste heat and poisonous chemicals and radioactive wastes into distant space or the sun, than to continue to foul this beautiful and delicately balanced planet that we live on.

If we should undertake a gradual transfer of industries to space, it seems reasonable to consider parts of the nuclear industry among the first. Some industrially useful radioisotopes, such as Californium 252, cost of the order of a billion dollars a gram or more! Plutonium for use in nuclear power reactors currently costs approximately $10,000 per kilogram, which is about an order of magnitude greater than the present costs of placing materials in earth orbit. The foreseeable worldwide market demand for plutonium is in the range of tens of thousands of kilograms per year within the next decade. The worldwide market demand for fabricated fuel elements containing plutonium or U-233 for power reactors is likely to be of the order of $100 billion per year by the end of this century. So these materials satisfy our requirement for high unit values and large expected markets.

Next I want to consider some of the possible advantages, other than material costs, of producing nuclear fuel materials in space. Although U-235 is the primary fuel in almost all power reactors in use or under construction, conversion to breeder reactors that convert the vastly more plentiful, naturally occurring, U-238 or thorium-232 to plutonium or U-233 is generally expected to start on a big scale during the 1980's.

In principle, all the foreseeable demands for plutonium of U-233 can be met by use of such breeder reactors. In practice, however, there are serious difficulties. Fast breeder reactor cores are inherently unsafe, and require considerable care, extensive engineered safeguards, and containment structures in order to assure that, under all credible circumstances, there can be no major release of radioactive products to the environment. Thermal breeders that use the thorium-U-233 breeding cycles are also under development, and there is some hope that the cores of such reactors can be made inherently safe against accidental loss of the capability either to cool the reactor or to shut down the reactor by insertion of control rods. In both types of reactors, however, the requirement that they produce more neutrons than are consumed to sustain a chain reaction imposes severe restrictions on the types of materials and design concepts that can be used. Furthermore, all breeder reactors now under development require extensive fuel reprocessing facilities to sustain an economic overall breeding fuel cycle. Such facilities produce huge volumes of radioactive wastes that must be contained and disposed of in ways that permanently assure that they will not flow into the natural environment.

If, however, natural uranium or thorium could first be converted to plutonium or U-233 by some means other than the use of breeder reactors, and supplied to the nuclear industry in fabricated fuel elements that, by use of suitable "burnable" poisons, could have sufficiently high fuel burnup efficiencies to avoid the need for breeding in power reactors or chemical reprocessing of fuel, the safety and radioactive waste disposal problems would be greatly alleviated. This possibility

would be economically attractive if the plutonium or U-233 could be supplied at a cost of about $10,000 per kilogram or less. This is the primary objective of the isotope production concept I shall briefly discuss.

Plutonium or U-233 can be produced by neutron capture in natural uranium or thorium. Neutrons for this purpose can be supplied in at least three ways: by fission in a reactor, by charged particle beams that produce neutrons in a suitable target, and by thermonuclear explosives. For reasons just given, I shall exclude the first.

Nuclear explosives are, by far, the cheapest sources of large numbers of neutrons that we have: a 10 Megaton thermonuclear explosion can be made to release enough neutrons to produce more than 5,000 kilograms of plutonium. The problem is to do this in such a way that the product can be contained and economically processed without seriously (or even catastrophically!) preturbing the environment. The plutonium can either be produced in the explosive device itself or by irradiation of a suitably placed and protected blanket that is not melted or vaporized by the explosion. Both concepts have been studied in some detail for use underground or on the earth's surface. We have recently done some preliminary thinking about the use of such techniques in space -- confining the explosions beneath the surface of the moon or, conceivably, a large asteroid, or irradiating blankets by sequential explosions in space. Partly because of the current ban on all nuclear explosions in space, however, we have concentrated more effort on a highly preliminary study of isotope production by the impact of beams of high energy charged particles on a suitable target in space. I shall therefore restrict the remainder of this discussion to that concept.

The concept consists of six primary components: A solar energy conversion source of electric power, a linear accelerator for producing a high energy beam of deuterons, a target within which the isotopes are produced, a facility for separating the isotopes after they have been made, a facility for fabrication of power reactor fuel elements, and supporting facilities required for operation of the system in space.

The spirit of this highly preliminary analysis has been to make all estimates on the optimistic side, to determine whether the concept can be definitely judged to be economically infeasible for the foreseeable future. As will be seen, we have concluded that the concept shows enough promise to warrant more detailed investigation, particularly if one is optimistic about prospects for sharp reductions in space transportation costs within the next several decades.

