Analysis of Selected Opportunities for Manufacturing in Space

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In this paper, four selected subject areas will be discussed which may be promising for manufacturing in space. In three of these areas, the opportunity arises mainly from the absence of a gravitational field, while in the fourth area advantage may be taken of the prevailing hard vacuum. The discussed line items are as follows:

1. Crystal growth and refinement.
2. Manufacture of perfectly shaped bodies.
3. Preparation of homogeneous mixtures and suspensions.
4. Ultrapurification of refractory metals in a vacuum.

It is generally concluded in this document that in spite of numerous technical uncertainties confronting the experimenter, it still may be a promising field of future space activities which deserves more general attention.

INTRODUCTION

The unique characteristics of space may offer an environment that can be exploited to fabricate materials or products that are not attainable in the terrestrial environment. These characteristics include vacuum, gravity-level control, low noise and vibration level, clean environment, natural solar radiation spectrum and an attenuation-free medium, and essentially unlimited volume. Singly, each of these characteristics is, in principle, attainable on Earth, with the exception of the zero-g condition, and even the effects of gravity may be circumvented in a limited sense. In space, however, it becomes possible to obtain an environment that possesses some or all of these characteristics. This situation offers a broad range of opportunities that might be exploited for manufacturing in space.

Opportunities to conduct commercially advantageous manufacturing activities in space may be anticipated as space capabilities become increasingly well developed, especially in at least three general ways:

1. Reliable operation of large-payload launch vehicles, capable of orbiting payloads upward to 200,000 lb in low-Earth orbit and joining separate payloads in orbit.
2. Development of techniques to dramatically reduce the unit costs of placing payloads in orbit.
3. Emergence of an operationally useful capability for man in orbit.

Satellites have already made inroads into several areas of commercial activity. The success of communication and weather satellites is well known, and advanced studies have indicated the advantages of surveying our Earth resources from satellites and have shown the utility of satellites as accurate navigational aids for ships and aircraft. Projecting into the foreseeable future, manufacturing would appear to be one of the ultimate steps in the sequence of advancing commercial activity in space.

Properties of the Orbital Space Environment Compared to Earth-Based Laboratory Capabilities

The most attractive properties of the orbital environment appear to be the almost unlimited volume of hard vacuum and the negligible gravity forces (10⁻⁶ to -10⁻¹⁴ g) acting on an orbiting vehicle. In addition, it may be of importance that these properties are available in an environment of comparatively low temperature. The prevailing vacuum pressure at 1 A.U. from the sun amounts to approximately 10⁻¹³ torr, while the hardest vacuum attainable in ground-based laboratories by fully exploiting today's technology is not much better than 10⁻¹² torr.

It is common knowledge that a near-zero-g environment can be, in principle, briefly simulated close to Earth either by use of drop towers or by taking advantage of suitable "free-fall" aircraft trajectories. Observation time, however, is limited to a few seconds in the case of drop towers and to a few minutes, at most, in airborne experiments. Such observation times are, however, grossly inadequate to simulate and evaluate the influence of zero-g conditions for most experiments concerned with space manufacturing. In this and other respects, the real space environment is naturally far superior. Only in regard to achieving low temperatures, does the Earth-bound laboratory's capability seem more impressive than what can be naturally attained in space. By use of such advanced techniques, as taking advantage of the magneto-caloric effect, temperature levels in an Earthbound laboratory have been reached which are only small fractions of a degree above absolute zero, while even the darkest parts of the surrounding universe still radiate like a blackbody of at least 30 K.

A simple parametric comparison of environmental conditions which can be obtained in space on the one hand and in the laboratory on the other may, however, be somewhat misleading. Laboratory experiments planned in an effort to reach new, hitherto unattainable A.U., from the sun, severe sacrifices in other respects. For example, in vacuum technology, meticulous standards of cleanliness generally have to be maintained on Earth to achieve an extremely hard vacuum. In another instance, it might be that, in an effort to reach extremely low temperatures, the available test volume would have to be kept impractically small. Therefore, all pertinent factors have to be objectively considered in attempts to evaluate realistically the merits of space manufacturing processes.
Philosophy of Investigation

The approach taken in this document is to treat the selected technical processes in a rather fundamental way and to describe specific features when these may be of critical importance. Where possible, the underlying physical principles have been identified. Experimental detail is discussed in cases where potential technical difficulties may be anticipated and where no adequate theoretical understanding is yet available.

Specifically, in this study selected answers are sought to the following two broad questions:

Which physical or technological processes are largely influenced by the action of gravity forces and could potentially benefit from a space environment? Which manufacturing processes could benefit from extremely rigid cleanliness standards or large volumes of hard vacuum?

Economical Outlook of Space Manufacturing

Wherever the opportunities of space manufacturing are discussed, one principal question raised is that of economical feasibility. In considering present-day costs of sending a pound of payload into an Earth orbit, one is tempted to jump immediately to the conclusion that space manufacturing expenses are by nature prohibitively high. Therefore, the argument goes, if the area is not economically attractive why bother to look at it?

However, there are good reasons for taking space manufacturing somewhat more seriously. Expenses may be high, but not necessarily prohibitive.

With the availability of such launch vehicles as Saturn IB and Saturn V, huge payload capabilities can be provided. The introduction of larger, more efficient launch vehicles and continuous improvement and uprating of present-generation vehicles may finally bring the payload costs for Earth-orbiting vehicles down to economically attractive levels. Delivery costs to an Earth orbit for a typical late-generation vehicle of large size are presently of the order of $1,000/lb. 2 Launch costs may drop to approximately $300/lb by 1975. This compares with a price of gold of approximately $600/lb, which brings the launch costs into the vicinity of the price of some medium-priced materials. Many exotic items command a much higher price per pound than gold. Naturally, inferences from such a comparison must be drawn with caution, but they do tend to suggest that launch costs are not necessarily the most serious limitation. Admittedly, launch costs alone represent only a partial assessment of the actual costs, which should also include laboratories, manufacturing, recovery, and others. At the present stage of development, meaningful estimates of actual space-product costs are very difficult, but long-range predications based on today's expectations seem to produce acceptable figures.

If available cost projections on reusable boosters are sufficiently realistic, transportation systems based on reusable boosters could finally bring down the unit space transportation costs to $50/lb or even less. A "surcharge" of $100/lb or even a conservative $1,000/lb for products manufactured in space could be quite acceptable for a variety of expensive products (high-quality single crystals and semiconductors) if no other more cost-effective production methods on Earth become available.

Analytical Approach to Topics of Space Manufacturing

In identifying broad areas of space-manufacturing opportunities, it has been found helpful to compare predominant forms of energy, or equivalent forces, which are primarily responsible for the occurrence of observable physical phenomena with simultaneously acting gravitational forces or energies. If the influence of gravity appears to be insignificant in comparison to other "formative" modes of energy (e.g., surface tension, thermal energy, or cohesive energy), then in a stable condition the influence of gravity as a first-order influence may be ignored and it may be concluded that absence of gravity in a space environment would not substantially influence the occurrence of ordinarily expected physical events. If, however, gravity forces turn out to be of a similar magnitude or even larger than apparently competing forces which act on the system, then the effects of gravity have to be carefully studied from case to case.

In each individual example the concept depends on the specific analytical model, whether the ratios used are those of forces or those of corresponding energies. In principle, the ratios of energies or forces may be considered to have equivalent effects upon a system that has reached a static condition, similar to the principle of virtual work.

Some dynamic phenomena, such as thermal convection currents and oscillatory movements of liquids, naturally cannot be analyzed in such an elementary manner. More detailed, sometimes qualitative, descriptions of phenomena must then be generated. Instead of an incomplete theory, sometimes experimental results are helpful to illustrate particular situations.

Line Items of Present Study

In this report, four selected subject areas which may show promising potential for space-manufacturing are discussed. Manufacturing opportunities for all of these areas primarily depend on the absence of the gravitational field; the fourth area, in addition, takes advantage of the hard vacuum (that is, the ultracleanliness) of space. These areas of interest are:

1. Crystal Growth and Refinement in Zero-g—Growing and refining single crystals and vapor deposition on clean crystalline surfaces in a zero-g environment.

2. Manufacture of Perfectly-Shaped Bodies—Obtaining ideal shapes of deformable bodies in zero-g and resulting opportunities to manufacture bodies of perfect configuration, such as spheres and other minimum-surface-energy configurations.
3. Preparation of Homogeneous Mixtures and Suspensions in Zero-g--Homogeneous suspension of high-density materials in temporarily molten matter of different density (in the absence of gravity), such as metal spheres homogeneously imbedded in a plastic matrix or exotic composite materials like those created by composite casting.


