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PRELIMINARY TERRESTRIAL BASED EXPERIMENTS OF GRAVITY-AFFECTED CRYSTAL GROWTH

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Ten crystals of tin were grown in a centrifuge at forces from 1 through 5 g. These crystals were etched for the purpose of observing the growth striations. Preliminary conclusions concerning the effects of gravity on the growth mechanisms are presented.

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PRELIMINARY TERRESTRIAL BASED EXPERIMENTS OF GRAVITY-AFFECTED CRYSTAL GROWTH

SUMMARY

Tin was melted in a heating assembly secured to the arm of a centrifuge. The furnace was allowed to pivot and reach its equilibrium angle of swing for the gravity force being experienced. The crucible was cooled during rotation to allow the growth of single crystals.

The crystals were etched for the purpose of observing the growth striations. Slices were removed from some of the crystals to permit observation of the striations in the interior. Visual analyses were made with a scanning electron microscope.

Preliminary conclusions relating the appearance of the striations to gravity forces and the affected growth mechanisms are presented. Further experiments that will verify these conclusions and determine other gravity effects are proposed.

INTRODUCTION

The influence of gravity on man and his environment is an area that until recently has been accepted and ignored. Prospects in the near future of zero-gravity and near zero-gravity environments require a readjustment of our earth-bound thinking if full utilization is to be made of the new environment. Precise determination of those parameters affected by gravity is required before processes can be developed and modified for operation in zero-gravity.

This study ascertains those gravity-influenced parameters that affect solidification and crystal growth. Single crystals will be grown in a centrifuge under different gravity forces. The effect of various gravity fields on the formation of striations, dislocation densities, growth direction, and growth mechanism will be studied. This initial report will be concerned with the observation of gravity-affected growth striations.

BACKGROUND

The term "growth striation" applies to the phenomena resulting from periodic distribution of impurities in a melt-grown crystal. These striations consist of periodic variations in the impurity concentration, bounded by regions of high dislocation density. The presence of striations is attributed to three possible growth mechanisms; platelet growth [1], supercooling, and convection.

Consider the edgewise growth of platelets (Fig. 1) containing an impurity that lowers the freezing point of the material. As growth proceeds, solute is rejected into the melt. At point A on the growth interface the impurity has less difficulty diffusing out into the liquid than at point B. To have a steep enough concentration gradient to remove the solute, the concentration at B must be greater than at A. Upon solidification more impurities are trapped at B than at A. The thickness of the platelets is a function of temperature and solute distribution at the platelet edge. Since points C and A are leading edges, their concentrations are similar, and a steep concentration gradient exists between B and C. The formation of edge dislocations [1] accommodates the resulting lattice misfit.

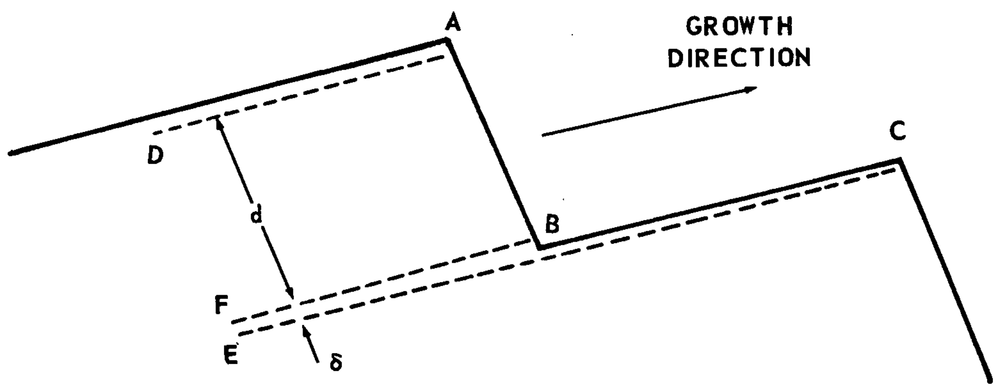

Figure 1. Schematic representation of platelets [1].