In order to review this concept in the context of large scale production operations in space, we have chosen values of the primary parameters that will appear very large to most people. If a concept such as this

were developed, it is clear that a development program would proceed through a large number of steps that would include many experiments and tests using much smaller components than those suggested in this paper.

We start from a premise that the production facility will produce 10,000 kilograms of plutonium or U^{233} per year, at a target cost of not more than $10,000 per kilogram, corresponding to a total annual production cost of the order of $100 million per year. This is comparable to the current total rate of consumption of special fissionable isotopes in power reactors in the United States today, and only a few percent of the expected worldwide consumption rate in 1985.

The plutonium or U^{233} is produced by capture of neutrons in U^{238} or Th^{232}. We propose that the neutrons be produced by the impact of approximately 200 MEV deuterons on a target that serves the triple purpose of yielding neutrons following deuteron impact, capturing the neutrons in fertile material, and radiating the deuteron and neutron capture energy into space. The deuteron accelerator is a linear accelerator of unspecified design that converts electrical energy, with high efficiency, to kinetic energy of the deuteron beam. The electric power source consists of a very large, spherically or parabolically surfaced solar energy collector that is used to concentrate the solar energy flux to produce sufficiently high temperatures for driving an electrical power generating system. Working backwards from the presumed plutonium production rate, we have derived the highly tentative production facility parameters shown in the following tables, using the indicated energy conversion efficiencies:

TABLE I

SOLAR ELECTRIC POWER SUPPLY

Electric power output	3,000 Megawatts
Total efficiency ($\frac{\text{electric power}}{\text{intercepted solar power}}$)	40%
Total intercepted solar energy	7,500 Megawatts
Area of solar energy reflector	5×10^{10} cm^2 (3.5 km^2)
Radius of solar energy reflector	1,100 meters
Thickness of aluminized milar reflector	10^{-3} cm = 10^{-3} g/cm^2
Mass of reflector material	5×10^4 kg
Mass of reflector supporting wires	5×10^4 kg
Maximum temperature of electric generator materials or working fluid	3000° K
Mass of electrical generators system (30 kw (e)/kg	10^5 kg

Table I, continued.

Average surface temperature of radiator	1300° K
Area of radiator (emissivity = 0.9) (14.3 watts/cm^2, 4,500 MW radiated power)	3.4×10^8 cm^2
Mass per unit area of radiator	.3 g/cm^2
Total mass of radiator	10^5 kg
Radius of radiator	110 meters
Total mass of power supply	3×10^5 kg
Total electric power/mass of power supply	10 kw/kg

TABLE II

DEUTERON LINEAR ACCELERATOR

Deuteron energy	200 MEV
Total beam power = electrical input	3,000 Megawatts
Beam current	15 amperes
Assumed length of accelerator	1,000 meters
Average electric field along accelerator	2,000 volts/cm
Assumed total weight of accelerator, including electric power conversion system, accelerating drift tubes, etc.	1.25×10^5 kg

TABLE III

TARGET AND BREEDING BLANKET

Assumed number of neutrons/incident deuteron	10
Power that must be dissipated by radiation from target (beam power plus neutron capture energy)	4,500 Megawatts
Assumed target surface temperature	2300° K
Area of target (σ = .8)	3.4×10^7 cm^2
Deuteron beam current density at target	4.5×10^{-7} amp/cm^2
Mass per unit area of target (U^{238} or Th^{232} + BeO + C)	20 g/cm^2

Table III, continued.

Mass of uranium or thorium in target (UC^2 or ThC^2)	5×10^4 kg
Total mass of target	6.8×10^5 kg
Total mass of plutonium or U^{233} produced per year	10,000 kg

TABLE IV

ISOTOPE SEPARATION
AND FUEL FABRICATION FACILITIES

Time between separations of Pu^{239}, Pu^{241}, U^{233}, U^{235} from uranium or thorium and fission products in blanket	1 year
Concentration of Pu or U in U^{238} or Th^{232} layers of blanket prior to separation	20%
Total mass of material to be separated	5×10^4 kg
Assumed total mass of isotope separation and fuel fabrication facilities	1.25×10^5 kg

TABLE V

SUPPORTING FACILITIES
REQUIRED FOR OPERATION OF SYSTEM

Assumed total mass of supporting facilities (manned space station, control equipment, auxiliary power supplies, life support equipment, station-keeping propulsion units, system assembly equipment, shops, etc.	5×10^5 kg
Assumed total annual mass that must be placed in orbit to supply facility with operating personnel, depleted supplies, and uranium or thorium	1.5×10^5 kg/yr