Specific conclusions relating to these selected areas are presented at the end of the sections, in which they are discussed.

CRYSTAL GROWTH AND REFINEMENT IN ZERO GRAVITY

Since the advent of transistor and solid-state laser technology, crystal growth has become a very important and active subject of research. Growing crystals is, however, still widely considered an empirical art with low general predictability. In the past few years, however, the theoretical know-how has increased markedly, leading to a generally better understanding of phenomena influencing crystal growth. In turn, this improvement of knowledge paid off in improved capabilities to grow high-quality crystals.

Expectations of Potential Improvements of Properties of Crystals Grown in the Weightless State

At this early stage of investigation, optimism should be the guide in an effort to stimulate interest in this quite promising but complex field. Preliminary investigation leads to the conclusion that the advantages derived from growing crystals out of melts in a zero-g environment or in a low-g environment could be in part quite significant.

In the ordinary 1-g environment, in the familiar Czochralsky method (Figure 1), in which a single crystal is drawn out of a melt, the seed crystal is barely able to pull a continuous mass of crystallizing material from the melt, subjecting the seed crystal and the surrounding newly attached solidified material to the danger of disjoining from the liquid phase. This "flowback" is the result of the downward pull of gravity, which for larger crystals quite easily may overcome the relatively small surface tension of the melt in the superheated condition. In order to sustain continued crystal growth from a melt, it appears necessary to prevent superheating (thus helping to maintain a higher surface tension) and to keep convective currents in the liquid phase at a low level. Superheating, however, is difficult to avoid entirely.

A zero-g environment would most likely still permit a melt of desired configuration to be retained in a crucible if the container shape and material were chosen properly. The crystals could be pulled from the side, the bottom, or the top of the crucible or from several sides simultaneously. The main requirement would be that the surface tension of the molten matter be larger than the adhesive force acting along the circumference of the hole.

Techniques and Problems Associated with Crystal Growing

It is well known that gravity is mainly responsible for the occurrence of convective currents in molten materials. The hotter parts of the melt are less dense than the cooler parts and exhibit a buoyancy in the field of gravity which tends to cause upward convection. It has been found in experiments that these somewhat irregular thermal convective currents contribute strongly to the observed undesirable irregularities (e.g., striations) in single crystals.

Temperature fluctuations on the order of 30°C, caused by turbulent convection, have been observed in melts during crystal growth. Frequency of fluctuations is on the order of 30 to 60 cpm. Besides convection, the phenomenon of "overstability," in which a synchronous coupling of the conducted and the convected heat flows occur, may be partly responsible for the observed temperature fluctuations. These large temperature fluctuations cause corresponding irregularities in the crystal growth rate. It has been shown that the amplitude of growth fluctuations is crudely proportional to the amplitude of the temperature fluctuations and inversely proportional to the stagnant boundary layer thickness, but rather independent of the frequency of temperature fluctuations. The boundary layer is basically the zone in which the melt solidifies. The pattern of growth fluctuations follows closely the temperature fluctuations.

Crystal growers have learned to reduce the size of growth fluctuations by applying one or several of the following methods: fluid baffling, a change in the mechanical or thermal environment, or application of a levitating magnetic field. One technique to better control the thermal environment is to heat the top of the crucible more strongly than the bottom and to use a radiation shield above the crucible. The use of magnetic fields may be a very effective means to obtain controlled conditions, that is, to reduce temperature fluctuations.

It has been stated that the absence of rapid temperature fluctuations, on the order of 1°C or more in amplitude, is necessary for the elimination of bubbles and voids in ruby crystals, but meeting this condition is not always sufficient. At any rate, nearly all high-quality crystals to date have been grown from melts which exhibit low temperature fluctuations. Experience seems to indicate that--at least in a normal-g environment--the existence of a temperature gradient in the melt may be partly responsible for the following undesirable phenomena:

1. Turbulent convection in the melt.
2. Undesirable shapes of the isotherms and the growth interface geometry and the creation of grain boundaries.

3. Influence on transport processes in the diffuse layer of the growth interface.

4. Thermal stresses in the grown crystals and resulting crystal imperfections.

The extension of the heat source around the melt and the provision of radiative heating sources may be remedies for large temperature gradients in the melt.

A significant improvement in the quality of crystals grown from melts has been achieved by rapidly spinning the growing crystal around its major axis. This movement introduces a centrifugal pumping effect which causes the melt to circulate more evenly from the bottom to the top. This may seem surprising at first, in view of the earlier statement that a suppression of convection currents will improve the crystal quality. A possible explanation of this discrepancy is that the most detrimental factors to ideal crystal growth are rapid and erratic fluctuations of temperature and concentration in the melt. Any means to improve the thermal "homogeneity" of the melt, either by preventing erratic circulation or by "smoothing" out local inhomogeneities, will for the most part improve the growth characteristics.

Free thermal convection in a normal-gravity environment may be described by a dimensionless parameter, the Rayleigh number $R$, which is defined as:

$$ R = \frac{L^3 \rho^2 \beta \Delta T c_p / \mu k}{L^2} \quad (1) $$

where

- $L$ = characteristic length (such as depth or diameter of container)
- $g$ = gravitational constant
- $\beta$ = coefficient of thermal volume expansion
- $\rho$ = density of liquid
- $\Delta T$ = temperature difference between wall and the test point in the liquid
- $c_p$ = specific heat
- $\mu$ = viscosity
- $k$ = coefficient of thermal conductivity

Laminar convection in a normal-gravity field sets in only at Rayleigh numbers exceeding a "no-convection" threshold value. Turbulent convection takes place when the Rayleigh number reaches still higher critical values. Therefore, it is important to keep the Rayleigh number as low as possible.

High thermal conductivities, such as those in molten metals and semi-conductors, naturally yield relatively low Rayleigh numbers, which would indicate basically little tendency to produce turbulent convection even in a normal-g environment.

The buoyancy induced part of thermal convection will naturally disappear in a zero-g environment. The physical reasons for the occurrence of another type of circulation, which may even persist under zero gravity, will be discussed in a later section.

Another familiar criterion to predict the occurrence of laminar or turbulent natural convection in a melt is the Grasshof number, $Gr$, which is defined (quite similar to the Rayleigh number) as:

$$ Gr = \frac{L^3 \rho^2 \beta \Delta T c_p / \mu k}{L^2} \quad (1a) $$

Thermal convection is laminar near a vertical flat plate if $10^4 < Gr < 10^8$. Thermal convection is turbulent near a vertical flat plate, if $Gr > 10^8$.

It has to be realized, however, that natural thermal convection is not the only potential source of imperfections in growing crystals. In principle, six other sources of disorders can be identified:

1. Seed crystal.
2. External stresses.
3. Thermal stresses.
4. Concentration gradients.
5. Condensation and migration of vacancies.
6. Trapping of impurities.

Thus, conducting crystal growth experiments in zero gravity may result in an improvement of crystalline properties but may not be a complete cure of all potential imperfections.

Quality Standards of Crystals, Especially of Ruby Crystals

For a number of applications, single crystals of certain materials are not yet available in adequate size or of the desirable degree of perfection. What are the properties of high-quality crystals? No attempt will be made to give a general definition of the properties of a "good" crystal. Specifically, it would be desirable to obtain relatively large crystals of high homogeneity and within a minimum of such imperfections as dislocations, twinning, and grain boundaries. The purpose for which the crystals will be used dictates the quality standards which the crystal must meet. Naturally, in laser technology the quality standards are optical in nature. In semiconductor technology, quality criteria are based mostly on the achievable uniformity of electrical conductive properties of the crystal.

In spite of significant improvement over the years, the art of crystal growing still leaves a lot to be desired. Needless to say, growing near-perfect crystals is the desire of most experimental crystal growers. Some of the following diagnostic methods are standards in determining the quality of ruby crystals. They are listed in order of increasing sensitivity:

1. Visual examination under polarized light and in the microscope.
2. Examination by Schlieren photography.
3. Application of the Schulz-Wei X-ray diffraction technique.
4. Use of the double-crystal X-ray spectrometer.
5. Chemical etching and counting of etch pits to determine dislocation densities.

By use of some of these methods, it can be shown that even quality ruby crystals contain at least microscopic flaws which have the appearance of streaks or filaments. Examination with optical microscopes indicates that the streaks consist of large numbers of closely-spaced spheroids approximately 2 μ in diameter or smaller. Similar streaks or filaments have been observed in good-quality ruby rods which have been deformed in compression at 1,900°C. The streaks have been primarily observed in regions which underwent a large amount of plastic deformation. Etching techniques reveal that many of the undesirable filaments terminate on subgrain boundaries.

