Kirk-Othmer Encyclopedia of Chemical Technology.

SPACE PROCESSING

The idea of processing materials in space originated at the NASA Marshall Space Flight Center (MSFC) during the Apollo program as the confluence of several different and essentially unrelated disciplines. Engineers responsible for propulsion systems needed to understand the behavior of liquids in tanks of orbiting stages. This led to the study of fluid mechanics in low gravity, where liquid behavior is dominated by interfacial forces. The need for welding and brazing in space was recognized for the eventual building of large space structures. Thermal designers considering the use of phase-change materials for thermal control of spacecraft were also interested in understanding how materials solidify in the virtual absence of gravity. A group of solid-state physicists, searching for new superconducting mechanisms, became interested in producing fine *in situ* dispersions of semiconductors (qv) in metals and performed the first low gravity monotectic alloy solidification experiments using the MSFC drop tower (1).

Because the residual accelerations resulting from atmospheric drag and gravity gradient effects in low Earth orbit are typically on the order of 10^{-6} times Earth-gravity, the term microgravity generally is used to describe this acceleration environment. Conferences were held at MSFC in 1968 and 1969 to develop concepts for using the space environment for the actual manufacturing of unique materials. The prospects for using microgravity to prevent convective mixing, reduce sedimentation, and eliminate contamination by containerless processing were recognized, as was the possibility of using space to create a nearly perfect vacuum. The disciplines that could benefit from space processing were identified as alloy solidification, crystal growth, and separation of biological materials.

Some simple preliminary microgravity experiments were carried out during return trips from the moon on *Apollo* 14 and 17, but the *Skylab* and *Apollo–Soyuz* missions in the mid-1970s offered the first opportunities to conduct materials processing experiments in dedicated facilities. The results of these experiments, though interesting, were not spectacular, and it became apparent that a much greater understanding of the subtle effects of fluid behavior in the virtual absence of gravity was needed in order to properly utilize this new environment. Further, it was realized that some of the early hopes of actually producing unique materials in space on a commercial basis would remain impractical ones for the foreseeable future.

On the other hand, it was recognized, at least by some, that the microgravity environment of low Earth orbit provided a unique laboratory in which various processes could be studied under greatly simplified transport conditions. It was believed that such experiments, if properly done, could lead to a better fundamental understanding of the role of transport in various processes that could suggest improved control strategies for use on Earth. Also, the prospect of being able to produce benchmark materials to serve as paradigms for Earth-based technologies may be useful for evaluating potential improvements in performance that could be expected from better control of heat and mass transport during the process. Thus, the goal of the original space processing program was redirected from one of space manufacturing toward a more scientific materials science and applications program for the U.S. Space Shuttle era.

Because by the mid-1990s the space shuttle has been operational for more than a decade, a large number of microgravity experiments have been conducted on various flights, as opportunities warrant. Several microgravity-emphasis missions, in which the shuttle is flown in an attitude that minimizes acceleration disturbances, have also been flown to accommodate experiments that are exceptionally sensitive to accelerations. The more academically oriented experiments designed to address fundamental issues of materials processing are sponsored by the NASA Office of Microgravity Science and Applications; experiments designed to address issues of more direct interest to industrial research are sponsored by the NASA Office of Space Access and Technology (formerly the Office of Commercial Programs).

1. Materials Experiments in Space

1.1. Protein Crystal Growth

As of the mid-1990s, the protein crystal growth experiments produced the most spectacular results of all the space processing experiments. The importance of x-ray crystallography as a mechanism for determining three-dimensional structure of complex macromolecules has placed new demands on the ability to grow large (ca 0.5 mm on a side), highly ordered crystals of a vast variety of biological macromolecules in order to obtain high resolution x-ray diffraction data. There are numerous difficulties encountered in attempts to grow macromolecular crystals of biological interest, and the ability to grow such crystals of sufficient size and quality has become an important step for advancement in this field.

The difficulties encountered prompted some investigators to consider growing protein crystals in reduced gravity. The motivation for these experiments was first the ability to suspend the growing crystals in the growth solution to provide a more uniform growth environment, and secondly to reduce the convective mass transport so that growth could take place in a diffusion-controlled environment. The effect of convection on the growth of crystals is not well understood, but it is generally accepted that nonuniform growth conditions that can result from convective flows are not conducive to good internal order.

