IMPROVED CRYSTAL QUALITY BY DETACHED SOLIDIFICATION INMICROGRAVITY

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Introduction

Directional solidification in microgravity has often led to ingots that grew with little or no contact with the ampoule wall. When this occurred, crystallographic perfection was usually greatly improved -- often by several orders of magnitude. Unfortunately, until recently the true mechanisms underlying detached solidification were unknown. As a consequence, flight experiments yielded erratic results. Within the past four years, we have developed a new theoretical model that explains many of the flight results[1-5]. This model gives rise to predictions of the conditions required to yield detached solidification, both in microgravity and on earth.

Beginning with Skylab in 1974, many investigators found directional solidification in microgravity often yielded ingots that appear to have grown without being in intimate contact with their containers. A wide range of surface features and behavior were observed. We classify these observations into the categories shown below. Note that a given ingot might display several of these features along its length, but not all of them.

1. The ingot easily slid out of its container, whereas sticking was observed when solidification was carried out on earth under otherwise identical conditions.
2. On its surface, the ingot had isolated voids or bubbles of various sizes, depths and contact angles with the ampoule wall. (Such surface bubbles are also frequently seen on terrestrially solidified materials, but to a lesser extent.)
3. With a triangular or rectangular cross-section ampoule, the ingot had cylindrical detached surfaces in the corners and a flat surface in contact the wall over most of each face.
4. With an ampoule containing grooves machined in it, the ingot contacted only the peaks of the grooves.
5. After correcting for thermal contraction, there remained a gap of about 1 to 60 μm between the ingot and the ampoule wall around the entire periphery. Irregular narrow ridges maintained limited contact with the ampoule wall and were predominantly axial. A variety of features were seen in the detached regions, including microfacets and periodic waves or lines.
6. There was a gap of up to several mm between the ingot and the wall, typically with a wavy surface and sometimes forming an hourglass-shaped neck adjacent to the seed. Although this gap generally extended around the entire periphery, sometimes it was confined to a portion of the surface.

For semiconductors, the last portion of the ingot to freeze often replicated the surface of the ampoule, showing that contact had become intimate (as on earth). Here, we are concerned primarily with 5 and 6 above, as these differ from all prior terrestrial experience and were completely unexpected prior to Skylab. Behaviors 1 and 2 often occur on earth. Behaviors 3 and 4 are not surprising, as one would not expect non-wetting (high contact angle) liquids to penetrate cavities.

Although detached solidification has been observed predominantly with semiconductors, it has also been observed with metals and inorganic compounds. This apparent predominance may reflect only the fact that most flight experiments on directional solidification have been performed on semiconductors. Detached solidification has been observed at both fast and slow freezing rates. Sometimes it occurred with one type of dopant and not with others. The type of detachment, indeed even whether detachment occurred or not, has not been reproducible.

Some investigators have chosen to avoid detached solidification by using a spring to press a piston or plug tightly against the end of the melt. This strategy appears to have been successful. On the other hand, detachment has occurred nonetheless when a plug only lightly contacted the end of the feed ingot. We can explain these observations in a fashion similar to that used to predict the influence of gravity on detached solidification. It has been claimed that detachment is sensitive to the residual acceleration. Unfortunately there have been so few measurements of residual acceleration, particularly the average value, that one cannot judge the validity of this claim from experimental evidence alone. Our theoretical treatment leads us to believe that acceleration can enhance detachment if it is of the correct direction and magnitude.

We now discuss briefly the wide variety of properties observed in materials solidified with detachment. It is interesting to note that there was seldom any correlation between the ridges and lines sometimes observed on the surface and any internal defects or composition variation. Axial and radial variations in impurity doping ranged from that expected for diffusion-controlled solidification to that corresponding to vigorous convection. Sometimes there was a variation in composition near the detached surface. Although impurity striations were rare, they were occasionally seen near the surface. Some detached surfaces were inadvertently coated with oxide, whereas even dissolved oxygen was not detected on others. An interesting result was obtained in Wilcox's Skylab experiments on GaSb-InSb alloys[9]. Large changes in composition occurred across twin boundaries only in the detached portions of the ingots.

Generally speaking, crystallographic perfection was much greater when detached solidification occurred. Very often, twins and grain boundaries nucleated only where the ingot contacted the ampoule wall. Dislocation etch pit densities were frequently orders of magnitude less when the solidification had been detached. In semiconductors, this higher perfection has led to substantial increases in charge carrier mobility.