A supercooling effect would produce periodic variation in the impurity segregation coefficient. As the material cools it falls below the melting temperature. Solidification begins rapidly and continues until the latent heat of fusion raises the temperature of the melt in front of the interface to the melting point.

The growth process stops until the melt again supercools, and the procedure repeats. The variation in growth speed is accompanied by a variation in impurity distribution.

The driving force for dendritic growth can be two types of supercooling: thermal supercooling and constitutional supercooling. Thermal supercooling is the process that lowers the temperature of the liquid beneath the solidification point by removal of heat from the melt. Constitutional supercooling results in many alloy systems when the solid freezes at a different composition from the liquid. Although the temperature gradient from the interface into the melt is positive, it still may be lower than the solidification point of the composition of liquid in the alloy near the interface.

Dendritic growth occurs when there is a temperature inversion at the growth interface. This set of conditions may cause the interface to become unstable and spikes to grow quickly out from the interface into the cooler liquid. The spike may form secondary or tertiary arms, depending on the temperature profile surrounding the arm.

Weinberg and Chalmers [2] observed dendritic growth of large single crystals of lead by decanting the remaining liquid during the solidification process. The structure was seen to consist of a series of parallel dendrite rows. Dendrites, which formed only in those regions where supercooling occurred, projected into the liquid ahead of the interface. As growth of the crystal continued, the space between dendrites was filled by the interface.

Studies of Pb-Sb alloys [3] indicate that the formation of dendrites on the interface passes through several transitions. At low growth rates, cellular growth occurs. As growth velocity increased the cross section assumed a cruciform shape in the 100 dendrite direction. When the dendritic direction made a large angle to the heat flow these cellular dendrites joined [3] to form platelets, possibly to insure a better path for heat flow. The resultant structure contained regions (platelets or columns) of high purity material surrounded by areas with a large concentration of impurities.

Convection in the melt, with its accompanying temperature fluctuations, has been shown to cause growth rate fluctuations. The growth variations in turn cause fluctuations in the impurity content of the crystal. The type of convection present in a system is indicated by the Rayleigh number [4]. At certain critical values, laminar or turbulent convection occurs. The Rayleigh number may be expressed as:

$$Ra = (L^3 \rho_l^2 Cp \; g\beta \Delta T)/\mu k$$

where L is a characteristic length (i.e. depth), g is the gravitational constant, β is the coefficient of thermal volume expansion, ΔT is a characteristic temperature difference (i.e. between two points in the melt), μ is the viscosity of the fluid, and ρ_1 is the density of the liquid. In the present experiment the gravitational constant will be the only parameter varied.

There are three temperature gradients contributing to convection in a melt. A temperature gradient is formed across the entire length of the melt by the process of cooling from one end of the crucible. A gradient exists between the center of the melt and the exterior as a result of either heating or cooling through the walls of the crucible. The third gradient exists at the interface. When the temperature of the liquid has fallen below the melting point, growth begins. As a result of the heat of fusion released at the interface, the temperature will rise at the interface above that of the neighboring liquid and solid and drop in the direction of either the liquid or the solid [5].

Because of its ease of handling and low melting point, tin was chosen for the preliminary material in this analysis. The β-phase has a body-centered tetragonal structure that can be thought of as a body-centered cubic structure with one shortened axis. Impurities in 99.95-percent Sn cause preferred growth along [110], whereas, purer tin (99.998 percent) has no preferred growth direction and does not exhibit striations [6]. The striations have been shown [7] to form along [110] when that is the growth direction of the crystal. They form at an angle to the growth axis when the orientation of the crystal is not [110].

APPARATUS

The apparatus consists of a 7.0-ft-lb, dc permanent magnet torque motor driving a symmetrical centrifuge arm (Fig. 2). The heating assembly, which was designed and fabricated by H. M. King of the Materials Division of Astronautics Laboratory, is allowed to pivot and reach its equilibrium angle of swing and is balanced about the axis of rotation by a pivoted counter weight. Rotation rate was determined by a photocell relay with a counter gate activated for 10-second intervals.