Further quality improvements are both desirable and necessary and could be accomplished by reducing the material strain which, although caused mostly by thermal effects, during the solidification process is also partially induced by gravity. As was previously mentioned, first-order temperature fluctuations can be reduced by preventing turbulent convection, which is a gravity-dependent phenomena. Thus, a zero-g environment could act beneficially in at least two ways to improve crystal growth in quality ruby crystals. As far as semiconducting materials are concerned, the electrical losses increase at the grain boundaries as frequencies increase. Therefore, attempts are made to replace, at the higher frequencies, polycrystalline materials by high-quality single-crystal material in sophisticated electronic devices. There is a similar tendency in the application of ferroelectric transducer material. It is obvious, then, that there is a need for further qualitative advances.

Pseudo-Convection in a Liquid or Melt by Bubbles

Most melts or heated liquids contain bubbles which may be attached to the bottom of the container or to the walls, or which may float freely in the liquid. In addition to thermal currents, moving and expanding bubbles may be an additional source of convection currents in the melt. It is normally recognized that the most important force acting on the bubbles is their natural buoyancy, which is proportional to the difference in specific weight between the vapor in the bubble and the surrounding liquid. In a zero-g environment, thermal convection would be expected to be completely arrested. Bubble-induced convection, however, will not disappear entirely because movement of the bubbles and the surrounding liquid do not depend on gravity forces alone. Pertinent phenomena are discussed in detail in Appendix A; a short description will suffice here.

The most important force acting on bubbles, besides buoyancy, is probably the dynamic force which does not disappear in zero gravity. This force may even increase in a zero-g environment. In brief, an expanding bubble sets the liquid along its boundary in motion and the momentum generated is transferred to the melt. The kinetic energy of the moving melt is finally consumed by internal friction. This phenomenon should be carefully studied, because bubbles in a zero-g environment grow larger and faster than in a 1-g environment as a result of the lack of surrounding hydrostatic pressure. They therefore displace more liquid, and the resulting dynamic force may be significant. In an effort to completely avoid convection, it is necessary to find means to entirely suppress bubbling in the melt.

Bubbles may also be moved by virtue of local variation of the surface tension in the melt. The surface tension depends strongly on the temperature. Therefore, temperature gradients in melts may indirectly contribute to bubble movement and, hence, to liquid convection.

Other Methods of Growing Crystals from Heated Melts

Attempts have been made to grow crystals in the laboratory by slowly dripping crystalline melts contained in a tungsten crucible through a pinhole opening in one end. However, these preliminary experiments have not been very successful, because as soon as the viscosity decreased to the point that the melt started to flow through the pinhole, there occurred almost immediately a sudden surge of melt. The rapidity of the mass transfer prevented orderly single crystallization. It may be possible, however, to perform such an experiment in a zero-g environment by applying a well-defined pressure force, such as provided by a piston on the side of the melt, which would squeeze the melt in a controlled way out through the hole. Long, single crystals could be grown, either in the vertical or horizontal direction. It seems, in principle, at least, that such a method could work in a zero-g environment. However, the feasibility must be verified.

Improvement of Crystal Quality by Zone Refinement

Crystals are commonly further purified after the growth process by "zone refining," in which a molten zone, created by an inductive coil, is moved slowly through the crystal. The higher solubility of the impurities in the liquid zone depletes and thus purifies the surrounding crystal of contaminants. The temperature of the liquid zone must be controlled in such a way that the molten zone does not significantly deform or collapse under its own weight. Naturally, this condition can be somewhat relaxed in the absence of gravity. The higher temperature tolerance in the liquid zone would suggest a greater solubility of impurities in the molten zone and possibly higher diffusion rates, hence a more effective purification process. It is possible to optimistically envision the maintenance of floating zones in a large specimen, say of 1-ft diameter.

The expectations regarding the merits of zone refining in zero gravity, however, are not in all respects favorable. The following arguments may even lead to the conclusion that in certain respects a zero-g environment could turn out to be partially detrimental to the process of zone refining:

1. Heat conduction in the sample and the uncontrollable action of the surface tension could cause the molten zone, regardless of the heating
method used, to assume shapes which would be unsuitable for efficient zone melting.

2. Mixing of the molten zone by natural convection in normal gravity may accelerate the diffusion process and, thus, the separation process in zone refining. Hence, as natural convection is largely absent in a zero-g environment, zone refining could become rather inefficient.

Most of these conflicting opinions are resolvable only by pertinent experiments in orbit.

**Crystal Growth from Supersaturated Solutions**

The merits of growing solid single crystals from a melt or a supersaturated solution in the absence of a gravitational field are difficult to assess. This process normally requires deposition of matter out of a melt or a solution on a seed crystal. The convective circulation, density gradients in the liquid, the surface tension and cohesive energy, and the concentration of impurities are factors which directly influence the growth behavior out of the liquid phase and indirectly influence the quality of the crystal.

Caution must be exercised in attempts to predict how growth rate, shape, and intrinsic properties will be affected at various g-levels, especially in a zero-g environment. Experimental results are available regarding the behavior of crystal growth in the high artificial gravity environment of a centrifuge. Some of the pertinent experimental observations are discussed below because they may be, in part, indicative of the phenomena to be expected in a zero-g environment if properly extrapolated in the "other direction."

**Crystal Growth by Centrifugation.** When a concentrated salt solution is rotated in a centrifuge, the crystalline matter in solution being denser than the solvent tends to concentrate in the area which is farthest away from the centrifuge axis. A concentration gradient establishes itself in a nearly saturated solution, a portion of the solution becomes supersaturated, and localized crystal growth may occur. The principal advantages of growing crystals by centrifugation are that disturbing impurities, air bubbles, and small crystallites are rapidly sedimented. They can be removed by permitting partial crystallization and decanting the remaining solution. Also, growth irregularities caused by convection currents are not very troublesome because the steady-state density gradient re-establishes itself rather rapidly as a result of the large artificial buoyancy forces.

An interesting, but not necessarily desirable, side effect of centrifugation is that most growing crystals assume shapes slightly different from normal under the action of high-g forces: mostly, the crystals become flatter. This behavior is attributed to the tendency to establish a minimum energy balance between surface tension and gravitational forces. A useful criterion to measure this phenomenon is the height-to-width ratio (H/W) of the equilibrium form of an isotropic crystal. It may be calculated according to the following equations:

\[ H/W = \frac{B W}{W + AV_g} \]  

\[ B = 1/2 + \frac{\sigma_{13} - \sigma_{23}}{2\sigma_{12}} = 1/2; \quad A = \frac{(\rho_1 - \rho_2)}{4\rho_{12}} \]  

In Equations 2a and 2b, \( \sigma_{13} \), \( \sigma_{23} \), \( \sigma_{12} \) are the surface energies per unit area at the crystal-solution, crystal-substrate, and solution-substrate interfaces, respectively. \( \rho_1 \) and \( \rho_2 \) are the densities of the crystal and the solution, respectively; \( g \) is the artificial gravitational acceleration acting on the solution in the centrifuge and \( V \) the volume of the crystal. \( AV_g \) is a very small, negligible quantity at the lower g-levels, but its value becomes very significant in high-speed centrifuges at g-values of 100,000.

In the "opposite" direction, that is at low-g levels or in a zero-g environment, \( H/W = 0 \); therefore, ratio \( H/W \) is expected to depend primarily on the surface energies \( \sigma_{13}, \sigma_{23}, \) and \( \sigma_{12} \). Small g-forces do not noticeably contribute to deformations of the crystals.

High-g forces will, however, influence the shape of crystals severely. For instance, Equation 2 applied to a 1-mm KBr crystal at a g-level of 200,000 theoretically yields for the \( H/W \) ratio a value of 0.152 instead of 0.5 in the normal 1-g environment.

It may be concluded from these experiments that a zero-g environment will hardly influence the natural \( H/W \) ratio in comparison to a 1-g environment.

A number of other characteristics of crystals grown from solutions which are being exposed to different artificial g-environments is more difficult to predict: homogeneity, transparency, concentration of impurities and dislocation, optical properties such as birefringence, and others. A systematic investigation of these properties will be required. As a preliminary conclusion, for a typical crystal grown from a saturated solution it may be guessed that provision of a zero-g environment would most likely not improve certain desirable crystalline properties. It could be argued, by extrapolating high-g experimental results over 1-g to zero-g, that the resulting "non-separation" of impurities, bubbles, and spurious seed crystals from the solution (resulting from a lack of gravity forces) will be, in effect, detrimental and not beneficial. However, circumstances may be different because of a number of hitherto unpredictable factors. Only a full-scale zero-g experiment will permit resolution of present uncertainties.

