Solidification of II-VI Compounds in a Rotating Magnetic Field

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Background

This project is aimed at using a rotating magnetic field (RMF) to control fluid flow and transport during directional solidification of elemental and compound melts. Microgravity experiments have demonstrated that small amounts of residual acceleration of less than a micro-g can initiate and prolong fluid flow, particularly when there is a static component of the field perpendicular to the liquid solid interface.[1] Thus a true diffusion boundary layer is not formed, and it becomes difficult to verify theories of solidification or to achieve diffusion controlled solidification. The RMF superimposes a stirring effect on an electrically conducting liquid, and with appropriate field strengths and frequencies, controlled transport of material through a liquid column can be obtained. As diffusion conditions are precluded and complete mixing conditions prevail, the technique is appropriate for traveling solvent zone or float zone growth methods in which the overall composition of the liquid can be maintained throughout the growth experiment. Crystals grown by RMF techniques in microgravity in previous, unrelated missions have shown exceptional properties.[2] The objective of the project is two-fold, namely (1) using numerical modeling simulate the behavior of a solvent zone with applied thermal boundary conditions and demonstrate the effects of decreasing gravity levels, or an increasing applied RMF, or both, and (2) to grow elements and II-VI compounds from traveling solvent zones both with and without applied RMFs, and to determine objectively how well the modeling predicts solidification parameters.

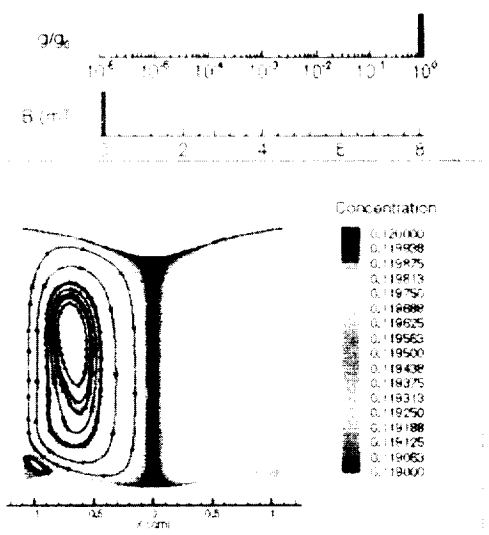
Microgravity Relevance

The traveling heater method (THM) of crystal growth potentially involves both temperature and solutal gradients and thus is considerably subject to buoyancy driven convection on earth. When the driving force for convection is reduced, as in a flight experiment, then transport through the solvent zone is predominantly by diffusion and the technique becomes prohibitively slow, and far too susceptible to variations in the microgravity environment such as g-jitter and the direction of the residual acceleration component. The application of a rotating magnetic field in unit gravity and in microgravity leads to a dramatic increase in the flow within the zone and to increased transport of solute material through the zone.

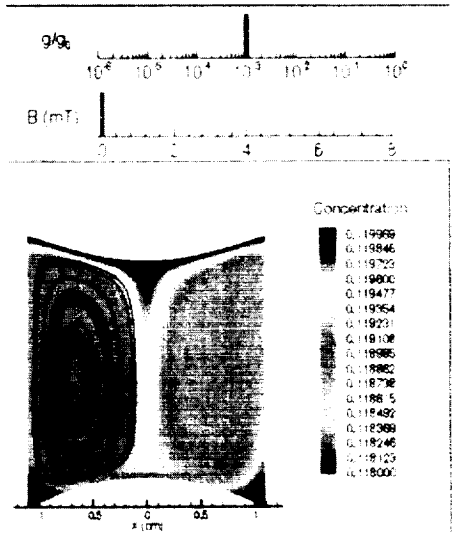
Cadmium telluride dissolved in liquid tellurium has been used to model a typical traveling solvent zone. During crystal growth a single crystal seed of CdTe is in contact with the zone at the solidifying end, while a source of polycrystalline CdTe is dissolved into the tellurium rich zone as the zone is translated. The aspect ratio of zone length to sample diameter is normally between ½ and 1. The temperature is set such that the zone maximum temperature is between the melting point of the solvent and the solute. In the case of CdTe-Te, a zone of approximately 750°C is used. This leads to a solute concentration of approximately 12% CdTe.