The heater is shown in Figure 3. The double-pointed graphite crucible used for crystal growth rests in a 3 1/4- by 1 1/8-in. diameter hole in a 2-in. diameter Lava Shell. Size 28 Chromel-P heating wire was wound through eight vertical 0.200-in. diameter holes. A 10-32 brass bolt placed flush with the

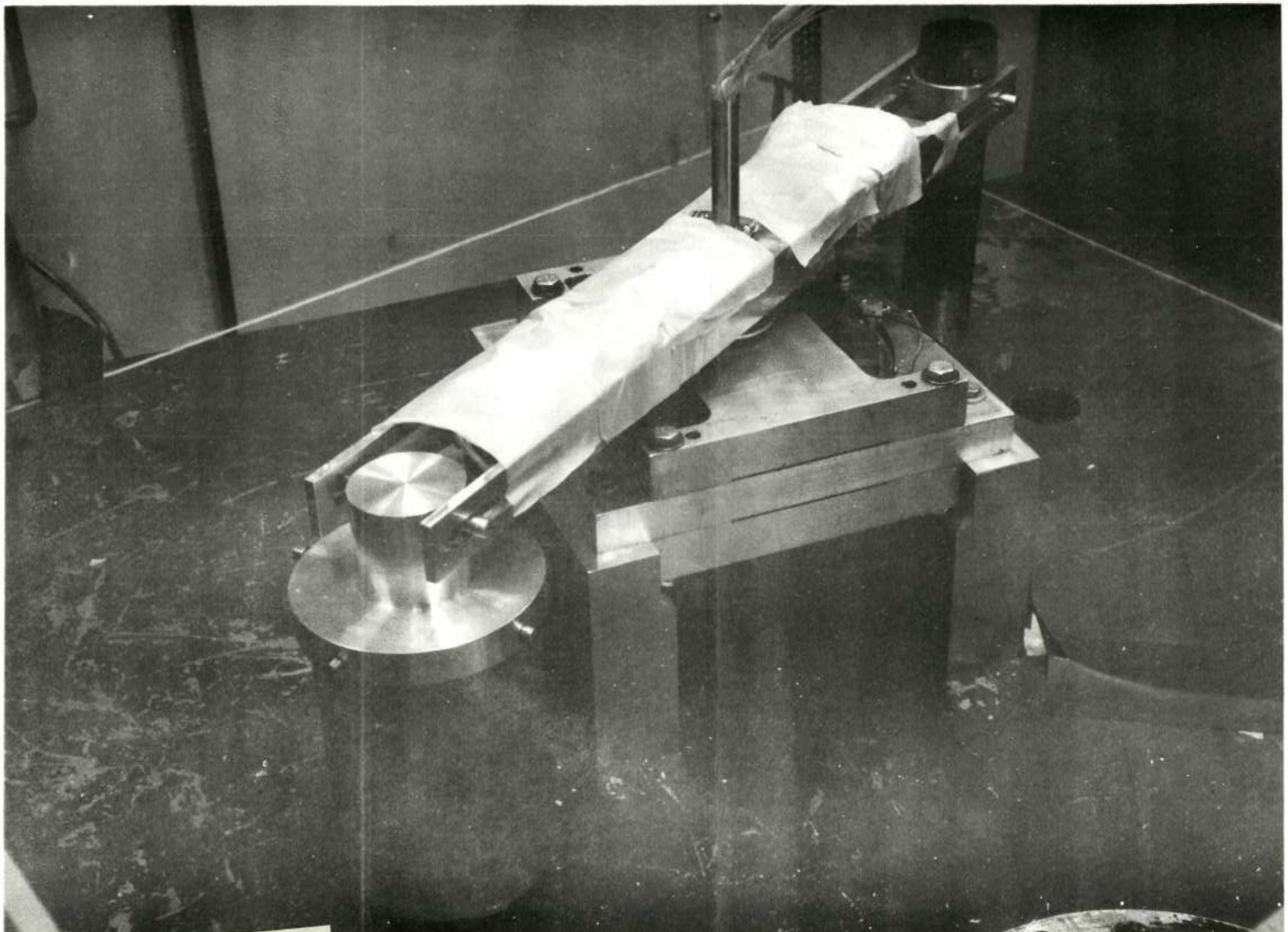

Figure 2. Centrifuge and heating assembly.