TABLE VI

SUMMARY OF
OVERALL SYSTEM PARAMETERS AND ECONOMICS

Total mass of facility	1.7×10^6 kg
Assumed useful life of facility, including non-nuclear materials for breeding blanket	20 years
Total operations supply mass placed in orbit @ 100,000 kg/yr	2×10^6 kg
Assumed cost per unit weight of transport to orbit and rendezvous with facility components	\$200/kg
Total cost of placing facility and operations supply mass in orbit	$\$3.7 \times 10^8$
Total value of fissionable matter produced in 20 yr operation, @ \$10,000/kg	$\$2 \times 10^9$
Total allowable cost of fabrication of all payloads, of ground support operations, and manual space operations to achieve "break even" point (Total value of fissionable material produced and recovered = total costs of 20 year operation)	$\$1.3 \times 10^9$

The parameters listed in the above table, though internally consistent, are first order estimates that are not based on a detailed analysis of a specific proposal for each component of the system. Since the entire concept is in the very early stages of conceptual design, I do not yet include any systematic description of the components. I have chosen, rather, to list the following qualitative points about some of the components.

1. Solar radiation pressure acting on the solar energy collector is apparently sufficient to maintain the shape of the collector mounted on a grid of thin, high strength wires, and to assure that the collector is directed toward the sun when it is not in the earth's shadow. A low power, high specific impulse propulsion system may be required to prevent the orbit from elongating. A stable configuration can be achieved by a parachute-like arrangement of the collector sheet, wires and appropriate masses.

2. A high temperature, closed cycle gas turbine appears to be an attractive method for converting the focused solar heat to rotational

kinetic energy. If a Brayton cycle engine is used, the working fluid (helium or argon, to have a high value of γ) can be cooled after the expansion part of the cycle by circulating it through a system of thin-walled radiator pipes before the compression part of the cycle. The peak temperature in the cycle is chosen to be as high as possible, to obtain a high efficiency, and to allow radiation of the waste heat at a high temperature. The expander, compressor, heating chamber, and radiator weights are based on a peak operating pressure of the order of 100 pounds per square inch. It is likely to be necessary to use superconductors to achieve the low weight per unit power assumed for the system to convert rotational kinetic energy to electrical energy. It is important to achieve a very high rotational velocity in both the engine and the generator, which can perhaps be combined in the same mechanical unit.

A variety of thermoelectric, thermionic, and magnetohydrodynamic conversion techniques may also be suitable, and perhaps require less mass per unit power output.

I realize that the electric power output per unit weight shown in Table I is several orders of magnitude greater than those now achievable with solar panel arrays. This is the combined result of using a very large, low mass collection and focussing system, very high surface temperatures for radiating waste heat, and the scaling benefits that come from using a very high power output system. We are currently studying the dynamics of such large collectors, when subjected to gravitational tidal forces, radiation pressure, and a variety of electromagnetic forces.

3. The deuteron accelerator should be designed from first principles, to assure that appropriate advantage is taken of the vacuum environment and state of weightlessness. If it saves mass, use should probably be made of superconductors. The thrust delivered by the deuteron beam is small -- of the order of a few kilograms -- and should therefore not produce significant tensions in the accelerator-target system.

4. The target should be sufficiently thick to stop the neutrons produced by the deuteron beam, requires moderating material to slow neutrons down to the resonance capture region, and must consist of materials that have a low vapor pressure at temperatures somewhat above the surface radiating temperature. We have, therefore, chosen uranium or thorium carbide, graphite, and beryllium oxide to make up the blanket. There is some optimum ratio of graphite to BeO that will minimize the total mass per unit area required for a given absorption probability per neutron. We believe that a thickness of $20 g/cm^2$ should guarantee capture of more than 75% of the neutrons, since the transport mean free path of several MEV neutrons in BeO is approximately 2.5 cm ($7.5 g/cm^2$). The UC_2 or ThC_2 would probably be distributed in thin sheets throughout the blanket, so that only they would have to be processed for isotope separation.

5. One of the likely reasons why this general type of isotope production facility may cost less to construct in space than on the earth's surface is the result of the requirement for an immense evacuated region to accommodate the deuteron beam and the accelerator's accelerating electrodes or drift tubes. For the values of the beam parameters we have chosen, the charged particle beam is likely to be several tens of meters in diameter, to maintain a stable beam. The very preliminary choice of a length of one kilometer was made to assure that there would not be problems of electron cascading between electrodes. The corresponding volume of the evacuated region is thus of the order of a million cubic meters which, though not necessarily completely beyond reason for a terrestrial vacuum, is orders of magnitude beyond any present experience. Further economic and technical analyses of this concept should obviously include comparisons between the costs of terrestrial and orbital facilities for producing the same product.

