Horizontal travelling heater method growth of $Hg_{1-x}Cd_xTe$ with crucible rotation

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A horizontal travelling heater method (THM) for growing cylindrical crystals from a partially filled solution zone has been investigated for the first time. By applying ampoule rotation, the whole cross section of the crystal is successively brought into contact with the liquid solution, which is effectively stirred by forced convection. This approach was used to grow single-crystalline $Hg_{1-x}Cd_xTe$ ingots from a Te-rich solution zone. The structural perfection and metallurgical homogeneity are equivalent to vertically-grown THM material.

1. Introduction

For many years the travelling heater method (THM) has proved successful for growing single crystals of a variety of compounds and alloys. The method combines solution growth, making relatively low growth temperatures possible, which result in low vapour pressures, and steady-state conditions between dissolution of the source material and crystallization on a seed. During the last decade, THM has been well accepted as a crystal growth technique especially suited to $Hg_{1-x}Cd_xTe$ and related alloys [1–4]. However, the large concentration changes during crystallization inherent in all solution growth methods present the problem of extremely small growth rates limited by the mass transport conditions. Several attempts have been made to improve mass transport in crystal growth from solution. Among them, accelerated crucible rotation technique (ACRT) [5,6], low-frequency vibrational stirring [7] and high-gravity crystal growth in a centrifuge [8] are the most prominent. While using different mechanisms, all these techniques are aimed at producing forced mixing of the solution, which is most important adjacent to the growth interface.

We have investigated THM growth of $Hg_{1-x}Cd_xTe$ using an experimental set-up with a cylindrical ampoule rotating about its horizontal axis. If the solution zone occupies at least half, but not the total volume between the cylindrical seed and feed (see fig. 1), gravitational acceleration will hold the liquid zone position at rest, although seed and feed are rotating together with the ampoule. As a result, the continuous tangential slip motion of the liquid phase adjacent to the solid will cause convective mixing, as with ACRT. However, contrary to the mixing produced by ACRT from the difference in rotation rates of the accelerated/decelerated ampoule and the inert liquid zone, in horizontal growth it is permanently effected by a constant rotation of the horizontal ampoule.

The method presented here is similar to the technique of Kumagawa, Ozawa et al. [9,10] for III–V mixed crystal layers and bulk crystals. The authors called it "rotationary Bridgman method" and used an arrangement inclined by an angle to completely wet the growing surface. They did not apply it to THM growth.

Horizontal THM arrangements without rotation are known from studies on crystal growth of III–V compounds from metallic solutions [11]. In all reported work on horizontal THM, use was made of approximately half-cylindrical seed and feed material. This results in the usual advantages of free surfaces and reduced strain due to

less container contact, but only in minor changes to the convective mixing conditions. Moreover, for substances with high vapour pressure, e.g. like $Hg_{1-x}Cd_xTe$, it is not possible to grow seed and feed ingots that do not completely enclose the zone region. It is the aim of this paper to describe the first results with this new approach to THM.

2. Theory

It is not within the scope of this article to give a complete description of convective motion in the solution zone in a horizontally rotating ampoule. Instead, we want to focus on that part of the complex flow pattern which most influences the solute transport rate. When there are no external mechanical forces on the horizontal THM growth system, fluid flow results from natural convection, caused by temperature and composition gradients, and surface tension (Marangoni convection). It is known that for a solvent with low viscosity, e.g. liquid Te, natural convection is a very effective mechanism of material transport [6]. This is true at least for some distance from the solid interfaces. In addition to density-driven convection and Marangoni convection, the influence of rotating boundaries in horizontal THM has to be considered. We want to separate the effects of the revolving cylindrical wall (ampoule) and the rotating discs (seed and feed interfaces), and suggest that the effect of the cylinder rotation on the liquid solution can be ignored. The argument for this is that natural convection, which will be enhanced by the rotating wall, has already been very effective in the bulk of the liquid zone. The limiting factor is the poor mixing adjacent to the crystal faces. In this way, the crystal and the feed rotating relative to the liquid zone govern the material transport conditions through the solution zone. It is proposed here that the model of a disc of infinite diameter rotating in a motionless liquid, which is quite common in hydrodynamics [12], is applicable. It is assumed that effects due to the edge or the confined volume may be neglected for the present case, where the boundary layer thickness is small compared with the disc radius. It is obvious that the liquid in the zone is actually far from being motionless.