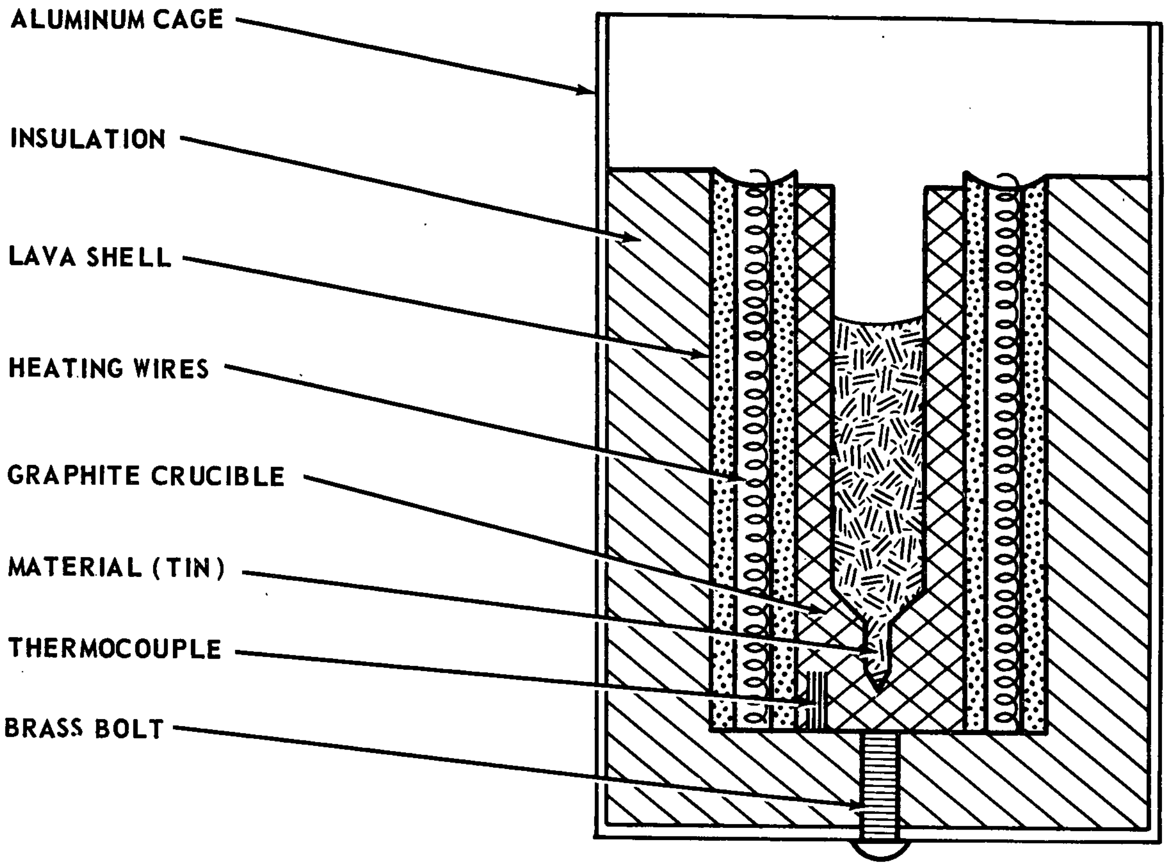

Figure 3. Furnace assembly.

base of the crucible provides a heat sink during the cooling process. The entire heating assembly is insulated by sodium-silicate foam, a low density foam for minimum weight purposes developed in-house by H. M. King. An ST124 platform slip-ring, not flight rated, was acquired from Astrionics Laboratory for connecting electrical leads to the heating assembly. The furnace is operated by an SCR power supply with a differentiating and integrating current adjusting-type control.