The first protein growth experiment in reduced gravity was carried out in 1983 (2) on *Spacelab* 1; crystals of lysozyme and β-galactosidase grew substantially larger in space than in ground control experiments. These results prompted the large number of other space protein crystal growth experiments conducted following that flight.

The first U.S. protein crystal growth experiment under reasonably well-controlled conditions was carried out in September 1988 on a space transportation system (STS-26), the first shuttle flight after the *Challenger* accident (3). The γ-interferon sample and the porcine elastase sample grew much larger than the ground control samples. The isocitrate lyase sample grew as discrete prisms, whereas the ground control crystals always grew dendritically. Crystals of all three of these proteins exhibited significantly higher x-ray diffraction resolution than any produced on Earth (4). This was true even when some of the smaller space-grown crystals were compared with larger Earth-grown crystals.

Following STS-26, there have been many other attempts to grow a variety of protein crystals in space. Considered as a whole, these experiments have produced a mixed set of results. In some cases the space experiments yielded no crystals or produced crystals that were inferior to those grown on Earth. However, there have been a number of cases in which the space-grown crystals were larger and better ordered than the best ever grown on Earth. In fact, the improvement in internal order obtained in several important proteins grown in reduced gravity has been so dramatic that structures have been solved or refined to higher resolution than had been possible using the diffraction data from the best available Earth-grown crystals. For example, a single crystal of human serum albumin (HSA) was grown on the first International Microgravity Lab (IML-1) that provided a data set with 15% more observations than the combined and averaged data sets from the best Earth-grown crystals, including those grown in gels (5). Crystals of satellite tobacco mosaic virus (STMV) grew 10-fold larger (by volume) than the largest ever grown on Earth and extended the resolution from 0.23 to 0.18 nm (6). Crystals of lysozyme, grown on *Spacelab* 1 and on IML-2, exhibited a reduction in mosaicity by a factor of 3, as determined both from rocking curve widths and Laue spot size (7).

The ability of a payload specialist on the first United States Microgravity Lab (USML-1) to mix the protein solutions actively and monitor the nucleation and early growth paid large dividends in the ability to grow crystals of several systems that had not been successful in earlier flight experiments (5). Malic enzyme that diffracted to 0.26 nm was grown in space, whereas the best crystals grown on Earth diffracted to only 0.32 nm. Similar results were obtained for Factor D, human α-thrombin, and HIV-1 reverse transcriptase. Bovine brain prolyl-isomerase crystals grown on Earth often form clusters and twins. The space-grown crystals were substantially larger and showed no clustering, twinning, or variations in diffraction quality.

However, there is still the question of why only some of the protein growth experiments in space were able to produce superior results, while many others did not. It should be remembered that not all experiments on the ground are successful; some are not reported. One possible explanation is that the growth process is developed and optimized on the ground before committing the experiment to flight. However, the conditions that are optimum under normal gravity may not take advantage of the microgravity environment. Therefore, it may be necessary to actually develop the optimal growth processes in space in order to improve the yield of protein crystal growth experiments in microgravity.

1.2. Solution Growth of Small-Molecule Crystals

At least some of the advantages obtained from growth of macromolecular crystals in microgravity appear to carry over to the growth of small-molecule crystals. Triglycine sulfate (TGS) crystals were grown from solution on *Spacelab* 3 and again on IML-1 using a novel cooled sting method (8). Supersaturation was maintained by extracting heat through the seed, which was mounted on a small heat pipe, and in turn was attached to a thermoelectric device. By growing under diffusion-controlled transport conditions, it was hoped it would be possible to avoid liquid–vapor inclusions. These inclusions are the most common types of defect in solution-grown crystals and are believed to be caused by unsteady growth conditions resulting from convective flows.

Typically, TGS crystals are grown on $\langle 001 \rangle$ oriented seeds, because growth on the $\langle 010 \rangle$ face tends to be nonuniform and multifaceted. However, in the absence of convection, growth on the $\langle 001 \rangle$ seeds on *Spacelab 3* was mostly around the periphery of the seed. Therefore, seeds with a natural $\langle 010 \rangle$ face were cut from a polyhedral TGS crystal for the experiments on IML-1. The crystal was grown in space with a 4°C undercooling, which produced a growth rate of 1.6 mm/d. Even though this is somewhat larger than typical growth rates (because of the limited time available) the quality of the space-grown crystal was extremely good. Growth was very uniform and the usual growth defects in the vicinity of the seed that form during the transition from dissolution to growth, known as ghost of the seed, were notably absent. High resolution x-ray topographs taken at Brookhaven National Laboratory (Brookhaven, New York) using the National Synchrotron Light Source indicated a crystal of exceptional quality. The only inclusions were from the incorporation of the polystyrene marker particles which had been added to the solution for flow visualization. As a pyroelectric detector for the far infrared, the detectivity, $D*$, of the space-grown crystal was significantly higher than that of the seed crystal, and the loss tangent was reduced from 0.12–0.18 for the seed to 0.007 for the space-grown material.