Models for detachment

Over the past 24 years, several models were proposed to explain detached solidification. We briefly review some of these below. When detached solidification was discovered in several

Skylab experiments, it was generally thought that the melt had lost contact from the ampoule wall because of the high contact angles of the semiconductor melts. Indeed, the phenomenon is still called "de-wetting" by some investigators[e.g.,10-12]. This view persists, in spite of microgravity experiments[13,14] and theory[15] showing that liquids do not pull away from the ampoule wall, no matter what the contact angle. The implicit assumption underlying this model is that the solid took the same shape as the liquid from which it froze. This would be like a person examining a Czochralski-grown crystal and concluding it came from a cylindrical melt of the same diameter as the crystal! In reality, the edge of a growing crystal does not even begin to follow the melt's meniscus -- it deviates by the so-called growth angle.

It is relevant to note that the voids found on the surface of Bridgman-grown crystals do not have the same shape as the gas bubbles had on the wall in the melt before solidification. In a parabolic flight experiment with InSb, gas bubbles on the wall moved when the freezing interface contacted them[15]. Such a bubble moved toward and partly onto the interface, so as to minimize the surface energy in the system. If one looks carefully at such cavities on a grown crystal, it can be seen that the angle with the ampoule changes as one moves around the periphery of the cavity. This is a manifestation of the interaction between the growing crystal and the bubble.

Some instances of detached solidification of metals in microgravity have been attributed to shrinkage during solidification. We believe this is erroneous. It is the inverse of the old discredited claim that one cannot grow semiconductor crystals by the vertical Bridgman technique because these materials expand when they freeze. To clarify the situation, let us consider the volume change that occurs as a semiconductor slowly freezes upward on earth. Solidification begins at the bottom of the ampoule, perhaps on a seed. If the density decreases upon freezing, then the top of the melt moves slowly upward to accommodate the increasing volume. Provided that enough head space remains for the entire volume change, solidification proceeds to completion without a problem. On the other hand, if the upward movement of the melt is blocked, then the ampoule breaks. The reverse situation occurs for metals that contract when they freeze. The melt surface slowly moves downward during solidification, while the melt and the solid both remain in contact with the ampoule wall.

If the coefficient of thermal expansion is greater for the ampoule than for the ingot, then during cooling from the melting point, the ingot is put under tensile stress while the ampoule is under compression[17-21]. Depending on the mechanical properties and the degree to which the solid sticks to the ampoule, the ingot may break free from the ampoule wall and form a gap, it may remain stuck and plastically deform, or it may remain stuck and break the ampoule.

Detached solidification has been attributed to a rough ampoule wall[10-12]. The idea is that a non-wetting melt cannot penetrate into cavities, especially if some residual gas is present in them. The problem with this model is that the interior of quartz growth ampoules is typically very smooth. Often it has been coated with shiny pyrolytic carbon. Artificially roughened ampoules did yield detached solidification between the peaks, while the solid was attached at the peaks[22-28].

Another proposed model invokes an oxide coating that acts as a container smaller in diameter than the ampoule. While this may have been true in some flight experiments, it has been rare. Ampoules were sealed in an inert gas and/or vacuum, sometimes with a gas getter installed. In the case of GaSb, for example, electron channeling patterns on the detached surface were sharp and showed no oxide[29,30]. No oxygen was detected by Rutherford back scattering measurements.

The meniscus model and results of recent theoretical modeling

In our new model of detached solidification a meniscus connects the edge of the ingot with the ampoule wall, similar to Czochralski growth but with much less distance between the ingot and the wall. Because of the curvature of the meniscus and the surface tension of the melt, the pressure in the gap must be greater than that in the adjacent melt. The gas filling this gap consists of one or more volatile constituents that are rejected by the growing solid. In most cases, this is the residual gas remaining in the ampoule that has dissolved in the melt. Although flight ampoules were generally sealed in a vacuum, outgassing would provide adequate gas to fill the gap. With only one known exception[23,25,27,28], the residual gas pressure has not been measured after flight experiments. In that one exception, it was about 10^{-2} torr, in spite of the use of gas getters in the sealed cartridge.