The rotating disc model is one of the few in hydrodynamics which has been analytically solved [13,14] and then adopted to crystal growth phenomena [15]. In the absence of external fields, a rotating disc imports angular momentum to the fluid in a thin layer adjacent to the disc and expels it centrifugally. This layer is known as the Ekman layer with a thickness proportional to $(\nu/\omega)^{1/2}$, where ν is the kinematic viscosity and ω the rotation rate. Following the mathematical treatment by Cochran and von Kármán [16], the angular motion results in a normal component $u_z(z)$,

$$u_z(z) = 0.51\omega^{3/2}\nu^{-1/2}z^2,$$

of the total convective flow for $z < (\nu/\omega)^{1/2}$, where z is the normal distance from the solid interface. It is this axial component which should

seed   crystal   zone   feed
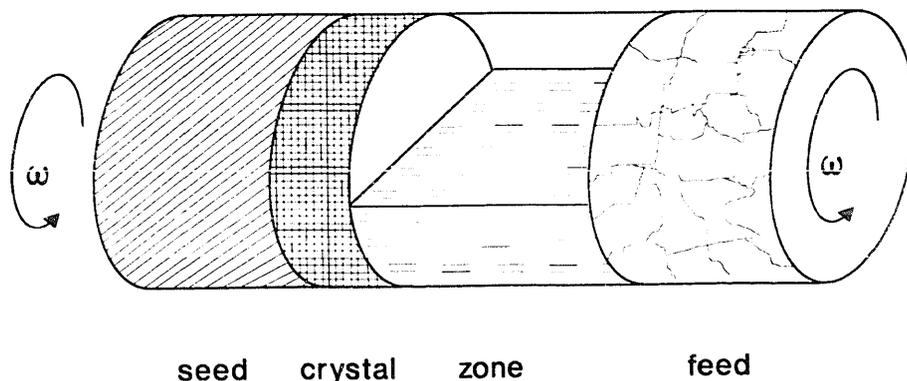
Fig. 1. Schematic representation of the horizontal THM crystal growth arrangement.

be as high as possible to increase crystal growth rate. We are mainly interested in the flow field out to a distance over which the solute field is varying, i.e. concentration gradients are not reduced by other kinds of convective mixing. This distance is usually called the solute boundary layer thickness and is again proportional to $(\nu/\omega)^{1/2}$ and well within the Ekman layer. As for the normal flow component of convective motion, the solute boundary layer thickness can drastically be reduced by the axially rotating disc, i.e. horizontally rotating seed and feed. A smaller boundary layer thickness results in more stable growth conditions with respect to constitutional supercooling theory. In a recent paper on ACRT applied to vertical THM [17], we gave a simple explanation in terms of constitutional supercooling criterion arguments. The same approach is valid for THM growth with horizontal crucible rotation, as we believe the same situation applies adjacent to the growth interface as in ACRT. The differences are the continuity of the slip motion, with the horizontal method, and the different cross sections of the liquid zone. Theoretically, the latter should results in a lower maximum growth rate for horizontal THM, since the smaller zone cross section has to provide the circular growth interface with the solute to be crystallized.

3. Experimental procedure

Horizontal crucible rotation with THM has been demonstrated for the growth of Hg$_{1-x}$Cd$_x$Te. Since the method had never been used before, the aim was to investigate whether it is possible to grow single crystals from a partially filled solution zone. Crystals of 15 of 16 mm in diameter and up to a length of 50 mm were grown from Te-rich solution zones, at a temperature of $510 \pm 20°C$, using ternary source ingots obtained from a previous THM run. Feed material preparation from off-stoichiometric melts was chosen to lower Hg vapour pressure and minimize the risk of explosion. Details of this approach have been reported elsewhere [4]. For THM crystal growth, use was made of single-crystalline CdTe seeds, being $\{111\}_A$- or $\{1\bar{1}\bar{1}\}_B$-

oriented, prepared from Bridgman-grown ingots. In a previous study [18] on vertically THM-grown Hg$_{1-x}$Cd$_x$Te, we could not confirm the results obtained by Colombo et al. [2] who found better growth conditions with $\{1\bar{1}\bar{1}\}_B$ seeds.

For a fixed temperature profile, the length and height of the solution zone are the most important process parameters which determine interface temperature and curvature of the phase boundaries. They are adjusted by varying the amount of pure solvent and by the original distance between seed and feed. These two parameters were calculated from the geometry and using the solubility data given by Brice [19]. Calculations were aimed at a zone height of approximately 0.6 times the diameter for a zone length of 15 mm. Deviations from the desired parameters cause differences in the height of the saturated solution zone. Zone preparation was done by melting the calculated amount of unsaturated tellurium in an H$_2$ atmosphere on the feed rod, while inclining the ampoule. In this way, the solidified Te zone becomes wedge-shaped so as to keep the distance between feed and seed ingots constant. The cylindrical seed with a mechanically polished surface was then placed next to the zone. The crystals were grown under a vacuum of 10^{-4} Pa in sealed silica crucibles which had been pre-coated with graphite.