6. Several concepts for separation of the fissionable materials from the isotope production blanket come to mind, and each of these should be examined in some detail before even preliminary choices of a specific method can rationally be made. Among the methods that might be especially attractive for use in space are chemical separation techniques, gas centrifuge methods, and any of several methods for electromagnetic separation. The assumed facility weights shown in Table IV are simply preliminary goals. We have taken a cursory look at the possibility of electromagnetic separation of ion streams of the fissionable isotope-bearing part of the production blanket, using the earth's magnetic field. Space charge defocussing of the ion stream appears to be a problem, but several space charge neutralization techniques at least appear to warrant further study.

7. The estimated and postulated costs given in these tables do not allow for fabrication of finished reactor fuel elements in an orbital facility. It is assumed, rather, that the separated fissionable materials would be packaged and returned to earth for incorporation into fuel elements in terrestrial facilities. It is possible, however, that some of the fabrication and processing techniques that have been discussed at this symposium, as well as other techniques that make use of the unique environments available in space may make it attractive to fabricate the fuel elements in space. We propose to examine this possibility further.

8. Estimates of the required supporting facilities and operations in space and on the ground are all highly speculative, and not based on any specific analysis. If the concept should be developed for production of a significant fraction of the fissionable material consumed in the world's power reactors several decades from now, production rates are likely to be an order of magnitude or more larger than the 10,000 kilograms per year assumed for our example. In this case, the number of operating personnel in space could be several hundred, without raising the total unit cost of fissionable materials above $5-10,000 per kilogram.

I should like to close by listing a few types of orbital experiments that relate to this concept and that appear worthwhile if it is assumed that more detailed study of the concept than we have carried out so far should make it appear practical and economical.

1. Observation of the dynamics of large, thin membranes subjected to forces due to the earth's gravitational field gradient, radiation pressure from the reflection of solar energy, reaction forces due to the strength of the membrane and its supporting elements, and electromagnetic forces due to charging of the membrane and its interatction with the earth's magnetic field and charged particles in space. Note that such experiments are relevant to many possible applications of large space power systems that use large collectors to focus solar energy.

2. Tests of relatively small scale prototypes of solar power generators of the type I have been discussing. A prototype with an electrical output of approximately 100 kw would require a total mass of the order of 100 kilograms or less, and a collector with a radius of approximately 10 meters.

3. Studies of the electron emission of various configurations of conductors subjected to electric fields of the same order (several thousand volts per centimeter) as those envisioned near the accelerating electrodes of a charged particle accelerator.

4. Observation of the radiation emission rates and material evolution rates from surfaces of materials that are candidates for high temperature radiators, as functions of temperature (up to approximately 1000° C.), and in the space vacuum environment. The measurement of surface material evolution rates may be difficult to make realistically in ground-based vacuum simulation facilities of reasonable size.

5. Tests of scaled prototypes of ultra-high velocity gas centrifuge isotope separation systems that make use of the state of weightlessness.

CLOSING REMARKS

Mathias P. L. Siebel

GEORGE C. MARSHALL SPACE FLIGHT CENTER
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In programs of the nature of space manufacturing, it is difficult to gage progress from day to day. However, if we compare the situation today with the situation last year at the time of our first meeting, I am more convinced than ever about the great future of this program.

Last November we had a first meeting. The purpose was to acquaint leading personalities in industry, government and universities with the potentials of space manufacturing: We talked about the production of materials from the melt, we talked about crystal growth, about membrane drawing and about the casting of composite materials. We described the bare bones of some proposed experiments and we made some inspired guesses about possible products such as metal spheres and turbine blades. We had no clear separation between process technology and products.

Last year, as this, we had a great deal of enthusiasm and somehow it caught on, for today very many people and organizations are involved and have worked on the program as evidenced by the excellent and original presentations you have heard during the last two days.

Today, we are talking not only about producing novel materials from the melt, that is solidification processes, but we are studying biological processes, space chemistry, diffusion reactions and separation processes applicable to isotopes, rare earths and pharmaceuticals. We have clearly defined and will fly some initial engineering experiments in the first earth orbiting workshop. Many other experiments are proposed for later flights such as the making of special glasses, high temperature high strength materials as well as composite materials, various crystals, polymers, vaccines, fermentation products and many others. In the last

year we have succeeded to separate, in our minds, the general processes from the specific products. Through a clear realization that an understanding of the process parameters is of prime importance, we have been able to initiate fundamental studies which will allow us to optimize the experiments and to judge proposals for feasibility and relevancy.