**Growth of Diamonds by Deposition of Carbon Atoms from Methane on Seed Diamonds**

In some instances, the cleanliness of space may create an opportunity for space manufacturing of crystalline material deposited from the vapor phase. One specific case will be discussed here: growth of diamond.

Industrial quality diamonds of limited size have been produced in industry since 1955 in a high-pressure environment (70,000 atm) at elevated temperatures. Under high pressure, the more densely packed diamond modification of carbon atoms is favored over the less densely packed graphite lattice structure, and a diamond crystal can grow. These industrial diamonds are mostly of low quality and small in size.

According to reports from a chemical engineering group at Case Western Reserve University, and independently from researchers at UCLA, the feasibility of growing diamonds from gaseous methane on a diamond surface recently was experimentally demonstrated. The experi-
mentors claim that a thin diamond layer has been grown in their experiments at very low pressures on the surface of large gemstone-size diamonds. The group hopes to further substantiate their claims and to improve the process and finally be able to grow synthetic diamonds of high quality from seed crystals to gemstone sizes.\(^\text{14}\)

On theoretical grounds, the possibility of diamond synthesis may be feasible in a temperature-pressure regime where diamond is actually thermodynamically unstable with respect to graphite. There is an activation barrier which prevents the spontaneous transformation of diamond to graphite below \(1,300^\circ\text{C}\). The likelihood that the mobile carbon atoms attach themselves to the diamond crystal is slightly greater than the probability of a buildup of ordinary graphite nuclei.

A similar problem is being investigated at UCLA under the supervision of Professor W. Libby. The long-range goal is, if preliminary attempts turn out to be successful, to eventually attempt to adapt this method to grow large-scale diamonds in space.

Hitherto, three major experimental difficulties have been experienced during the past 2 years since the start of pertinent research at UCLA:

1. Obtaining clean surfaces.
3. Producing monatomic carbon.

Attempts of cleaning surfaces by ion bombardment were only partially successful. So far, local heating by electron guns mostly transformed carbon from the diamond modification into undesirable graphite. Better cleaning methods have to be developed.

During the deposition process, practiced at UCLA, methane is passed at 1,000-1,300\(^\circ\text{C}\) over natural gem-size diamonds. Methane decomposes at 1,000\(^\circ\text{C}\) into \(\text{C}\) and \(\text{H}_2\). Thus far, \(\text{C}_2\), \(\text{C}_3\), and longer carbon radicals always seem to form in company with monatomic carbon, which is the only desirable component. The reason for preferring monatomic carbon as the gaseous phase is that single carbon atoms can be more easily incorporated into the diamond lattice structure than longer chains.

The diamond formation on the surface of the seed diamond is--if at all verifiable--a very slow process and the extensive formation time thus far experienced will certainly be a handicap. The deposition of a few milligrams of very low-grade "diamond-like" substance requires time on the order of days. The newly grown "diamonds" appear in hard lumps, which are sintered together. Depending on the graphite content, their visual appearance is gray or black. As a long-term speculation, however, the cleanliness of space may make in the future a commercial exploitation of this process not only feasible but also attractive. At the present stage of development, reliable predictions are premature, because it has not been verified beyond doubt that the deposited layers are really crystalline in nature.

Prospects for Development of New Materials in a Zero-\(g\) Environment

Occasionally, the opinion has been advanced that a zero-\(g\) environment could lead to opportunities to manufacture basically new materials and compounds. While such a possibility cannot be completely ruled out, it seems that chances for the formation of hitherto unknown compounds by sole virtue of a zero-\(g\) environment are rather remote. The fundamental reasons are as follows.

The processes of crystallization are primarily controlled by the combined action of lattice and surface energies which have the tendency to create an orderly structure: the crystal. These forces are opposed by randomized thermal agitation and the disturbing influence of impurity atoms which tend to upset the state of order. In any case, normal gravitational forces are rather unimportant in this respect, because their magnitude is negligible in comparison to intrinsic crystalline forces. There is, however, a marked influence of gravitation during the process of crystal solidification, while the crystal is still in a plastic state.

The relative significance of gravitational forces can be simply envisaged if the average cohesive energy of a molecule in a crystal—interlattice energy—is compared with the potential energy an atomic-size particle can gain in the Earth's gravitational field, when moving a distance comparable to a lattice dimension. In short, the lattice energy in a pure metal crystal is on the order of several electron volts, and it has been shown in Appendix B that the exhibited potential energy of the gravitational field is many orders of magnitude smaller. The approximate ratio of cohesive forces versus gravitational forces is shown for various parameters of \(\Delta T/M\) in Figure 2. \(\Delta T = \text{temperature difference between crystal and vaporization temperature; } M = \text{molecular weight. A more sophisticated model has been deemed superfluous in the present "zero-order" analysis.}

Attempts have been made at various solid-state physics laboratories in recent years to grow ferroelectric and ferromagnetic crystals, such as barium titanate of relatively high density from molten salt fluxes of much lower densities. These attempts have not been very successful so

![Figure 2](image-url)
far in a normal gravity environment because the crystals have a tendency to rapidly sink to the bottom of the crucible, are subject to damage by the walls, or interfere with other crystals. It has not been feasible so far to simply suspend seed crystals in a melt and completely avoid contact with contaminating foreign bodies.8

A zero-g environment in space may open new avenues of experimentation regarding such melt-grown crystals. Besides manufacturing of crystals, it has been speculated that certain glassy materials of great purity could also benefit from a zero-g environment.

It must be kept in mind, however, that initially the raw materials must be very carefully prepared to avoid bubbles and undesirable trace impurities in the melts, because these potential contaminants will not be separable in a space environment, because of the absence of gravity sedimentation.

Conclusions Regarding Crystal Growth and Refinement in Zero Gravity

Thermal Convection. Uncontrolled, sporadic convection currents in crystal melts, which occur in the familiar Czochralsky crystal-growth method, and associated temperature fluctuations are for the most part gravity-dependent and detrimental to perfect crystal growth. Greatly reduced convection and elimination of weight and thermal stresses in the crystal during the formation process in a zero-g environment could improve the quality of crystals. Bubbling of the melt should be avoided, because it could cause pseudo-convection. Also, movement of bubbles by virtue of changing surface tension may cause circulation of the melt and its influence should be studied.

Other Growth Methods. An alternate method of crystal growth that shows little promise in an Earthbound laboratory may be effective in a zero-g environment: slowly dropping a molten material contained in a crucible through a pinhole opening under gentle piston pressure. The feasibility, however, has to be verified.

Zone Refining. The process of zone refining of single crystals could probably be improved in a zero-g environment. (The influence of the lack of convection on the effectiveness of zone refining is still a controversial subject, and needs further investigation.)

Supersaturated Solutions. Crystal growth from supersaturated solutions most likely will not benefit from a zero-g environment; impurities and unwanted seed crystals are not readily sedimented because of the absence of gravity-induced buoyancy forces.

New Crystalline Structures. The possibility of forming new compounds and materials in space by virtue of zero gravity is probably precluded by the predominance of lattice and thermal forces in a solid lattice in comparison to gravitational forces. But the quality of some crystalline structures of crystals grown out of melts or the purity of glasses could be improved in a zero-g environment.

Diamond Growth by Vapor Deposition. The merits and feasibility of growing diamonds in vacuum by carbon deposition on clean seed diamonds needs to be verified in the laboratory.

Simulation Techniques. A study is required of selected laboratory simulation techniques which may permit evaluation of crystal growth behavior in a zero-g environment. Use of a centrifuge in crystal-growth experiments may yield first order indications of the behavior of crystalline properties in zero gravity through a cautious extrapolation.