Modeling incorporates the momentum balance as governed by the incompressible Navier-Stokes and the continuity equations, but with three velocity components to account for the azimuthal flow. The force term includes thermal and solutal buoyancy forces and also the electromagnetic stirring force. Thermal boundary conditions are imposed on the THM system, and it is assumed that the dissolution and growth rates are equal. The complete model has been described in a journal article.[3]

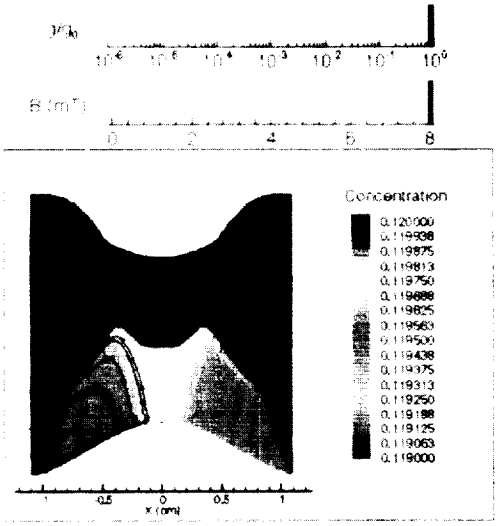
In Figure 1a, the THM technique is shown as configured for terrestrial gravity. This technique has proved to a useful method of producing CdTe, but suffers from the time required to transport the material through the zone. Too fast a translation leads to increased tellurium inclusions. The figure shows the flow pattern, superimposed on the CdTe concentration field. It can be seen that the solidifying interface is a complex shape with the curvature mainly concave as seen from the melt. Under these conditions any defects that are propagated from the edges of the sample will continue to grow through the crystal. In Figure 1b, the same geometry and thermal field have been applied for the conditions of $10^{-3}g_0$. In this case the transport is purely diffusion controlled and the flow rates are considerably slower. The composition varies almost linearly through the zone. The interface shape, now convex as seen from the melt, has been modified and is now more favorable for the growth of high quality crystals. Defects propagating from the interface will be eliminated upon reaching the walls. Figure 1c shows the effect of applying a 8 mT rotating magnetic field of 60 Hz on the ground. The single roll cell has been replaced by a complex, mainly double cell arrangement as the buoyancy induced cell is pushed upwards by a recirculating Ekman cell at the interface. While, in principle, an increase in field strength should result in two cells, the flow velocities become very large and the solutal transport is too intense to be modeled. The interface shape is, however, improved as compared to the non-magnetic case. This two-dimensional representation does not show the azimuthal flow which attains a maximum of approximately 1 mm/sec for each 1mT of applied field. Transport rates through the zone are considerably increased. In figure 1d the RMF is applied to a zone in low gravity. The RMF produces two Eckman recirculating cells which overwhelm the residual convection and result in efficient transport of material. At higher field strengths than shown here, the two cells are more uniform. This illustration is meant to show the onset of the double Ekman cell configuration. The situation is ideal for controlled transport, even when the acceleration level is only as low as $10^{-3}g_0$. Thus the combination of low, but not exceptionally low, acceleration levels with a weak applied rotating magnetic field is able to produce controlled flow ideally suited for zone growth.



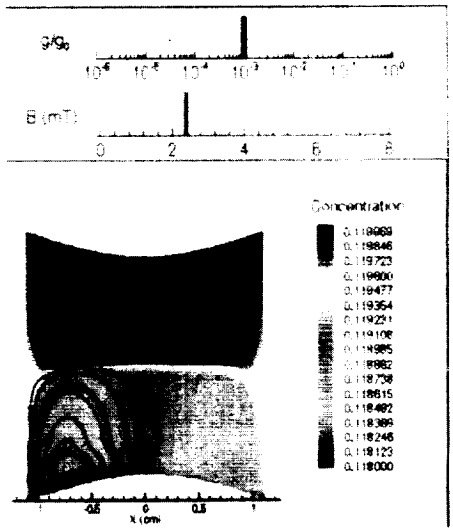
a. Terrestrial Gravity, No Field



b. Microgravity, No Field



c. Terrestrial Gravity, 8 mT



d. 10^{-3} g_0, 2.2 mT

Figure 1. Calculated Flow Patterns and concentration fields in cadmium telluride within a tellurium solvent zone