A simple one-zone furnace was used, resulting in axial temperature gradients of 50 K cm^{-1} in the liquid adjacent to the phase boundaries. The ampoule was mounted on a goniometer head to adjust its axis to the rotation axis of the motor. The rotation rate was virtually constant at 100 rpm. Translation was driven by a stepper motor combined with two reduction units resulting in a very smooth motion of about 80 steps per μm. Most of the experiments were carried out with a translation rate of about 5 mm per day. Higher growth rates were not used during this study. Growth was terminated by inclining the whole apparatus to remove the liquid zone from the grown crystal and to solidify the zone on the remaining feed while slowly cooling the furnace. The crystals were cut by a wire saw, lapped and mechanically/chemically polished. Metallurgical homogeneity was measured by electron probe

microanalysis (EPMA) using the Cd Lα line. Structural perfection was characterized by X-ray topography using Cu Kα radiation.

4. Results and discussion

All crystals grown by this horizontal THM process are cylindrical and are indistinguishable from vertically grown ones. This was not true for the zone region. In the first experiments, the rotating crystals were cooled down in the horizontal position. This resulted in a free volume between the grown crystal and the residual feed because the zone material had been crystallized at the two front faces. Only by horizontal quench-

ing, which affects the structural perfection of the last-to-freeze part of the crystals, does the liquid keep its original shape when rotation is ceased. In more recent growth experiments, attempts were made to avoid this by inclining the whole apparatus during cool-down to decant the solution zone from the grown crystal. The result was the same as before, which is probably due to sublimation processes caused by the relatively high vapour pressures in the Hg–Cd—Te system.

An X-ray reflection topograph of a $\{\overline{111}\}_B$-oriented slice cut perpendicular to the crystal axis is shown in fig. 2. It can be seen that the slice is single-crystalline with some twins. The structural perfection is comparable with the vertically-grown THM crystals of the same material using growth

Fig. 2. (620) X-ray reflection topograph of a $\{\overline{111}\}_B$ surface of a $Hg_{1-x}Cd_xTe$ single crystal (15.2 mm diameter) grown by horizontal THM.
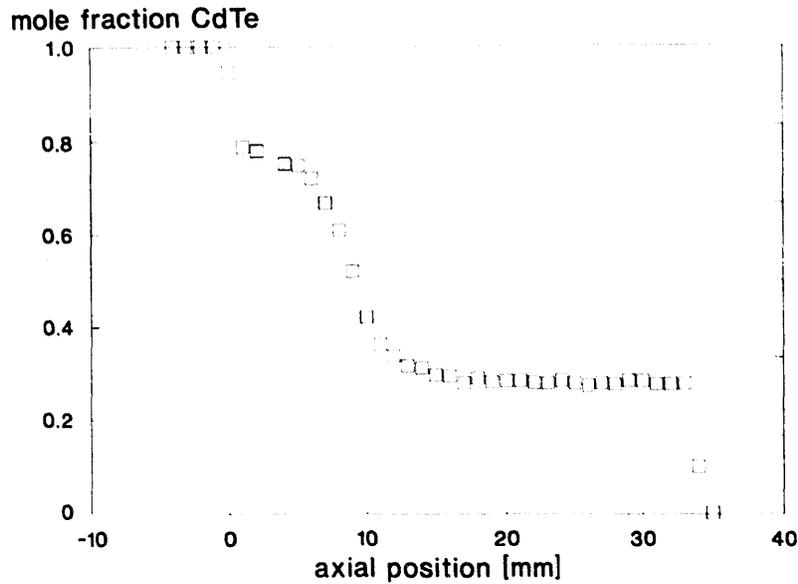
mole fraction CdTe

Fig. 3. Axial distribution of mole fraction, x, along a $Hg_{1-x}Cd_xTe$ crystal grown by horizontal THM on a CdTe seed. Source ingot ($x = 0.28$) was grown by a first (vertical) zone pass. EPMA measurement using Cd Lα radiation.

rates as low as 1–2 mm per day [18]. Clearly, the rapid changes between liquid solution and vapour atmosphere experienced by the growing interface during constant rotation are not detrimental. It is to be expected that there will always be a thin liquid film wetting the crystal face. If rotation rates are high enough, which is apparently so

with 100 rmp, the thermal system is sufficiently stable to prevent the interface temperature from suffering major fluctuations.