MANUFACTURE OF PERFECTLY SHAPED BODIES

It has been suggested that an opportunity exists8,15 for space manufacturing of perfect spheres, or possibly hollow ball bearings of extremely high spherical symmetry, in a zero-g environment. While it is premature to question such a possibility in principle, it may be important to point out some of the apparent difficulties which would probably have to be overcome. Undeniably, the equilibrium configuration of a liquid or melt in a zero-g environment is largely dominated by surface-tension forces, and perfectly shaped bodies could be manufactured in principle if secondary influences could be sufficiently suppressed. However, it may be debatable whether apparent disturbances can be eliminated to a degree that the created shapes will meet the desired extremely close tolerances. In view of the heavy emphasis placed on this space-manufacturing opportunity, a more detailed discussion seems appropriate. Of particular importance is a study of such side effects as the oscillatory behavior of large liquid masses, the configuration which the liquid medium assumes, and potential causes of thermal distortion occurring during the solidification process. The discussion in this section borrows heavily from several experimental studies.16-18

Deformative Relaxation Times of Liquids

A liquid which has not yet attained its equilibrium configuration will oscillate around its minimum energy configuration until finally dampened by friction. The relaxation times of small quantities of some liquids, such as alcohol or mercury are sufficiently short (a few seconds) to validly simulate zero-g behavior by use of drop towers.16,17,19

The theory of the kinetic behavior of a liquid mass is reasonably well developed, and the agreement with experimental data is fair.18,19 In spherical containers, for instance, the deformation times T_a and T_b of the liquid in two vessels of radius R_a and R_b and of kinematic surface tensions β_a and β_b can be related as follows:

\[ T_a = T_b \left( \frac{R_a}{R_b} \right)^{3/2} \left( \frac{\beta_b}{\beta_a} \right)^{1/2} \]

More meaningful, the modulus of decay \( T_D \), that is the time in which the amplitude of oscillation of a liquid drop of diameter D decays to \( e^{-1} \) of its original value, is given by the equation17

\[ T_D = 4(4n - 1) \left( \frac{\eta g}{\rho g} \right) \frac{1}{(2n + 1)} \left( \frac{D^2}{2} \right) \left( \frac{\Delta D}{D_0} \right) \sim e^{-t/T_D} \]

where

\[ \eta = \text{viscosity of the fluid in the globule} \]

\[ \rho = \text{density of the fluid} \]

\[ g = \text{acceleration due to gravity} \]

\[ n = \text{degree of stratification} \]

\[ \Delta D = \text{change in diameter} \]

\[ D_0 = \text{initial diameter} \]

\[ t = \text{relaxation time} \]
$p_g =$ mass density of the fluid in the globule

$n =$ harmonic order of the oscillation (n = 2 for the simplest vibratory mode)

$\Delta D =$ measure of the oscillatory amplitude

As an example, for spheres of 10-in. diam, the relaxation time can be as large as 1 hour, while for a sphere of 100-in. diam, the equilibrium relaxation will require times of the order of weeks. Hence, if one wishes to manufacture perfect spheres, the problem and duration of oscillations must be carefully considered during the process of solidification of the melts. Otherwise, major deviation from the desired shape may result. It may be advisable to preshape the raw material into spheres, if this does not cause storage problems or makes it difficult to efficiently heat spherically shaped material to the desired temperatures.

Often, as a basic criterion for the velocity of the deformation, the deformation rate $\nu/\eta$ (which has the dimensions of a velocity) is being used. $\nu$ is the surface tension and $\eta$ the viscosity of the liquid. While $\nu/\eta$ is on the order of 0.5 to 4.0 x $10^4$ cm/sec for water and many common molten metals, it is much smaller (~1 cm/sec) for engine oil. Hence, the equilibrium shape is much more swiftly attained in molten metals and water than substances similar to engine oil.

Configuration of Liquids in Spherical Tanks

Configurations of wetting and nonwetting liquids under a variety of different circumstances are shown in Figures 3, 4, 5, and 6. In general, the following observations have been made for wetting and nonwetting liquids in spherical tanks:

Any direct contact with a solid wall will cause major deviations from sphericity. The assumed shape depends on the contact angle, which in turn depends on the minimal surface interaction of the point of contact of the solid material and the liquid. Obviously, in zero gravity, the radius of curvature of the free liquid surface remains constant between the solid boundaries.

The following discussion of experimental results regarding the equilibrium configuration of liquids in containers will make it quite obvious that pertinent "free-casting" techniques have to be individually conducted according to the particular materials involved. Clear distinction will be necessary between "wetting" and "nonwetting" liquids or melts, because these behave in distinctly different manners when in contact with solid matter.
Nonwetting Liquids, Such as Mercury. Nonwetting liquids exhibit the following characteristics:

1. The radius of curvature remains the same for any part of the liquid-vapor interface in the weightless state. This can be seen from the configuration of Mercury in a 1-g environment in Figure 3.

2. The contact angle itself is unaffected by a gravity field.

3. An important quantity with regard to the equilibrium configuration in spherical tanks is the liquid-to-tank volume ratio. Below 80%, the liquid-vapor surface is convex; above approximately 80%, the liquid-vapor surface is concave. Therefore, at approximately 80%, the liquid-vapor surface remains flat. The liquid-to-volume ratio is a significant similarity parameter regarding the configuration of liquids in solid containers of similar shape.

4. Figure 4 shows the behavior of a totally nonwetting liquid in zero gravity. The liquid forms a noncontacting sphere in the tank surrounded by vapor. Such an arrangement may serve in principle as a means for creating spherical configurations in space.

Wetting Liquids, Such as Methyl Alcohol, Ethyl Alcohol, and Water. Wetting liquids exhibit the following characteristics:

1. The equilibrium configuration for ethyl alcohol in partially filled spherical glass tanks is a completely wetted tank. Below approximately 80%, the liquid surface behaves as indicated in Figure 6. (This case may serve as an example to illustrate manufacturing of hollow spheres.)

2. The time required to totally wet the surface of a container depends on the ratio of liquid density to surface tension. A calculation shows that it is directly proportional to the square root of density to surface tension. 17

Manufacture of Specifically Shaped Bodies, Such as Spheres, in a Zero-g Environment

It is difficult in a normal-g environment to effectively manufacture perfectly spherical bodies because of the oblatting effect of gravity on matter while it is in the non-solid state. It seems obvious that the influence of the gravitational field increases with the larger masses. Large liquid masses simply will break up under their own weight. The influence of gravity on the shape of a spherical deformable body can be illustrated by the following simple analysis.

Assume that a small spherical droplet of density \( \rho \) and radius \( r \) is resting on a solid surface in a normal-g environment. If more liquid is added to the droplet, the surface energy, \( \Delta E_S \), will increase by \( \Delta E_S = \gamma dA = 8\gamma r dr \), and the potential energy, \( E_g \), of the center of gravity through upward displacement by \( dr \) by

\[
d E_g = V \cdot \rho \cdot g \cdot dr = 4/3\pi r^3 \cdot \rho \cdot g \cdot dr \]

Therefore, the ratio obtained is

\[
d E_S = \frac{6\gamma}{2 \cdot \rho \cdot g} \cdot (\frac{dr}{r^2})^{1/2} \]

Solving Equation 5 for the radius yields

\[
r = \left( \frac{6\gamma}{g} \cdot \frac{1}{1/2} \cdot \frac{E_g}{\Delta E_S} \right)^{1/2} \]

For a given molten material or liquid, the deviation from sphericity approximately increases with the square of the diameter and is inversely proportional to the square root of the level of acceleration to which the deformable mass is subjected. In practice, a space manufacturing module in an Earth orbit will be subject to drag forces which will result in a deceleration on the order of \( 10^{-6} - 10^{-13} \) g. For the creation of perfect spheres, it will be necessary to compensate for this natural deceleration by a low-thrust propulsion system. Otherwise a slight deviation from sphericity will result.

It may be noted as a matter of historical curiosity that the process of zero-g manufacturing of small spherical objects has been practically applied for many years to create small metal spheres from hot metal melts by "free fall casting" from drop towers. Naturally, this old method cannot be used to manufacture large spherical objects of close tolerances.

If the demand for near-perfect spheres could justify the high expense, undoubtedly spherical configurations could be, in principle, manufactured in a zero-g environment. Rotating deformable minimum-surface-energy bodies would allow the creation of rotational ellipses of specified shapes. Naturally, great care would have to be exercised so that no significant mechanical oscillations were induced while handling the metal and that no other disturbances were "frozen" into the solidifying product, while the mass spun around its rotational axis. Another technical problem would be the successful separation of the required mechanical support device from the metal and the control of non-uniformities in the angular velocity exhibited by different points of the melt. Also, mutual mass attraction of the space facility and the melt might be a cause of distortions.

A special situation would be the production of hollow spheres. Some recent studies seem to indicate a need, e.g., for hollow ball bearings. 8, 15 Manufacturing of such hardware items would appear to be basically feasible in a zero-g environment.