As regards "flying machines", that is the vehicles in which to perform experiments and in which to transport men and materials: Last year we were talking about an initial space station which was very limited in payload and which had no serious follow-on except that we had expected some kind of space station in the late 1970's. Today, we can look back on a successful lunar landing. We can look forward with assurance to the AAP orbital workshop in 1972 with a great payload capability. We can look forward to a follow-on workshop a year or two later. NASA and the President's Space Task Group, chaired by Vice-President Agnew, have put forward a plan which includes a large earth orbiting space station and a shuttle plane to ferry materials and people from earth to the station and back -- this within the next 7 - 10 years. The space station, most likely, will have attached to it individually launched experiment modules of various kinds, including manufacturing development modules. These will allow you to begin the commercial exploitation of the know-how gained during the experimental phases in the AAP orbital workshops. You will have access at a reasonable cost to this unique zero "g" environment and will find there facilities in which to develop products useful on earth.

A year ago we had no detailed plan or NASA policy for the participation of industry. We did however extend an invitation to you to come and work side by side with us at Marshall if you deemed this appropriate. Today, we have in the making a detailed policy by NASA which will allow you to participate in our flight programs. We will announce flight opportunities, we will have procedures directed at safeguarding your patent and proprietary rights.

As I listened to the papers in this meeting, I was reminded of young Tom Barton who in 1894 went to his boss at the Patent Office and tendered his resignation. When asked why he wanted to terminate a promising career so early in his life, his answer was that he did not see what else could be patented, almost all things possible had already been invented. In short, he did not see a future in the Patent Office. Gentlemen -- I urge you not to become latter day Tom Bartons. Not all has been invented, space manufacturing technology has barely started. Many gaps exist

in our technology and many areas of application of the weightless environment remain to be discovered. Much more work, of course, is needed by all of us to bring the program to fruition and to make it commercially attractive.

Last year I concluded my remarks by inviting you all to come and fly with us -- this year I repeat the invitation. And I add -- gentlemen let's go to work right now for the flight opportunities are suddenly much closer than they seemed a year ago.

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APPENDIX B
BIOGRAPHICAL SKETCHES

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Dr. von Braun is Director of NASA's Marshall Space Flight Center. He received his Ph.D. in physics from the University of Berlin at the age of 22, and later served as technical director of the Peenemuende Rocket Center, where the V-2 was developed. In 1945 he came to the United States under contract to the U.S. Army, and was active in the Army rocket and missile programs. He was responsible for the technical development of the Redstone and Jupiter missiles, modifications of which were used to launch the earliest United States payloads into earth orbit and into deep space.

WILLIAM O. ARMSTRONG

Mr. Armstrong, with NASA Headquarters, received his B.S. in aero engineering from the University of Alabama in 1951. More recently he completed a course in Management Development at Harvard. Currently serving as Director of Payloads in the Office of Manned Space Flight, Washington, D.C., he has spent 18 years in the aero engineering field and has authored or co-authored 14 technical papers.

DR. EMIL W. DEEG

Dr. Deeg, with the American Optical Corporation, received his doctorate in physics from the University of Wuerzburg, Bavaria, Germany, in 1965. Presently Chief of Ceramic Research, he has spent 15 years in the field. Dr. Deeg has published more than 60 articles in professional journals and books on glass and ceramics; a book, Glas im Laboratorium; articles on glass in the Brockhaus Encyclopedia; and has more than 30 patents.

DR. EDWARD C. HENRY

Dr. Henry received his Ph.D. and Cer.E. degrees from Pennsylvania State University, his M.S. from the University of Nevada, and his B.S. from Rutgers. Presently a Consulting Engineer at the Space Sciences Laboratory of the General Electric Company, he has spent many years in university teaching

and research. From 1961 to 1969 he was chairman of the National Academy of Sciences — National Research Council's Committee on Ceramic Chemistry.

ROBERT H. WITT

Mr. Witt holds BMetE and MMetE degrees from the Polytechnic Institute of Brooklyn and has taken additional graduate courses at New York University. Presently a Welding Group Leader in the Advanced Manufacturing Development Department of Grumman Aerospace Corporation, he has 20 years of diversified experience in the fabrication of aluminum, steel, high-temperature metals, and refractory alloys. Mr. Witt has over 20 published articles on welding and metallurgical studies.

DR. R. THOM FROST

Dr. Frost received his A.B. and Ph.D. in physics from Johns Hopkins University. Presently Manager of the Space Physics Section of General Electric's Space Sciences Laboratory, he has spent many years in research and helped pioneer the development of basic experimental reactor physics methods and data. Dr. Frost has published numerous papers and articles in professional journals.

DR. JOHN T. A. POLLOCK

Dr. Pollock received his B.S. from the University of Glasgow and was awarded the DIC and Ph.D. by Imperial College, London, in 1966. Presently a Staff Scientist for Tyco Laboratories, he is engaged in research on continuous high strength sapphire ribbons and filaments.