A regulating thermocouple was placed in a hole in the tip of the crucible. The hole was drilled as close as possible to the end of the melt for an accurate determination of temperature. During solidification the temperature was displayed on a strip chart recorder.

EXPERIMENTAL TECHNIQUE

Tin (20 mesh-99.95 percent pure) was melted in the experimental apparatus in air without rotation. The oxide slag was removed from the surface, and the melt was allowed to solidify. After cooling the slug was removed, etched (10 percent HCl, 10 percent HNO_3, 80 percent H_2O), and examined. Most of the samples at this stage were polycrystalline. The prepared slug was replaced in the heating assembly, which was then secured to the centrifuge arm by four bolts. Rotation of the assembly was begun before the furnace achieved maximum temperature. When the furnace reached temperature the power was turned off and the furnace allowed to cool at its own rate. Rotation was continued until the sample cooled to room temperature. It was removed and etched until surface striations appeared. The crystal at this time was also checked for small grains.

For observing the striations in the interior of the crystal, it was cut with a diamond wheel saw, parallel to the axis, and polished with successively smaller grit to 900 grit polishing compound. The slices were etched in a 10-percent HCl, 10-percent HNO_3, and 80-percent H_2O solution until the striations appeared (Figs. 4, 5, 6, and 7).

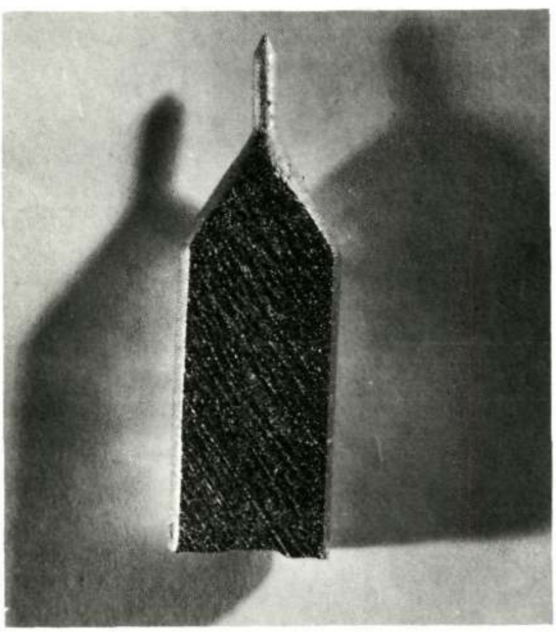

Figure 4. Interior striations of 2-g single crystal.

RESULTS

Ten crystals of 99.95-percent tin were grown in a centrifuge. The gravity force was varied from 1 through 5 g's.

Crystals grown at 1 g, when etched, display dendritic growth patterns. As the force is increased to 1.3 and 1.5 g, the patterns become areas of parallel lines, the orientation of the lines differing with each area. Crystals grown at forces 2 g and greater display one set of parallel lines completely encompassing the crystal (Fig. 8). At 5 g only polycrystalline samples containing no striations were obtained. This last result was not entirely