It may be, however, necessary to insert another word of caution at this point regarding the feasibility to attain perfect shapes in a zero-g environment:

1. The formation process will naturally take place in the liquid state; the finished product, however, is only useful in the solid state. The transition requires cooling, mostly by radiative dissipation of heat. The cooling process will induce thermal stresses into the material which could lead to additional deformations, if the process is not carefully controlled.

2. Non-uniformity in the surface tension of the liquid matter may cause surface irregularities and unevenness within the solidifying material.

It can only be hoped that these potentially detrimental phenomena can be sufficiently kept under control.

Figure 7 indicates the dependence of the ratio \( E_g/E_S \) on the radius for a variety of materials in the liquid state in a normal-g environment.
weight, is a useful parameter which crudely characterizes the configuration of a liquid when exposed to natural or artificial accelerations. For small spheres, the surface tension energy dominates over the gravitational energy; thus, deviations from sphericity are small. For spheres larger than, say, 1 cm the gravity force is the dominating parameter.

Conclusions Regarding Manufacture of Perfect Shapes

Configuration in a Gravitational Field. The gravitational field and the surface tension are the most important parameters influencing the equilibrium configuration of large masses of liquids or melts, and space could be, in principle, a good medium to cast perfect spherical bodies. A variety of secondary effects, however, has to be carefully studied if there is to be any hopes of achieving precision spheres.

Oscillations in Liquids. Oscillations around the equilibrium configuration may constitute a major source of disturbance in efficient free casting in space, because the oscillatory relaxation times for larger spherical bodies (of the order of 100-cm diam) could amount to days or weeks.

Configurations of Liquids in Null Gravity. The configuration of liquids in containers depends on the contact angle between the liquid and solid surfaces, which remains a constant. The liquid surface in zero gravity exhibits a constant radius of curvature. The contact angle depends on the properties of both the liquid and the wetted solid. Each material will require specific technical considerations.

Configuration Criteria. An important similarity parameter regarding the surface shape of a specific liquid in a spherical container in zero gravity is the ratio of liquid volume to total volume. The most suitable shape of the liquid container for use in a zero-g environment has to be specifically determined in order to achieve individual objectives. In some cases, internal surface coating with nonwetting materials may help to retain the liquid in the container, simply because of a more favorable contact angle.

Behavior of Totally Wetting Liquids. A totally wetting liquid that partially fills a spherical container encloses a spherical vapor bubble of the size of the unfilled volume. Totally wetting liquids have to be kept in sealed containers.

PREPARATION OF HOMOGENEOUS MIXTURES, SUSPENSIONS, OR FOAM MATERIAL IN ZERO-GRAVITY

Gases in Gravitational Fields

The influence of gravitational fields with regard to the change of density as a function of altitude is, of course, well understood from studies of the atmosphere of the Earth and other planets. A useful quantity in elementary atmospheric calculations is the scale height \( H_i = kT/mg \) which defines the altitude where the average density has dropped to 1/e of the zero altitude value. By employing such a scale height concept, the well-known barometric height equation can be written as function of altitude, \( h \), in the following form:

\[
\frac{p_h}{p_0} = \exp\left(-\frac{mg h}{kT}\right)
\]

Assume that in a column of gaseous material (for an unspecified purpose) a certain homogeneity requirement exists which stipulates that the density tolerance should not exceed a specified fractional number, say \( \Delta p/p_0 \leq a \), over the length, \( h \). This may be written as

\[
\frac{\Delta p}{p_0} = \frac{p - p}{p_0} = 1 - \frac{p}{p_0} = 1 - \exp(-h/H_i) \leq a
\]

For

\[
\frac{p}{p_0} \ll 1, \log (1 - p/p_0) = -\Delta p/p_0 = -h/H_i
\]

Hence, Equation 9 permits determination of the length, \( h \), of a gas column in which the homogeneity requirement, \( (p_0 - p)/p_0 \leq a \), is still fulfilled:

\[
h = -H_i \Delta p/p_0
\]

For instance, if the homogeneity requirement in air under the action of gravity stipulates a homogeneity of better than one part in 103, the height of the column according to Equation 10 should not exceed 7.5 m. More stringent homogeneity requirements would naturally further reduce the length of the respective column. Homogeneity in density, therefore, in a column of a one-species gas could be markedly improved in a gravitation-free environment by virtue of an "infinite" scale height, \( H_i \). The discussed gaseous system would naturally be of little practical value. This model would, however, be useful to analyze matters of more practical importance: manufacture of solid homogeneous suspensions of materials of different densities in each other. This will be explained in the following paragraph.
Suspension of Solid Particles in a Liquid Medium

If colloidal particles of zero electrical charge are suspended in a liquid, a characteristic distribution of the number density as a function of height takes place. The Brownian movement tends to distribute the suspended particles equally--in the steady state--over the container volume, while countering gravity forces tend to sediment the heavy particles on the bottom. Because the scale height must be at least on the same order of magnitude as the scale height of the gas atmosphere. If, however, values for particle density, $p = 1.1 \text{ g/cm}^3$; temperature, $T = 300\,\text{°K}$ are inserted, for a normal gravity environment, the following is obtained:

$$n_1 = \exp \left[ -\frac{mg(p - p_f)N}{\rho RT} (h_1 - h_2) \right]$$

where $\rho$ and $p_f$ are the particle and liquid densities respectively, $N$ is Avogadro's number, and the other terms have their usual meaning.

The number of particles, $n_1$, at height $h_1$ is related to the number density $n_2$ at height $h_2$.

$$\frac{n_1}{n_2} = \exp \left[ -\frac{mg(p - p_f)N}{\rho RT} (h_1 - h_2) \right]$$

$$= \exp \left[ -\frac{mg}{kT} \left( 1 - \frac{p_f}{p} \right) (h_1 - h_2) \right]$$

The equivalent scale height $H_1$ is

$$H_1 = \frac{kt}{mg} \frac{p_f}{\rho - p_f}$$

The parameters in this relation are, in principle, the same as those used for the scale height in a gas, except for the buoyancy correction factor $p_f/(p - \rho_f)$. The mass, $m$, of a suspended particle may, however, be many orders of magnitude larger than that of single gas molecules; therefore, the scale height in the suspension is largely reduced, from kilometers in case of gases to the order of centimeters or much less in liquid suspensions. That is, the particle density gradient resulting from the gravitational field is very steep. It is easy to see that in this case, gravitation is a force of dominating importance.

Relaxation Time of Solid Particles in a Liquid to Achieve Homogeneity

Small solid particles, even in a nonconvecting liquid, will be subject to Brownian motion, which makes the particles diffuse at random through the order of the thickness of one-particle layer.

Therefore, assuming $H_1 (\text{Min}) = 2r$, the following is obtained as a "critical" particle radius for establishing a suspension of neutral particles in a normal gravitational field:

$$r_{\text{crit}} = 1.063 \cdot 10^{-5} \cdot \left( \frac{T}{\rho - p_f} \right)^{1/4} \text{ cm}$$

For $T = 1,000\,\text{°K}; \rho = 1.1 \text{ g/cm}^3$; and $p_f = 1 \text{ g/cm}^3$; $r_{\text{crit}} = 10^{-4} \text{ cm}$ is obtained.

In another typical case, where $T = 300\,\text{°K}$; $\rho = 2 \text{ g/cm}^3$; and $p_f = 1 \text{ g/cm}^3$; $r_{\text{crit}} = 2 \times 10^{-5} \text{ cm}$ is obtained.

From this consideration, it is concluded that it is not feasible in equilibrium to maintain a suspension of electrically neutral, solid particles ($\rho \neq p_f$) in the presence of normal gravity, if the particle diameter exceeds $10^{-4} - 10^{-5} \text{ cm}$, because of sedimentation. However, the "almost" homogenous suspension of very small colloidal particles (of less than $10^{-6} - 10^{-5}$ cm diam) in a normal-$g$ environment by means of natural sedimentation is not a major problem as long as the container height is not excessive. Hence, if it is desired to achieve homogenous distributions of particles of high density and diameters larger than $10^{-5} \text{ cm}$ suspended in a melt of a lighter material, provision of a zero-$g$ environment may be essential. By the same token, a variety of foamy materials, such as metal sponges, may be manufactured only in a zero-$g$ environment, because the heavy material will otherwise sediment immediately.