Fig. 3 shows the longitudinal distribution of the CdTe mole fraction measured along the periphery of the ingot. As expected, there is no significant difference in the macroscopic segrega-

mole fraction CdTe
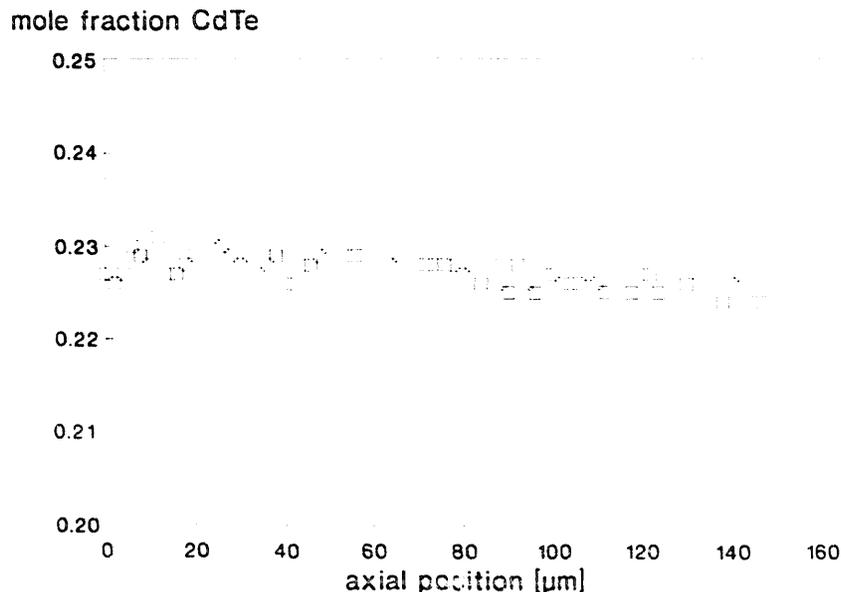
Fig. 4. Microscopic distribution of the mole fraction along the crystal axis of horizontally grown $Hg_{1-x}Cd_xTe$ (detection limit, $\Delta x = 0.003$, of EPMA measurements, Cd Lα radiation).
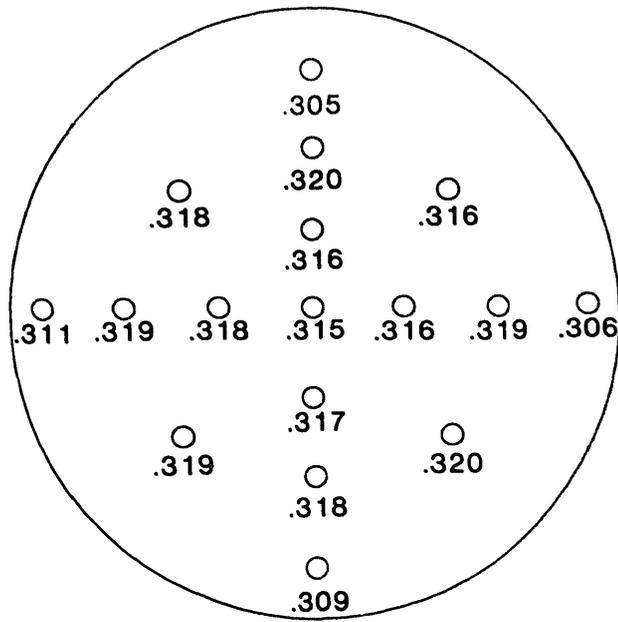
Fig. 5. Typical radial plot of mole fraction, x, for a 16 mm diameter slice of a $Hg_{1-x}Cd_xTe$ single crystal.

tion behaviour compared to vertically-grown crystals. The initial transition region, which depends on the segregation coefficient and amount of solution in the zone, is approximately half as long as it would be with a totally filled solution zone of the same length. Reaching steady-state conditions, after the transient region, the crystal homogeneity is good and has the same mole fraction as the feed ingot. Results on the microscopical mole fraction distribution along the crystal axis are depicted in fig. 4. The measured distance of 150 μm lies within the steady-state region of the crystal. The standard deviation of 2×10^{-3} of the mole fraction, which corresponds to the detection limit of EPMA, suggests little microscopic inhomogeneity. With a rotation rate of 100 rpm and a translation rate of 5 mm per day, rotational striations would have spacings as low as 35 nm and, if stable, would not to be resolved by EPMA. This is not to be expected, as shown by Gray et al. [20]. A typical plot of the radial distribution of mole fraction in a slice cut perpendicular to the growth axis is shown in fig. 5. Again, there is no marked difference from the results obtained by the vertical method. Slightly better uniformity achieved with vertical experiments [4,17] may be attributed

to a higher stage of optimization reached in those techniques.

5. Summary

Horizontal THM growth with crucible rotation has been demonstrated for the first time. Crystal rotation with respect to the partially filled solution zone is necessary to crystallize the whole cylindrical cross section of the ingot. It causes an effective stirring of the solution zone adjacent to the growing interface which has been described in terms of the rotating disc model.

Experimental evidence has been given for the growth of $Hg_{1-x}Cd_xTe$ single crystals. Structural perfection and metallurgical homogeneity are promising and comparable with results on vertically-grown THM crystals of the same material. Further work will be directed to the detailed theoretical understanding of forced convection within the solution zone and optimization of rotation and translation rates.

Acknowledgments

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