1.3. Bridgman Growth of Electronic and Photonic Materials

The early *Skylab* experiments demonstrated that growth striations in doped semiconductors (qv), believed to be caused by unsteady convective flows, could be eliminated in microgravity and that diffusion-controlled growth conditions could be established (9). This prompted a number of attempts to grow bulk multicomponent alloy-type systems with the objective of obtaining better compositional homogeneity necessary to achieve uniform electronic and optical properties. This goal, as of ca 1996, has not yet been realized because of the small (micro-*g*) quasisteady residual accelerations from atmospheric drag and gravity gradient effects. Many systems of interest have Schmidt numbers (ratio of viscosity to chemical diffusivity) that are on the order of 10^2–10^3. In order to achieve good homogeneity, it is necessary to keep the product of Grashof and Schmidt number on the order of unity (10). This requires an acceleration level below the typical micro-*g* available in low Earth orbit. For this reason, NASA is considering the development of furnaces with imposed magnetic fields for the space station, to further suppress the small residual flows.

In many of the Bridgman growth experiments in reduced gravity, however, the solidified ingot was found to be smaller than the growth ampul, and the melt appears to have pulled away from the ampuls during the solidification process. A satisfactory explanation for this effect has been offered (11). According to this model, the newly grown crystal initially pulls away from the ampul wall because of differential thermal expansion. In the absence of hydrostatic pressure, a meniscus forms between the solid and the wall and the subsequent growth front tracks this meniscus, causing the diameter of the growing crystal to become progressively smaller. This continues until the meniscus angle reaches the value required for constant diameter growth. This effect certainly alters the thermal boundary conditions and opens the possibility for surface tension-driven (Marangoni) convection to disturb the diffusion-controlled transport conditions. However, crystals grown in this manner frequently exhibit fewer dislocations, twins, and other growth defects (12). In fact, it has been suggested that this low gravity effect may provide more important benefits related to Bridgman growth than the establishment of diffusion-limited growth conditions (13).

1.4. Vapor Crystal Growth

For materials that lend themselves to physical or chemical vapor transport, growth from the vapor offers some attractive alternatives to growth from the melt. Growth can take place at temperatures considerably lower than the melting point, thus avoiding some of the higher temperature problems associated with melt growth. Gravity-driven convection definitely influences the growth process, perhaps in ways that are not yet completely understood or appreciated. For example, it has been shown that compositional gradients arising from the interaction of multicomponent systems with any vertical wall always results in horizontal density gradients which produce buoyancy-driven convective flows (14). However, since the Schmidt numbers characteristic of the vapor growth process are ca 1, diffusion-limited growth conditions can be obtained under far less stringent acceleration conditions than those required for melt growth (15).

Several crystal growth experiments on the shuttle have produced provocative results that are not at all understood, eg, growth of unseeded GeSe crystals by physical vapor transport using an inert noble gas as a buffer in a closed tube on STS-7 (16). In the ground control experiment, many small crystallites formed a crust inside the growth ampul at the cold end. The flight experiment produced dramatically different results; the crystals apparently nucleated away from the walls and grew as thin platelets that eventually became entwined with one another, forming a web that was loosely contained by the ampul. Even more striking was the appearance of the surfaces of the space-grown crystals. These were mirror-like and almost featureless, exhibiting only a few widely spaced growth terraces. By contrast, the crystallites in the ground control experiments conducted under identical thermal conditions had many pits and irregular closely spaced growth terraces.

Another vapor growth experiment was carried out on USML-1 in which $Hg_{0.4}Cd_{0.6}Te$ was grown by closed-tube chemical vapor deposition on HgCdTe substrates using HgI_2 as the transport agent. Again, considerable improvements in the flight samples were observed in terms of surface morphology, chemical microhomogeneity, and crystalline perfection (17). These improvements were attributed to the sensitivity of the $Hg_{1-x}Cd_xTe$–HgI_2 vapor transport system to minute fluid dynamic disturbances that are unavoidable in normal gravity.

