Crystal-Growing in Space: Significance Still Up in the Air

More than a dozen crystal-growing and related metallurgical experiments were carried out on Skylabs 2, 3, and 4 over a period of several months ending a year ago this month. Many results are now in, and they are characterized by materials scientists as sufficiently encouraging and interesting to merit further space processing studies, such as those that will be on the joint American-Russian Apollo-Soyuz test program later this year or that are being planned for the Space Shuttle–Space Lab program in the 1980's.

Some researchers hope that the results of such experiments will one day lead to the manufacturing, in space, of high quality materials with carefully specified properties for electronic and other applications. Others in a still somewhat divided materials science community have yet to be convinced that the near-zero gravity environment of a satellite orbiting Earth has much to offer materials manufacturers. All agree that such space manufacturing is still a long way off at best and must await the outcome of much more research.

The National Aeronautics and Space Administration (NASA) program in space processing had its origin several years ago when engineers were concerned with the ways to construct and repair orbiting space stations. No one knew, for example, if metal welding would be possible in space.

As it happened, the development of large booster rockets made it feasible to orbit prefabricated space stations. By the time Skylab was launched in May 1973, the emphasis had shifted from metals joining processes, such as welding and brazing, to more basic metallurgical studies, including the possibility of growing single crystals of electronic and optical materials with high purity and few detrimental defects and the possibility of fabricating metallic materials with controlled microstructures and unique properties.

The experiments finally chosen to fly on the various Skylab missions are best characterized as a mixed bag of studies designed to observe the effect of microgravity on a variety of phenomena ranging from solidification of molten semiconductors to joining metals by brazing. The majority of the experiments were accomplished with the same furnace under somewhat restricted conditions. Thus, experiments were designed (and materials selected) not only for scientific value but also on the basis of whether they could be done or not. On the whole, and given the limitations, the researchers involved have been pleased with how well the experiments turned out.

One caveat to be borne in mind, however, is related to the fact that reports of improved materials quality in space-grown crystals compare materials processed exactly the same way in space and on the ground, the only difference being the presence or absence of gravity. While this approach may be scientifically valid for isolating the effect of gravity, the ultimate practical significance of space processing will be evident only when space-grown crystals are compared with the best crystals grown on Earth by any economically and technically viable method. Some of the effects observed on Skylab, according to some scientists, could have been produced on Earth if different experimental techniques had been used.

Microgravity of Earth Orbit

The absence of gravity, of course, is the one feature of the space environment that is not easily duplicated on Earth. Gravity is thought to affect the properties of materials solidified from a molten liquid or deposited from a vapor in a number of ways. Gravity-induced convection may be one of the more significant such effects. For example, a molten liquid in a temperature gradient such that the bottom portion is hotter (and hence of lower density) than the top will be unstable. That is, the high density, cool liquid will sink to the bottom, forcing the low density, hot material to the top. As the hot liquid cools, the process repeats itself.

Along with this convection cycle come thermal fluctuations, so that, for example, the position of the interface between the liquid and the solid being formed may change slightly from moment to moment. In a semiconductor such as silicon, the concentrations of impurity dopants control the electrical properties of the semiconductor. Since the concentrations of the dopants incorporated into the solidifying crystal depend on the instantaneous growth rate, the thermal fluctuations give rise to fluctuations in concentrations, which may adversely affect the semiconductor.

August Witt, Harry Gatos, and their associates at the Massachusetts Institute of Technology (MIT) demonstrated that such convection-caused composition fluctuations were absent when indium antimonide (InSb) crystals doped with tellurium were grown on Skylab by melting and resolidifying single crystals previously grown on Earth. Furthermore, analysis of the distribution of tellurium along the length of the InSb as obtained by electrical measurements indicated that the tellurium was homogeneously distributed, as is predicted by theory when convection is absent.

A similar set of experiments on germanium doped with gallium was carried out by John Yue and Fred Voltmer of Texas Instruments, Inc., Dallas. Because of the nature of InSb, the MIT researchers were restricted to a technique called the Hall effect that limited the resolution of the profile of tellurium to distances of 0.5 millimeter or greater. At Texas Instruments, investigators were able to use a technique (spreading resistance) that permitted a resolution of 10 micrometers. Thus, so-called microsegregation (concentration fluctuations with a periodicity less than about 100 micrometers) could be measured as well as macrosegregation. In both cases, reductions of fivefold or more in the fluctuations were observed in both radial and axial directions when germanium was solidified aboard Skylab.

Convection effects are also postulated to occur when crystals are grown by deposition from a vapor. Heribert Wiedemeier and his colleagues of Rensselaer Polytechnic Institute showed that crystals of germanium telluride (GeTe) and germanium selenide (GeSe) grown in space by chemical vapor deposition contained about one-tenth the number of some kinds of defects as compared to Earth-grown crystals.

A quantitative measure of the effect of convection was obtained by Anthony Ukanwa of Howard University. Ukanwa measured the self-diffusion of a radioactive zinc isotope in molten zinc. The experiment consisted of bonding the zinc isotope (zinc-65) to the end of a zinc specimen, melting the zinc for a predetermined time, solidifying the melt, sectioning the resulting ingot along its axis at intervals of 1 millimeter, and measuring the activity of the zinc-65 in each section. The profile of the diffused zinc-65 is matched with theory to extract a diffusion coefficient.