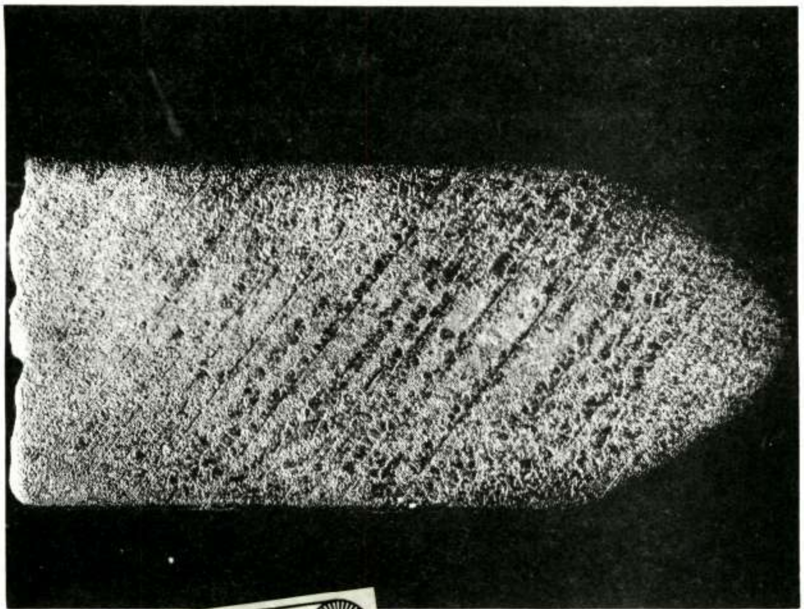

Figure 5. Interior striations of 3-g single crystal.

Figure 6. Striation in 3. 5-g single crystal (100X).

Figure 7. Striation in 3.5-g single crystal (2000X).

unexpected since an increasing number of smaller grains occurred on the surface of the crystals with increasing gravity force (Fig. 9).

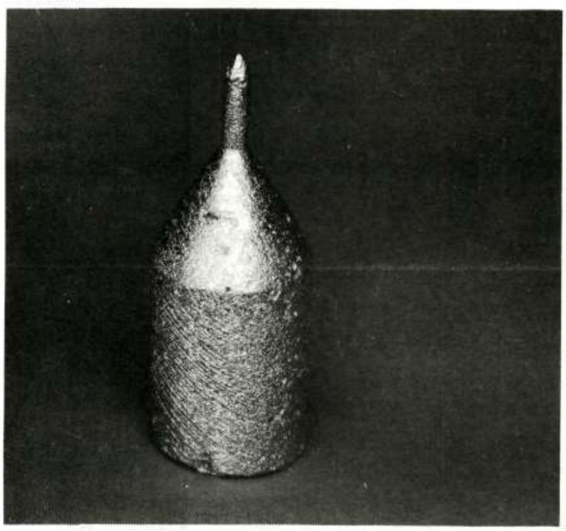

Figure 8. Surface striations of 3.5-g single crystal.

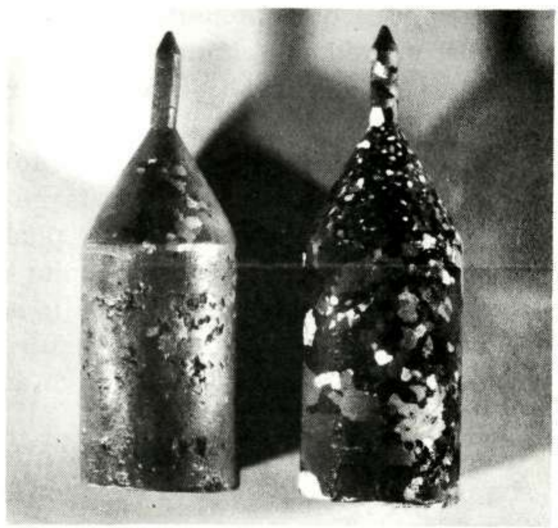

Figure 9. Comparison of 4- and 5-g crystals showing increase in number of crystallites.

In this experimental apparatus a low negative, almost nonexistent, temperature gradient was imposed upon the material. This allows the crystallographic properties of the crystal and the thermal properties of the interface to control solidification. Convection and temperature fluctuations are encouraged as well as dendritic growth.

The crystals appear to be passing through two stages of growth effects; one between 1 1/2 and 2 g, in which growth changes from dendritic to platelet-dendritic, and one above 4 g, in which growth changes from platelet to polycrystalline. The ability to grow pure (99.999-percent) tin single crystals without these effects indicates they are purity related, thus substantiating our assumption of high concentrations of impurities at the striations.

The increasing gravity force increases the amount of convection, eliminates the supercooling growth mechanism, and subsequently eliminates dendritic-type growth. It has been shown that columnar dendrites occur under growth conditions not extreme enough to warrant true dendritic growth. These are aligned parallel and will combine on adjoining sides to form series of flanges or platelets. Scanning electron microscope studies reveal columnar formations in the tin crystals (Fig. 10), substantiating the assumption that our growth mechanism has progressed from dendritic at low g-force to columnar-platelet type growth at 2 through 4 g to spurious nucleation at 5 g.