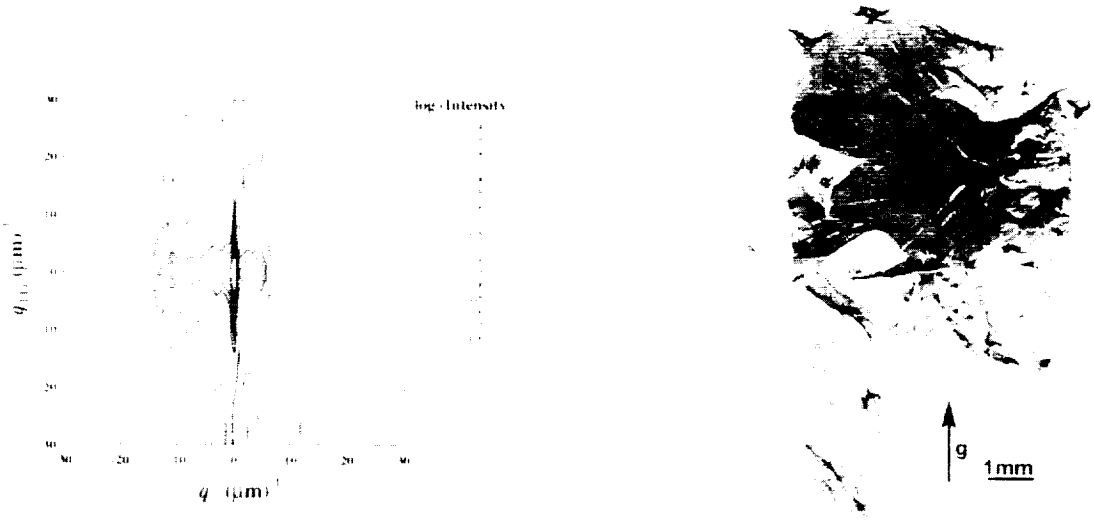


Figure 2. Typical results of growth of a high Cd HgCdTe alloy grown by traveling heater method with an applied rotating magnetic field
a. Triple axis x-ray diffraction b. Synchrotron white beam topograph

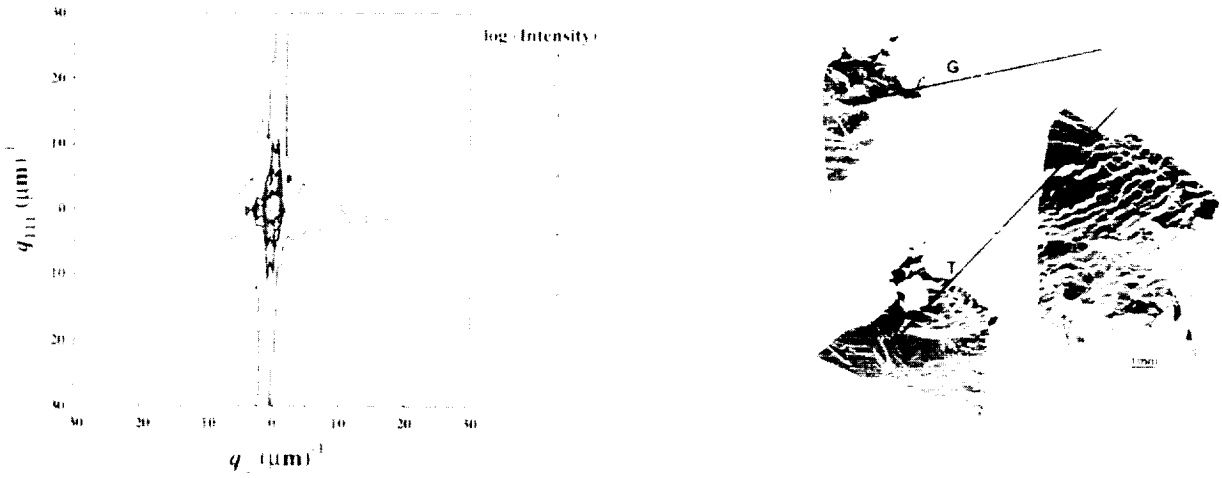


Figure 3. Typical results of growth of a high Cd HgCdTe alloy grown by traveling heater method – conventional (no magnetic field)
a. Triple Axis Diffractometry b. White Beam X-ray Synchrotron Topograph