In practice, a variety of manufacturing processes could be envisioned in which the homogeneous embedding of particles of various densities and sizes into a medium of different density, such as molten plastic would yield very homogenous particle distributions which could not be otherwise achieved in a normal-$g$ environment. The following product groups may be potential candidates for space manufacturing:

1. High-altitude radiation shielding for aircraft electronics, made by imbedding high-density metal particles in a plastic matrix.
2. Nuclear and thermal heterogeneous shielding structure, made by suspending certain compounds in a non-metal matrix.
3. Complex high-strength fittings, high-temperature structures, high-strength brazing alloys or cermets made by dispersion of high-strength materials and fibers in a suitable metal matrix (composite casting).

In Figure 8, the characteristic length (in which a specified homogeneity requirement is still fulfilled) is plotted for a normal gravitation environment against the homogeneity requirement as a function of particle density, $\rho$; melt density, $p_f$; temperature, $T$; and particle radius, $r$. The constraints are very severe. In space, the equivalent capability is almost unlimited.

Relaxation Time of Solid Particles in a Liquid to Achieve Homogeneity

Such a result is, of course, meaningless because the scale height must be at least on the
liquids. After a certain relaxation time, $\tau$, the particle distribution will reach a steady state and be fairly uniform, unless a superimposed gravitational field establishes a vertical density gradient. The steady-state density distribution in a gravitational field has been discussed in Equation 11. In a zero-g environment, the particles will slowly diffuse at random and finally occupy the total volume of the liquid. It is of importance to estimate how the initial state of particle distribution will influence the relaxation time required to reach the final steady-state distribution. It is quite obvious that the more uniformly the particles are initially distributed, the sooner the equilibrium state of equal distribution will be reached.

In an effort to estimate the average "equal distribution" relaxation time, let us consider the well-known formula by Einstein regarding the Brownian motion which relates the mean square of the random migration path $X^2$ to other typical characteristics of the suspension. If $T$ is the observation time, the following is obtained:

$$X^2 = \frac{2kT}{6\pi\eta r} \tau$$

(15)

where

- $r$ = particle radius
- $\eta$ = viscosity of liquid
- $k$ = Boltzmann constant
- $T$ = absolute temperature

$X$ can be identified, e.g., as the average distance between centers of inhomogeneity, and its magnitude depends mainly on the premixing condition; $\tau$ is a crude estimate of time necessary to reach the steady state.

A few examples of characteristic relaxation times follow. If centers of inhomogeneities are on the average, e.g., 10 cm apart, it may take approximately 3 years to obtain a steady-state distribution in a convectionless liquid of viscosity $\eta = 10^{-2}$ poise (water or liquid metal) and a particle radius of $10^{-6}$ cm. If the inhomogeneities are, however, on the average 1 cm apart, the relaxation time would be reduced to 10 days. If the average distance between the particles approaches the particle diameter, thus $X = 2r$, the following is obtained from Equation 15:

$$\tau = \frac{12\pi T r^3}{k T}$$

(16)

The average time it takes the particles to exchange their position shrinks to the order of $10^{-4}$ sec.

These crude estimates indicate that intensive premixing of the suspended particles in the melt or liquid will be required if the steady-state (homogeneous) distribution is to be attained within an realistic time span.

Conclusions Regarding Preparation of Homogeneous Mixtures and Suspensions in Zero Gravity

In a normal-g environment, particles larger than approximately $10^{-5}$ to $10^{-4}$ cm cannot be homogeneously suspended in steady state in a liquid melt without counteracting fields. Homogeneous imbedding of heavy particles in a melt, matrix of a material of different density, followed by freezing, may constitute an important and versatile capability of space manufacturing. Several potential applications of these techniques have already been suggested. In order to avoid excessive relaxation times to homogeneity, careful premixing would be required.

ULTRA-PURIFICATION OF MATERIALS IN SPACE

Discussion of Experimental Findings

In many manufacturing processes, undesirable impurity trace elements and/or gaseous contaminants are widespread and difficult to eliminate. Quite often, the material has to be accepted in a rather impure condition because no efficient methods are known for further refinement, and the properties of the contaminated material are falsely assumed to be very similar to those of the pure material. It has been shown, however, that some material properties of metals, such as strength and ductility, undergo dramatic changes when they are manufactured in the ultraclean state. For example, "whiskers" (very clean metal single crystals) show great strength in comparison to "commercially pure" specimens of the same base metals. The discovery of ductile tungsten, for example, resulted from a careful elimination of oxygen and other trace elements. While ordinary beryllium is very brittle, it is believed that this metal in an ultrapure state exhibits reasonable ductility. This would greatly increase its utility because it would permit use of simplified forming techniques.

Some metals contain impurities that are hard to extract even by applying very sophisticated processes. "Pure" iron, for example, mostly retains residual carbon which easily diffuses back into the hot metal from the contaminated environment after refinement. The critical level of impurities, at which some sensitive properties, such as hardness and ductility, change radically, is sometimes a fraction of one part in a million.

It may be concluded from these random examples that an economical method of ultra-
refinement in space could revolutionize some of the cumbersome conventional forming techniques of exotic metals or other materials.

In reactor technology, it is well known that certain impurities in stainless steel core structures, for example cobalt, act as centers of local radioactive "hot spots" that in time cause embrittlement of the surrounding material. Because of a high thermal-diffusion rate, the chance of a spread of contamination is most severe while the ingot is at elevated temperatures.

The problem of contact contamination has been overcome in some ingot specimens by avoiding contact with mechanical support elements through levitation techniques, a process in which the clean specimen "floats" in a superimposed magnetic field without mechanical support. This method is, however, successful only with relatively small ingots of metal, mainly because of the enormous magnetic fields required.

The costs of creating ultraclean conditions on Earth as a means to obtain ultraclean products are, in principle, very high. Even high incremental expenditures would scarcely improve the vacuum environment and the cleanliness condition enough to warrant the mounting costs. Therefore, if purity requirements continue to become more stringent for some materials the space environment may in due time become an attractive and even cost-effective alternative to the Earth-bound manufacturing laboratory.

A hard vacuum combined with elevated temperature also affects weight, size, and density of oxides of various refractory metals, such as beryllium, magnesium, zirconium, and thorium isotopes. Noticable changes in density occur. In the case of beryllium oxide, for instance, the density changes from 1.3 g/cm³ at 1,000°C to approximately 2.8 g/cm³ at 2,000°C. It is difficult to predict whether such property changes will lead to new ceramic materials of interest for industrial use.

Conclusions Regarding Ultrapurification of Materials in a Vacuum

Certain properties, such as ductility, change drastically in some refractory materials when they are refined from an averagely pure to an ultrapure state. The necessary standards of cleanliness in an Earthbound laboratory are hard to achieve and even harder to preserve, if large specimens of metals are to be refined. Space may turn out to be an ideal medium for ultra-refinement of such exotic materials. Certain ultrapure metals may be easy to form in space because of their high ductility.

GENERAL CONCLUSIONS

In brief, the conclusions from the study effort reported in this paper are as follows:

1. In melt-grown crystals at normal-gravity turbulent convection currents, which are gravity-dependent and associated temperature fluctuations are a major hindrance to high-quality crystal growth. Even in a zero-gravity environment, however, convection may not disappear entirely because of the influence of moving bubbles. Special precautionary measures have to be taken to eliminate potential sources of imperfections. The technique of zone refining for large single crystals may be expected to work well in space. The merits of applying other methods of growing crystals in space remain inconclusive before actual space experiments can be performed.

2. The opportunity of manufacturing perfectly shaped bodies of minimum energy surfaces in space must be studied in greater detail. It may be difficult to take full advantage of such techniques without a variety of special precautionary measures. Minor irregularities in the configuration may be caused by internal motion of the liquid, buildup of internal stresses during the cooldown phase, nonuniformities in surface tension and viscosity while relaxing to the new shape, fluctuating spacecraft accelerations, and others.

3. It can be shown from analytical models of particle suspensions that, in space, a high degree of homogeneity may be obtained for heavy particles in a melt, provided the suspended material is properly premixed. For the larger particle sizes, however, even small g-forces may disturb the achievable homogeneity significantly. The dimensions of the particles exert the greatest influence on homogeneity (in the presence of g-forces) and to a lesser degree the density difference between liquid and solid particles and the temperature that can be considered. The use of "composite casting," among other methods, has been suggested for high-strength fittings and for nuclear and radiation shields.

4. The ultraclean space environment could be useful for refining certain refractories and their oxides. This conclusion is supported by laboratory studies regarding the behavior of refractories in a hard vacuum. It may be worthwhile to check the feasibility and effectiveness of refining high-purity refractories in a space environment.