RALPH A. HAPPE

Mr. Happe received his B.S. in Met. E. from the Carnegie Institute of Technology in 1946. Presently a member of the Technical Staff, Advanced Material and Process, Space Division, North American Rockwell Corporation, he has previously worked in metallurgical joining materials selection, titanium alloy development, and conceptual design for the Apollo Telescope Mount.

DR. L. F. MONDOLFO

Dr. Mondolfo received a doctorate in engineering from the Polytechnic in Milano, Italy, in 1933. Presently Manager of the Metallurgical Research Department at Revere Copper and Brass Incorporated, he has previously worked in industry and as a professor of metallurgical engineering. He has written two books and a score or so of papers dealing mainly with aluminum alloys and solidification of metals.

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Mr. Reger received his B.S. and M.A. degrees in chemistry from the University of Texas, and his M.S. degree in engineering science from the University of California at Los Angeles. Presently part of the Technical Staff of TRW Systems Group, he is the principal investigator in programs dealing with energy conversion and properties of materials. Mr. Reger has had sixteen years' experience in research and development and has several patents and patent applications.

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Dr. Saunders received his B.S. from Duquesne University, and his M.S. and Ph.D. degrees in chemistry from Georgetown University. Presently Environmental Biology Chief in Bioscience Programs, Office of Space Science and Applications, NASA Headquarters, he is a recognized research authority in general cryobiology, tissue transplantation, and physical biochemistry. Author of numerous scientific and technical reports, he also lectures and has edited and narrated four films about the Biosatellite Program. Dr. Saunders is a member of numerous organizations and received the 1962 Authur S. Flemming Award in Science as "One of the Ten Outstanding Young Men in the Federal Service."

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Mr. McCreight received his B.S. and M.S. degrees in ceramic engineering from the University of Illinois. Presently Manager of the Materials Research and Development Section of General Electric's Space Sciences Laboratory, he has spent many years in the ceramic field. Mr. McCreight is the author of several articles for professional journals and co-author of two books on ceramic fibers.

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Presently Chief of Space Biomedical Research for Martin Marietta Corporation's Denver Division, Dr. Jordan received his doctorate in microbiology and virology from the University of Michigan School of Medicine. He has done much work in immunology and has served on the medical staffs of three universities.

P. GORDON PARKS

Presently Chief of the Welding Development Branch, MSFC, Mr. Parks studied welding at the University of Pittsburgh. He specializes in manufacturing research and development of specialized equipment and processes for metals joining, and has authored numerous technical papers.

ROBERT V. HOPPES

Mr. Hoppes studied mechanical engineering at Purdue and Alabama Universities. Presently Deputy Chief of the Manufacturing Engineering Welding Development Branch, MSFC, he has worked in welding research and development since 1962.

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Dr. Wechsler received his doctorate in chemical engineering from the Massachusetts Institute of Technology in 1960. Presently Group Leader of the Engineering Research and Experiments Group for Arthur D. Little, Incorporated, he specializes in heat flow and heat transfer.

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Dr. Mazelsky was awarded an A.B. in chemistry from Hofstra University in 1954 and a Ph.D. in Inorganic Chemistry in 1958 from University of Connecticut. Presently Manager of Inorganic Preparation and Crystal Growth for Westinghouse Electric Corporation, he has previously done research on various properties of luminescent, laser, and oxide materials. Dr. Mazelsky has authored and coauthored over 25 scientific papers.

DR. ARUN P. KULSHRESHTHA

Dr. Kulshreshtha received his M.Sc. in physics in 1959 from the University of Agra, India, and his Ph.D. in 1965 from the Moscons State University, USSR. He is now working as a National Academy of Sciences Research Associate in the Thermal Environment Physics Branch of Space Sciences Laboratory, MSFC, and has previously taught at the Indian Institute of Technology, Delhi, India. He has published over 15 papers.

JOHN H. KIMZEY

Mr. Kimzey received his B.S. degree in chemical engineering from Virginia Polytechnic Institute. Presently an Aerospace Technologist at the Manned Spacecraft Center, he was previously a naval aviator and is a member of various professional societies.

HANS F. WUENSCHER

Mr. Wuenscher received his B.S. degree in mechanical and aeronautical engineering from the State College for Technology, Chemnitz, Germany, and did his graduate studies in Berlin, Prague, and Frankfurt. Presently Assistant Director for Advanced Projects, Manufacturing Engineering Laboratory, MSFC, he specializes in space vehicle research and development. Mr. Wuenscher has published many technical papers and has received numerous patents in the United States and Germany.