Experimental Results

Several systems have been examined as candidates for the THM technique. While the original proposal called specifically for II-VI compounds, the possibility of examining transport in simpler systems with materials, particularly elements, which are easier to characterize, has also been contemplated. Of the possible selections, the growth of the group IV elements, particularly germanium has been considered. Growth of germanium from a lead solution has been tried, but the solubility is low and there is a need to process at above 820°C to achieve the desired zone configuration. The resulting crystal of germanium contained lead inclusions. We are now proceeding with the growth of germanium from a germanium-silver eutectic. The eutectic temperature is 651°C and so growth will be at temperatures similar to those used for growth of II-VI compounds. While the modeling has been done for pure CdTe, compounds have been grown, namely CdZnTe and HgCdTe. In all cases the thermophysical properties of the zone were assumed to be those of pure tellurium. The measurement of the viscosity, electrical conductivity and density of the tellurium alloys will be made with an oscillating cup viscometer.[4] The modeling effort is now being extended to include the HgCdTe alloys.

The growth configuration consists of four separate heaters on one translating stand. Of these small, single zone furnaces, two are equipped with rotating magnetic fields and two are not. Thus, we run parallel experiments, with and without the field. Some typical early results for HgCdTe alloys grown with a translation speed of 1 mm/day are shown in Figure 2 and 3. When the zone is translated with the field applied, the result is a structure in which there are many low angle boundaries and a mosaic structure results. Figure 2a shows results from a triple axis x-ray diffractometer which maps reciprocal lattice space. The multiple peaks confirm the presence of sub-grains, and the breadth of the peaks illustrate a high defect density. Figure 2b, taken from an adjacent wafer, is a reflection white beam x-ray synchrotron photograph in which the diffraction spot is enlarged to show the structure. The material has a very high defect density with a myriad of overlapping segments to the reflections. The photograph confirms that the quality of material is not high. Other wafers from the same boule showed similar results. Results from the parallel experiment with HgCdTe grown conventionally without the field are shown in Figure 3. In Figure 3a, the triple axis diffraction demonstrates a strong "surface streak" running vertically. This is an indication of good crystal quality. The material, however is not free of low angle boundaries. This structure is typical of the THM method. The improvement can be seen more dramatically in Figure 3b, where the white lines delineate low angle boundaries, as do the dark lines within the sub-grains. The sub-grain size is large fractions of mm, however, and is another indication of high quality. In this case the tilt across small angle boundaries is 1-4 minutes, while the dislocation density within the sub-grains is 10^4 - 10^5 /cm^2. Modeling analysis, which was done for the simpler case of CdTe, shows that the flow in the ground based sample is extremely complex in the presence of the field (see figure 1c), while low gravity conditions with the field applied would lead to a superior product as the flow across the interface would control the thermal field (figure 1d). The more complex cases of the II-VI alloys are now being modeled.

Conclusions

Numerical modeling has demonstrated that, in the growth of CdTe from a tellurium solution, a rotating magnetic field can advantageously modify the shape of the liquid solid interface such that the interface is convex as seen from the liquid. Under such circumstances, the defect structure is reduced as any defects which are formed tend to grow out and not propagate. The flow of liquid, however, is complex due to the competing flow induced by the rotating magnetic field and the buoyancy driven convection. When the acceleration forces are reduced to one thousandth of gravity, the flow pattern is much simplified and well controlled material transport through the solvent zone can be readily achieved.

Triple axis diffractometry and x-ray synchrotron topography have demonstrated that there is no significant improvement in crystal quality for HgCdTe grown on earth from a tellurium solution when a rotating magnetic field is applied. However, modeling shows that the flow in microgravity with a rotating magnetic field would produce a superior product

References

1. Donald C. Gillies, Sandor L. Lehoczky, F. R. Szofran, Dale A. Watring, Helga A. Alexander and Gregory A. Jerman, J. Crystal Growth, 174 (1997),
2. M. Fiederle, C. Eiche, W. Joerger, M. Salk, A. S. Senchenkov, A. V. Egorov, D. G. Elbing and K. W. Benz, J. Crystal Growth, 166 (1996), 256-260.
3. Chahid K. Ghaddar, Cheo K. Lee, Shariar Motakef and Donald C. Gillies, To be published in Journal of Crystal Growth.
4. Konstantin Mazuruk, Ching-Hua Su, Sandor L. Lehoczky and Franz Rosenberger, J. Appl. Phys. 77 (10), 15 May 1995, 5098-5102.