By carrying out self-diffusion experiments on Earth and in space, Ukanwa found that a convection velocity of only 4 micrometers per second could increase the effective diffusion rate about 50 times as compared to the case when no convection was present.

Some researchers believe that temperature fluctuations due to gravity-induced convection can affect the microstructure of multiphase systems, such as eutectics. A eutectic occurs when a two-component alloy, for example, has a melting point that is lower than that of either component by itself. A characteristic eutectic microstructure consisting of either fibers or lamellae rich in one component embedded in a matrix rich in the other component occurs at the alloy composition which has the minimum melting temperature.

Alfred Yue and his colleagues at the University of California, Los Angeles, studied eutectics consisting of sodium fluoride fibers embedded in a sodium chloride matrix with the hope of obtaining fibers that were continuous along the length of their samples. Such fibers, in similar materials, could serve as optical waveguides akin to glass optical fibers, but very closely spaced together. The UCLA scientists observed continuous fibers over a distance of 6 centimeters in their space-grown eutectics, but they obtained only discontinuous fibers from the experiments on Earth.

Earl Hasemyer and his co-workers at NASA's Marshall Space Flight Center, Alabama, carried out experiments on copper-aluminum eutectics. In this binary system, the eutectic structure consists of alternating lamellae of an aluminum-rich phase and an aluminum-copper compound (Al_2Cu). The NASA scientists observed some decrease (10 to 20 percent) in the frequency of defects, but continuous microstructures through the entire crystal were not seen.

On Earth, surface tension is sometimes overshadowed or at least balanced by the effect of gravity. For example, gravity can both hold a liquid in its container and force the wetting of the container surface. In an Earth orbit where the gravity is about 10^{-6} that on Earth, surface tension may have a role not ordinarily exhibited.

The MIT researchers observed such an effect in their experiments with tellurium-doped InSb. They found that the InSb liquid did not wet the surface of its quartz container, and as a result the melt contacted the container only by a network of ridges over a sizable portion of its length. Indium antimonide that had no intentionally introduced impurities or that was doped with tin did not exhibit this effect. Evidently, the dopant has a controlling effect on the surface properties of the liquid semiconductor, but why this happens is not yet understood.

The effect of surface tension in the absence of gravity may enable the production of large masses of defect-free semiconductors by such containerless methods as float-zone crystal growing. The float-zone method has not been widely used on Earth to commercially grow silicon crystals up to now, but interest in the use of this method is increasing. The advantage of this method is that the molten portion of the semiconductor is supported by surface tension between unmelted, solid semiconductor. No crucible or container is contacted, and hence there is no contamination by impurities, which otherwise can be a problem. In addition, for other materials with very high melting points or that are very reactive, it is difficult to find any container at all.

Containerless Crystal-Growing

Hans Walter of the University of Alabama, Huntsville, observed that when InSb was melted and resolidified in such a way that no container was contacted, it had approximately a tenfold reduction in the density of dislocations, a common defect in semiconductors and metals. However, the distribution of impurities was quite inhomogeneous in a sample intentionally doped with selenium.

In studying the phase equilibria of metallic systems, it is usually assumed that the only reactions that need to be considered are those between solid phases, liquid phases, or solids and liquids. Vapor phase reactions are not considered significant. However, David Larson, Jr., at Grumman Aerospace Corporation, Bethpage, New York, and his associates have found the success of this simplifying assumption in some materials may be due to the presence of gravity. A hydrostatic head (ρgh, where ρ is the density, g is the gravitational acceleration, and h is the height) can create a pressure on the interior of a liquid metal that suppresses the vapor. In microgravity, the absence of this force permits the evolution of a metal vapor from within a molten material. In effect, three-phase equilibria, solid-liquid-vapor, now need to be considered, according to Larson. A number of unusual microstructures, such as highly porous metal foams, conceivably could be made, provided that the phase equilibria can be controlled.

In some multicomponent systems, the liquid is not homogeneous but may consist of two separate liquid phases with different properties. Such systems are said to be immiscible. Under the influence of gravity, two liquids of different densities tend to separate, much as oil and water. As a result, the solid that finally forms is quite heterogeneous and does not display the equilibrium structure appropriate for its overall composition.

Experiments on three such immiscible systems by Jo Reger of TRW Systems Group, Redondo Beach, California, and his co-workers have established that the absence of gravity does increase the homogeneity of solidified material and that, in some cases, metallic phases similar to those that can otherwise be produced only by solidifying extremely rapidly may have been produced. Improved electrical properties were also observed.

NASA's ultimate goal is to develop space processing technology to the point that industry will want to participate on a commercial basis. Not only might potentially useful and unique materials that could not easily be made in any other way be produced, but the overall space program would also receive a big boost.

At present, however, a more modest goal is to encourage increased research participation by the materials science community, which remains divided on the question of how significant crystal growing in space really is. In the past, some respected researchers have declined to participate in Skylab and other zero-gravity programs. According to NASA officials, as the results of the Skylab experiments have become known, there seems to be increasing interest among scientists. How much that interest is transformable into research on just what space has to offer and how it can be exploited would seem the question to be answered before manufacturing of materials in space can be more than fanciful speculation.

—ARTHUR L. ROBINSON

Additional Reading

1. *Proceedings of the Third Space Processing Symposium: Skylab Results* (National Aeronautics and Space Administration Report No. M-74-5, Washington, D.C., 1974), vols. 1 and 2 (available from National Technical Information Service, Springfield, Virginia 22151, at $10.25 per volume).