One may draw an analogy between our mechanism of detached solidification and the formation of "worm holes" or gas tubes inside growing solids. Formation of such tubes is commonly observed in ice and organic compounds. The mechanism underlying tube formation is as follows. Residual gas dissolves in the melt, e.g. air in the case of water being converted to ice cubes. The dissolved gas is much less soluble in the solid, and so accumulates at the freezing interface. When its concentration becomes large enough, a gas bubble nucleates and grows. If conditions are right, it remains at the interface and blocks the solid from growing under it. The diameter and stability of the resulting tube depends on the transport of dissolved gas into the bubble. One can regard detached solidification as the reverse geometry, i.e. the gas bubble surrounds the growing solid rather than vice versa.

Over the last several years, we have been developing our theoretical model for detached solidification. Numerical calculations were performed for InSb, which has exhibited detached solidification in numerous microgravity experiments. Steady state in the absence of buoyancy-driven convection was analyzed numerically[3]. We found that detached solidification in zero gravity is favored by a low freezing rate, increased concentration of volatile constituent, large contact angle for the melt on the ampoule wall (poor wetting), low surface tension for the melt, and a large growth angle.

Although Marangoni convection had a large effect on the local concentration field, surprisingly, it did not strongly influence the total flux of gas into the gap and, therefore, the tendency for detachment. One would expect Marangoni convection to influence the axial and radial variation in impurity doping in the crystal. Flight experiments with detachment have yielded a wide spectrum of results. In some cases, axial and radial concentration profiles corresponded to diffusion-controlled conditions. In other cases, there was clear evidence for Marangoni convection, ranging from gentle to vigorous. Why was Marangoni convection not always exhibited with detached solidification? If the gap is very narrow, our calculations show that the region of perturbed composition should also be very narrow. Thus, one might still achieve an axial concentration profile expected in the absence of convection, particularly if the freezing rate is not low. Another possible explanation for diffusion-controlled segregation with detached solidification involves a surface-active impurity that concentrates on the meniscus surface. One would expect, for example, that dissolved oxygen would concentrate on the surface of semiconductor and metal melts. Such impurities strongly inhibit the movement of a free liquid surface. For example, surfactant can stop Marangoni motion of a gas bubble in a temperature gradient and retard its rise velocity in a gravitational field. The influence of a surfactant increases as the bubble size decreases. Thus, for a given oxygen concentration in a semiconductor melt, we would expect Marangoni convection to manifest itself only for large gap widths during detached solidification.

We examined the stability of steady-state detached solidification in microgravity[4]. The shape of the meniscus is destabilizing in a fashion similar to Czochralski growth. If, for example, the crystal begins growing toward the wall, the meniscus shape tends to accelerate the change in diameter. Thus, if only the meniscus is taken into account, one predicts that both Czochralski growth and detached solidification are unstable. Since this is contrary to experimental observations, other factors must stabilize the growth. We considered gas transport and heat transfer as stabilizing mechanisms for detached solidification. We found that while gas transport into the gap is necessary for detached solidification, it is sufficient to stabilize detachment only for a short distance, on the order of the gap width. On the other hand, heat transfer strongly stabilizes detached solidification, as it does for the crystal diameter in Czochralski growth.

We considered the influence of gravity on detached solidification[5]. In the usual vertical Bridgman configuration, we must add the melt's hydrostatic head to the gas pressure in the gap required to maintain the meniscus shape (or the spring pressure when a piston is used in a microgravity experiment). At low g, the streamlines are nearly straight into the freezing interface. As g is increased, buoyancy-driven convection increases and eventually overpowers the flow due to growth. Gentle buoyancy-driven convection increases the flux of volatile species into the meniscus when it moves from the center toward the meniscus and carries segregated materials with it. At high g, the buoyancy-driven convection mixes the melt and decreases the flux into the meniscus even when the melt flow is directed radially outward along the freezing interface. Thus, for vertical Bridgman growth with a fixed convex freezing interface, there is a maximum in flux versus acceleration. On the other hand, with a concave interface, the flux decreases monotonically as acceleration increases because the convection near the interface is away from the gap. With the normal vertical Bridgman growth on earth, a slightly convex interface is indicative of the thermal field required to cause the flow favoring detachment. Thus, it is interesting to note that detached solidification was recently observed on earth for germanium with a slightly convex interface[6-8]. Use of a mirror furnace enabled observation of the ampoule in the neighborhood of the freezing interface. The appearance was exactly as expected from our model.

Future plans

We have recruited two new graduate students to work on this program. One will continue the theoretical development of the meniscus model as outlined above. The other will attempt to achieve detached solidification on Earth using a transparent, low-melting material so that the interface shape and convection in the melt can be seen.

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