5. From a cost-effectiveness point of view, space manufacturing techniques could be applied at the present time only to products which are feasible only in space. However, with further progress in space technology, it may even be possible to compete economically with difficult Earth-bound manufacturing techniques, provided that the cost of space delivery and recovery can be reduced to acceptable levels.

APPENDIX A

INTERNAL MOTION OF HEATED LIQUIDS OR MELTS IN ZERO-G

In the consideration of crystal growth in a convection-free environment, it might be assumed that natural convection will occur only in the presence of a gravity field, and results from a buoyancy force acting on the hotter, less dense portion of the liquid. Buoyancy is, however, not the only internal force at work in a heated liquid. At higher temperatures, where bubbles form from vapor of impurity materials and the heated melt, other forces may cause sporadic convection. "Bubbling forces" which may be partially active even in a zero-g environment could keep the melt in circulation and are discussed briefly below. The basic arguments of this discussion describe experiments that investigate boiling in liquids in a zero-g environment created by use of a 100-ft drop tower. Also only alcohol, water, and mercury were used as liquids in these experiments and the observation times in the weightless condition were limited to less than 0 sec. It is still believed that a certain similarity exists which may be, in principle, indicative of the behavior of
melts of solids at elevated temperatures in a zero-g environment.

Some of the significant forces which have been identified as acting in boiling aqueous solutions and bubbling melts of solids are buoyancy, surface tension, pressure, drag, and dynamic forces.

Buoyancy Forces

The difference between the external hydrostatic pressure force on the top surface of an object submerged in a liquid and the external hydrostatic pressure force on its bottom surface causes buoyancy. The magnitude of the buoyancy force, \( F_B \), is defined as

\[
F_B = (V - V_b) \cdot \rho_L \cdot g \cdot g_c \quad (A-1)
\]

where

\( V_b \) = bubble volume directly over the bubble base which is attached to the wall surface (cm\(^3\))
\( V \) = total bubble volume (cm\(^3\))
\( \rho_L \) = density of the liquid (g/cm\(^3\))
\( g \) = acceleration due to gravity cm sec\(^{-2}\)
\( g_c \) = gravitational constant (g-mass/g-force) cm sec\(^{-2}\)

Surface-Tension Forces

These forces are generated at the boundary of a liquid and an adjacent substance, such as a vapor or a solid. Only the vertical component, \( F_s \), of this force has significance, while the horizontal component is cancelled out:

\[
F_s = \sigma_s \cdot \pi \cdot d_b \cdot \sin \phi \quad (A-2)
\]

where

\( \sigma_s \) = surface tension
\( d_b \) = base diameter of the bubble
\( \phi \) = contact angle

In addition, bubbles move in a liquid medium of changing surface tension. A change in surface tension may be induced by a temperature gradient in the liquid matter.

Pressure Forces

In a bubble is completely surrounded by a liquid, the pressure force is completely balanced by the surface tension. When the bubble is, however, attached to a surface, the net internal pressure force acting on the spherical surface area of diameter \( d_b \) directly over the base is unbalanced:

\[
F_p = \frac{1}{2} \left( \frac{d_b}{R_t} \right)^2 \sigma_{sat} \quad (A-3)
\]

where

\( R_t \) = radius of curvature of the liquid-gas bubble interface
\( \sigma_{sat} \) = surface tension of the liquid with regard to saturated vapor

Drag Forces

A detached bubble moving through a liquid is subject to a drag force, \( F_D \) which can be expressed\(^{17} \) as:

\[
F_D = 12 \mu_c \pi R_{max} V \quad (A-4)
\]

\( \mu_c \) = viscosity of the liquid; \( R_{max} \) = maximum bubble diameter
\( V \) = bubble velocity

Dynamic Forces

A growing bubble in a liquid or melt displaces an equivalent amount of matter and transfers a momentum to the displaced liquid which is subsequently consumed by friction. It is rather difficult to give a clear analytical description of this force, but its magnitude can be quite significant for fast-growing bubbles. This force is independent of gravity and causes a pseudo-convection of the liquid or melt.

Experiments have been performed from drop towers to show the "force history" of bubbles in water in a zero-g environment\(^{16} \) (This force history can be compared to the equivalent conditions in a 1-g environment.) As expected, at a low-subcooling, normal-gravity condition, the gravity-dependent buoyancy force considerably influences the motion of the bubbles. Therefore, at a comparable rate of subcooling in zero-g, the dynamics of the bubbles would be altered because of the absence of a buoyant force. Accordingly, in the experiments, the formal and zero-g force histories proved to be significantly different. The bubbles still separated, however, from the surface in free fall because of an expected increase in the dynamic force. Therefore, bubbling should be avoided in crystal melts as a source of pseudo-convection.

APPENDIX B

ESTIMATE OF THE RATIO OF COHESIVE FORCES IN CRYSTALS VERSUS GRAVITATIONAL FORCES

In an effort to estimate the average cohesive energy of an ion in a "non-pure" crystal (which differs markedly from the ideal lattice energy), it may be reasonable to take the value of the surface energy, \( \gamma_s \), that is necessary to create 1 cm\(^2\) of new surface and then divide this quantity into the number of particles in this surface area, \( n^2/3 \). This is an estimate of the average surface energy per article.

\[
n = \text{number of atoms/cm}^3
\]

\[
n_s = \text{number of atoms/cm}^2 \text{ in the surface}
\]

\[
A = \text{Avogadro's number} = 6.02 \times 10^{23} \text{ atoms/mol}
\]
p = density gm/cm³  
M = atomic weight of substance 

\( \gamma = \text{surface energy} \) erg/cm²  
\( E = \text{cohesive energy} \) erg/particle

Then

\[
E = \gamma \cdot \left( \frac{d-A}{M} \right)^{-2/3} \times \frac{1}{1.6 \times 10^{-12}} \text{[eV]}
\]  
\( n_g = \frac{E}{1.6 \times 10^{-12}} \text{particles/cm}^2 \)  
\( m, g, d \)  

This crude calculation yields the following approximate values for cohesive energies in metals:

- Iron: 0.425 eV/particle
- Copper: 0.35 eV/particle
- Mercury: 0.1 eV/particle
- Tin: 0.3 eV/particle

Values for the ideal cohesive energy reported in the literature¹⁴ yield 4.36 eV for pure iron and 3.5 eV for pure copper, on the average one order of magnitude larger than the energies in an impure lattice.

One arrives at surprisingly similar results (within 20%) of the above estimate if one assumes that each lattice ion exhibits on the average a thermal energy of \( \frac{3}{2}kT \) and that at the vaporization point of the substance \( T_v \) the thermal energy approximately equals the cohesive energy. Thus,

\[
\gamma (N)^{-2/3} = \frac{3}{2}k(T_v - T)  \tag{B-2}
\]

where

- \( T_v = \text{vaporization temperature (°K)} \)
- \( \gamma = \text{surface tension (dyne/cm)} \)
- \( N = \text{Avogadro's number} \)
- \( k = \text{Boltzman's constant (erg/°K)} \)

Equation B-2 provides a rough estimate of the temperature dependence of the cohesive energy. The surface tension diminishes to very small values near the vaporization temperature \( T_v \). The average cohesive energy of the metal lattice will now be compared to the gravitational energy. The movement of a particle of mass \( m \) in the lattice will be limited to about one lattice distance, which will be less than \( 5 \times 10^{-8} \) cm. Therefore, the gain in potential energy of an ion of atomic weight, say 100, will be limited to m.g. d-10⁻²⁶ erg - 5 x 10⁻¹⁵ eV. In comparison, the average thermal excitation energy at 1000°K amounts to 1.3 x 10⁻¹ eV, 14 orders of magnitude larger. The conclusion is that gravity forces normally do not exert any substantial influence on the intrinsic structure of crystals because the ratio

\[
\frac{m.g.d}{3/2k (T_v - T)} = \frac{m.g.d}{3/2k\cdot\Delta T}  \tag{B-3}
\]

is a very small quantity in comparison to the lattice binding energy, provided the temperature of the material is well below the boiling point, and the material is still in a ductile or solid state. This simple consideration, of course, breaks down near the boiling temperature itself, but gains new significance in a qualitative sense above the boiling point, where the material is naturally in the vapor state. The "qualitative" similarity of Equation B-3 above the boiling point, \( \frac{mgd}{3/2k\cdot\Delta T} \), with the exponent of the barometric height relation \( \frac{mgd}{kT} \) is obvious. (See Equation 7 of main text.) This comparison may help (at least qualitatively) to build a rather shaky bridge from the relative influence of gravitation in a solid to that of matter in the gaseous state.

REFERENCES


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