When thin films of copper phthalocyanine, CuPc, were grown on Cu substrates by physical vapor deposition in a similar experiment on an earlier shuttle flight, a dramatic difference in appearance of the space-grown film as compared with the ground control experiment was also found (18). The central portion of the space-grown samples had a distinct opalescent quality (18). Detailed analysis of the films using a variety of optical, x-ray diffraction, and sem techniques revealed not only a significant difference in the growth morphology, but also a new polymorph of CuPc that had never been seen. The film on the ground control samples, when viewed by sem, had the appearance of a shag carpet in which the individual columns of crystalline CuPc were relatively sparse and were quite irregular. By contrast, the central portion of the space-grown films had the appearance of a thick pile carpet. The columns of CuPc were closely spaced and vertically aligned.

Mercuric iodide crystals grown by physical vapor transport on *Spacelab 3* exhibited sharp, well-formed facets indicating good internal order (19). This was confirmed by γ-ray rocking curves which were approximately one-third the width of the ground control sample. Both electron and hole mobility were significantly enhanced in the flight crystal. The experiment was repeated on IML-1 with similar results (20).

Mercuric iodide forms a layered structure, similar to graphite, in which the A–B planes are bonded by van der Waals forces. Consequently, the crystalline structure is very weak, especially at the growth temperature, and it was believed that the performance of the materials as a room-temperature nuclear spectrometer was limited by defects caused by self-deformation during the growth process. This was the original motivation for the flight experiments. It is not clear as of ca 1996 whether the improved quality of the flight crystals was the result of the elimination of the weight of the crystal during its growth, or of the diffusion-controlled transport conditions that produced a more uniform growth environment.

1.5. Test of Dendritic Growth Models

The microgravity environment provides an excellent opportunity to carry out critical tests of fundamental theories of solidification without the complicating effects introduced by buoyancy-driven flows. This advantage was used to carry out a series of experiments to elucidate dendrite growth kinetics under well-characterized diffusion-controlled conditions in pure succinonitrile (SCN) (21). This constituted a rigorous test of various nonlinear dynamical pattern formation theories that provide the basis for the prediction of the microstructure and physical properties achieved in a solidification process.

Dendrite tip velocities were measured as a function of undercooling over a range from 0.05–1.5 K. Comparing these measurements with ground-based measurements, it was possible to show that effects of convection are more significant at the smaller undercoolings and are still important up to undercoolings as large as 1.3 K. Even in microgravity, a slight departure in the data was noted at the smallest undercooling, which was attributed to the residual acceleration of the spacecraft. These data also allow the determination of the scaling constant important in the selection of the dynamic operating state, which the present theories have been unable to provide.

1.6. Electrodeposition

Electrodeposition experiments in reduced gravity have produced some intriguing results. An early experiment on the German TEXUS rocket, using higher current densities than can normally be used on Earth, reported the deposition of amorphous Ni on Au substrates (22). In a series of experiments on the Consort Rocket, it was possible to repeat this result and a mechanism by which this occurs was proposed (23). Careful analysis of the x-ray-transparent Ni films produced in low gravity revealed that a significant amount of hydrogen had been incorporated into the deposit to form NiH. This distorted the lattice, destroying long-range order to the extent that x-ray diffraction peaks could no longer be observed. It was conjectured that the difference in the morphology of the hydrogen bubbles collecting on the cathode surface owing to buoyancy effects must have been responsible for the increased hydrogen incorporation into the film in the low gravity experiments. Ground-based experiments using a frit between the electrodes were partially successful in duplicating some of the effects observed in low gravity (24).

This group also carried out a series of codeposition experiments in which diamond dust was incorporated in Ni coatings and chromium carbide was incorporated in Co coatings. These experiments led directly to a new ground-based technique for electrodepositing a bone-like hydroxyapatite coating on prosthetic implants, which provides significantly better adhesion, and unlike the presently used plasma spray coatings, does not damage the hydroxyapatite (25–27) (see Prosthetic and biomedical devices). This is highly significant in developing implants that do not loosen with time. Also, during this investigation, a new plating process was also developed using Cr(III) which poses significantly few environmental problems than the more common Cr(VI) process (28). Exciting spin-offs such as these are likely to be the most important return from the microgravity program.

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