DR. JULIUS SIEKMANN

Dr. Siekmann received his doctorate in Germany from the Technische Hochschule Karlsruhe in 1955. Presently Professor of Engineering Scientifics at the Georgia Institute of Technology, he has spent many years on the staffs of various universities in Germany and the United States.

DR. WOLFGANG H. STEURER

Dr. Steurer received an M.S. degree in mechanical engineering and metallurgy in 1937 and a Ph.D. in 1941 at the University of Stuttgart, Germany. Presently engaged in materials and manufacturing research for

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JOHN R. RASQUIN

Mr. Rasquin of the Manufacturing Engineering Laboratory, MSFC, has his B.S. in electrical engineering. He has 15 years experience in metal working and 20 years experience in electrical engineering, specializing in electronics and optics.

DR. R. M. HOUSLEY

Dr. Housley has his B.S. in physics from Reed College and his Ph.D. from the University of Washington. He is presently with the Solid State Physics Group of North American Rockwell Corporation, and has spent some time studying in The Netherlands.

TOMMY C. BANNISTER

Mr. Bannister received his B.S. and M.S. degrees in physics from the University of Alabama. Presently with the Space Sciences Laboratory, MSFC, he has been actively engaged in research in the fields of thermal control and solidification physics. Mr. Bannister has published 13 scientific papers while at MSFC.

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Dr. Roy received his B.S. in metallurgical engineering from B.I.T., Sindri, India; his M.S. from Sheffield University, England; and his doctorate from Max-Planck Institute of Metal Research, Stuttgart, Germany. Presently a National Academy of Sciences Research Associate at MSFC, he is engaged in many projects, including the establishment of a materials research laboratory at the University of Alabama in Huntsville. Dr. Roy has published eight scientific papers.

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Dr. Davis received his doctorate in physics from Clemson University. Presently Associate Professor of Physics at the University of Alabama in Huntsville, he has published numerous scientific papers.

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Dr. Grodzka received her B.S. and M.S. degrees in chemistry from Wayne State University, and her doctorate from the University of Michigan. Presently with Lockheed Missiles and Space Company, she has worked in the applications of solid-liquid phase change and solid state thermodynamics. Dr. Grodzka was previously an instructor at Smith College.

E. C. McKANNAN

Mr. McKannan received his B.S. in physics and mathematics from West Chester State College, Pennsylvania, and his M.S. in engineering from the University of Alabama. Currently Chief of Metallic Materials Branch of the Materials Division, MSFC, he has worked on space lubrication and environmental effects on the properties of materials. Mr. McKannan has authored several scientific papers and co-authored a book.

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Mr. Fogarty is a Chemical Processing Group Leader in the Advanced Manufacturing Development Department of Grumman Aerospace Corporation. He holds a B.S. degree in chemistry from Clarkson College of Technology, and has 10 years of experience in the development of chemical processes for aircraft and spacecraft applications.

DR. WILLARD F. LIBBY

Dr. Libby, Professor of Chemistry at the University of California at Los Angeles, received the 1960 Nobel Prize in Chemistry for the Radio Carbon Dating Technique. He is Consultant to several universities and corporations, and has received over 15 merit achievement awards from various societies, colleges, and academies.

DR. THEODORE B. TAYLOR

Dr. Taylor received his B.S. in physics from the California Institute of Technology, and his Ph.D. from Cornell University. Currently, he is President of the International Research and Technology Corporation, a firm which he founded. Dr. Taylor was the recipient of the Ernest Orlando Lawrence Memorial Award of the Atomic Energy Commission in 1965, for his work on the development of nuclear weapons and of the TRIGA Research Reactor.

DR. MATHIAS P. L. SIEBEL

Dr. Siebel attended the University of Bristol, England, and holds his doctorate in mechanical engineering. Presently Director of the Manufacturing Engineering Laboratory, MSFC, he previously worked in industry, several universities, and developed an independent consulting practice. He holds several U.S. and British patents.

R. C. LITTLEFIELD

Mr. Littlefield has his degree in engineering from the University of Southern California and is presently a member of the technical staff, Office of Manned Space Flight, NASA Headquarters. Previously he was involved in manufacturing engineering liaison activities for MSFC.