If one assumes that the dendritic growth mechanism predominates, but is modified in intensity as it passes through the gravity ranges, the platelets may be viewed as primary and secondary dendritic stalks. The stalks, conforming to 100 growth directions, are coplanar on (001).

When the dendrites join to form platelets, a phenomenon expected when the direction of heat flow is at large angle to the dendrite direction, the platelets would occur on the 001 plane. In the presence of an impurity, such as Sb, that raises the melting point of the material, dendrites resulting from constitutional supercooling contain a high concentration of the impurity. Subsequent etching of the sample then reveals the impurities. In the present case, the highest concentration of antimony would be on the 001 planes.

In Table 1 the angles which (001) makes to the axis of the crystals are shown. A definite shift in the growth direction as the gravity force increases is evident. The striations coincide with the 001 planes only in the case of 3 1/2 g. What must then be considered as happening is that because of the fast growth rates and the high angle which (001) makes with the crystal axis, the striations are forming at a "compromise angle" between (001) and the

Figure 10. Columnar formations in tin crystals
(4000X; reduced 14 percent in reproduction).

TABLE 1. ANGLES BETWEEN (001) AND CRYSTAL AXIS

Gravity-Force	(001) Angle with Axis
1 1/2	8 deg 9 min
2	11 deg 40 min
2	14 deg
3	16 deg 52 min
3 1/2	28 deg

direction of heat flow. This phenomenon has been shown to occur in tin by previous experimenters [7]. As (001) shifts towards the axis the striations more nearly coincide with this plane and crystalline perfection increases. Too great a shift in the growth direction, as occurs above 4 g, is an intolerable growth condition and the boule becomes polycrystalline.

The importance of convection during crystal growth is influenced by the temperature gradient, growth rate, impurity concentration, and gravity force. For a rapid rate of growth, such as exhibited by our samples, it is possible that the area of high impurity concentration lies within the "stagnant" layer of melt near the interface. As the degree of convection is increased with gravity g force, this layer gradually becomes perturbed. Altering the amount of impurities present would alter the degree of convection necessary to change the method of growth. If the above analysis is correct, it should be possible to predetermine at what gravity force platelet growth will appear by controlling the level of impurities present.

If any preliminary extrapolation to zero gravity can be made at this point in the experiment, it is that by eliminating convection in zero gravity we are greatly enhancing dendritic growth capabilities. Unless the moment of nucleation and beginning growth of the crystal and the growth rate itself are carefully controlled, a single crystal grown in zero gravity might be expected to exhibit impurity banding and possible dendritic growth.

To ascertain if the stated conclusions are accurate further experimentation must be conducted in which the growth conditions are more closely controlled. An apparatus is being designed that will enable a seed to be introduced to the bottom of the melt and growth begun from a predetermined orientation. The effects of the gravity force can then be more fully determined from the consequent crystalline perfection and lattice strain.

Future studies will include the variation of one of four parameters: temperature gradient, impurity concentration, growth rate, and material. These studies lead to further knowledge of convection effects, interface morphology as controlled by growth rate and impurity concentration, and growth mechanisms. A further system for study is InSb, which is similar to GaAs and is presently under study in this laboratory. Alloys containing materials with different densities also provide interesting questions for study.

CONCLUSIONS

Two obvious conclusions can be drawn; it is possible for large single crystals to grow while experiencing high gravity forces and increasing the gravity force initiates changes in the predominant growth factors.

While the slight negative temperature gradient in the crucible encourages convection, it also encourages dendritic growth. Crystals grown from 1 through 1.5 g exhibit definite dendritic patterns on their surfaces. These patterns change to parallel striations at the higher gravity forces. Preliminary results from X-ray examination indicate a change in the growth direction with increasing gravity force.

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APPROVAL

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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