APPENDIX C
LIST OF ATTENDEES

INDUSTRIES AND RESEARCH

Dr. C. E. Dixon
Aerojet General Corp.
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Mr. L. P. Langan
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Mr. Leonard B. Griffiths
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Mr. George L. Anderson
Ball Brothers Research Corp.
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Mr. Robert von Eschen
Ball Brothers Research Corp.
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Dr. Roman J. Wasilewski
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Dr. W. Oldfield
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Mr. James F. Miller
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Dr. James H. Bredt
Bellcomm, Inc.
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Mr. Saul L. Penn
Bellcomm, Inc.
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Dr. Thomas C. Tweedie
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Mr. George R. Seeger
The Bendix Corp.
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Mr. Jaime B. Fernandez
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Mr. Roger Weddell
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Mr. Carl Struever
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Fairchild Hiller Corp.
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Mr. John W. Seeger
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LIST OF ATTENDEES (Continued)

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LIST OF ATTENDEES (Continued)

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LIST OF ATTENDEES (Continued)

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Mr. D. C. Goldberg
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Mr. William F. Moore
National Aeronautics & Space Council
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Mr. H. Steffen Peiser
National Bureau of Standards
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National Bureau of Standards
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National Bureau of Standards
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Captain Carl J. Schulze
Andrews Air Force Base (SCSSS)
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Col. George W. Brock
Air Force System Command
Andrews AFB, Maryland

Mr. Roy W. Rice
Naval Research Laboratory
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Mr. James J. Murray
U.S. Army Research Office
Durham, North Carolina

Mr. Donald B. Cook
U.S. Army Metrology Center
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Mr. James J. Mattice
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Dr. Eloise Rowland
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Dr. Richard C. Leonard
University of Alabama at Huntsville
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Dr. Curtis H. Adams
University of Alabama in Huntsville
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LIST OF ATTENDEES (Continued)

Mr. Paul Bisenius
University of Alabama in Huntsville
Huntsville, Alabama

Mr. John S. Renfro, Jr.
University of Alabama in Huntsville
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Mr. Singh Mehta Rajinder
University of Alabama in Huntsville
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Mr. Joseph L. Mercier
University of Alabama in Huntsville
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Dr. Leo J. Hirth
Auburn University
Auburn, Alabama

Dr. Donald H. Denholm
Auburn University
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Dr. Charles L. Rogers
Auburn University
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Mr. Richard H. Sforzini
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Auburn, Alabama

Dr. Luther Haynes
Auburn University
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Dr. Alfred S. Yue
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Dr. Milton C. Shaw
Carnegie Mellon University
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Mr. J. C. Purcupile
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Dr. Donald G. Burkhard
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Dr. Helmut F. Bauer
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M. I. T.
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Mr. Edward R. Lawson
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Dr. William A. Jesser
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Mr. W. H. Gray, MSC
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LIST OF ATTENDEES (Continued)

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Mr. George D. Adams
Mr. Addo S. Ahmed
Mr. Bill R. Aldrich
Mr. W. Angele
Mr. Gary M. Arnett
Mr. Robert M. Avery
Mr. William Bailey
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Mr. Ernest Bayless, Jr.
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Mr. H. G. Harber
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Mr. G. B. Heller
Mr. W. R. Henry
Mr. James G. Holland
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Mr. Harrell L. Landreth
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Mr. Norman Levine
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Mr. A. G. Loughead
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Mr. Hans Martineck
Mr. Paul H. Maurer
Mr. James McCaig
Mr. W. M. McCampbell
Mr. Truman E. McClard
Mr. James W. McKee
Mr. Charles M. Mitchell
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LIST OF ATTENDEES (Continued)

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Mr. Robert Paetz
Dr. Palmer N. Peters
Mr. Richard M. Poorman
Mr. John L. Ransburgh, Jr.
Mr. Fred A. Reeves
Dr. Gerhard H. R. Reisig
Mr. J. B. Rendall
Miss Barbara E. Richard
Mr. Werner H. Rubel
Mr. Rudolph C. Ruff
Mr. Robert L. Saidla
Mr. T. L. Shaner
Mr. R. J. Schwinghammer
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Dr. Werner H. Sieber
Mr. William C. Snoddy
Dr. Robert S. Snyder
Mr. Walter H. Stafford
Mr. T. T. Starkey
Mr. R. T. Stein
Mr. Robert L. Swain
Mr. Charles A. Swanson
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Mr. William F. Taylor
Dr. Heinz H. Trauboth
Mr. Lemuel F. Vaughan
Mr. Jack H. Waite
Mr. Edward O. Walker
Mr. William A. Wall
Dr. H. Walter
Mr. John K. White
Mr. William A. Wilson
Mr. Leon D. Wofford, Jr.
Mr. Perley H. Wormell
Mr. I. C. Yates
Mr. Phil H. Yohannan

LIST OF ATTENDEES (Concluded)

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Astronaut
MSC

Dr. Philip K. Chapman
Astronaut
MSC

LCdr. Bruce McCandless, USN
Astronaut
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