

## Zone Leveling and Crystal Growth of Peritectic Compounds\*†

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Homogeneous samples of peritectic semiconducting compounds have been prepared for optical and electrical characterization by combining zone leveling concepts with Bridgeman crystal growth techniques. Proper temperature distribution in the zone leveling equipment must be established on the basis of the phase diagram for the material, and by considering the rate process accompanying solidification and crystal growth. The ingots produced by this method are substantially uniform and homogeneous in composition, whereas normally frozen or Czochralski-grown crystals contain concentration gradients.

### INTRODUCTION

THE principles of zone refining and crystal growth that have been developed by Pfann<sup>1</sup> for congruently melting materials can be applied to peritectic compounds. Although Goodman<sup>2</sup> has indicated briefly that the zone leveling technique can be used in principle to prepare homogeneous peritectic samples, there have been no published reports of a reduction to practice and it has not received the attention which it merits. The techniques which have been developed and used in making ingots of several different peritectic compounds are reported.

### DESCRIPTION

The pertinent principles can be illustrated by considering the formation of the peritectic compounds in the system CdTe-In<sub>2</sub>Te<sub>3</sub> shown in Fig. 1, which has been investigated by Thomassen and Mason.<sup>3</sup> The compound CdIn<sub>2</sub>Te<sub>4</sub> precipitates along the liquidus line ranging between 63 mol % In<sub>2</sub>Te<sub>3</sub> and 785°C, and 93 mol % In<sub>2</sub>Te<sub>3</sub> and 702°C. The compound decomposes at 785°C to form a cadmium telluride phase and liquid. The solid does not disappear completely below 835°C. In order to precipitate the solid with the composition of 50% In<sub>2</sub>Te<sub>3</sub>, a liquid having a composition between 63 mol % In<sub>2</sub>Te<sub>3</sub> and 93 mol % In<sub>2</sub>Te<sub>3</sub> must be used. However, at the solidifying interface, a large excess of In<sub>2</sub>Te<sub>3</sub> is rejected by the solid, thus increasing its concentration in the liquid drastically. Hence, the diffusion of the excess In<sub>2</sub>Te<sub>3</sub> through the liquid film ahead of the advancing interface, the mixing of the liquid zone, and the rate of zone travel are much more critical in these circumstances than in normal zone refining operations.

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<sup>1</sup> W. G. Pfann, *Zone Melting* (John Wiley & Sons, Inc., New York, 1958).

<sup>2</sup> C. H. L. Goodman, *Research (London)* **7**, 168 (1954).

<sup>3</sup> L. Thomassen and D. R. Mason, *J. Electrochem. Soc.* **106**, 206c (abstract) (1959).

### Mode I

In setting up the zone refining system two different modes of operation can be used. In mode I a liquid zone containing over 63 mol % In<sub>2</sub>Te<sub>3</sub> is established and an ingot with a nominal composition of 50 mol % In<sub>2</sub>Te<sub>3</sub> is used as the charge ingot. The liquid zone is normally less than one-fifth the total length of the sample. The sample is placed in a zone refining furnace, as shown in Fig. 2, with the liquid zone at about 800°C, which is above the peritectic temperature of 785°C. Although the liquid zone can be formed below the peritectic temperature, it has been found that the peritectic feed ingot does not dissolve readily in the liquid zone without being raised above its decomposition temperature. The entire sample is maintained at a temperature of 710°C, which is above the next lower transition temperature of 702°C. Hence, any precipitation of the  $\gamma$  phase is impossible, and the homogeneity of the resulting  $\beta$ -phase ingot is increased. The compositions, temperatures, and solid-liquid boundaries then are as shown in Part A of Fig. 2.

As the zone advances through the polycrystalline charge ingot, the liquid composition remains relatively constant, and the composition of the precipitated  $\beta$  phase also remains constant, as shown in Fig. 2(b). Successive zone leveling passes may be made by reversing the direction of the zone travel in order to equalize any variations which might have originated from the charge ingots.

### Mode II

Because the vapor pressure of these materials at the liquidus temperature is moderately high, the samples are processed inside sealed, vitreous silica tubes, and the ambient temperature must be high enough to inhibit vapor condensation in the coldest region of the container. In practice, it is somewhat tedious to prepare a zone refining sample with two separate composition regions. Such a sample requires the preparation of two charge ingots of different composition, which then must be resealed into another vitreous silica tube, with opportunity for additional contamination and loss of the sample.

These objections can be overcome in part by using

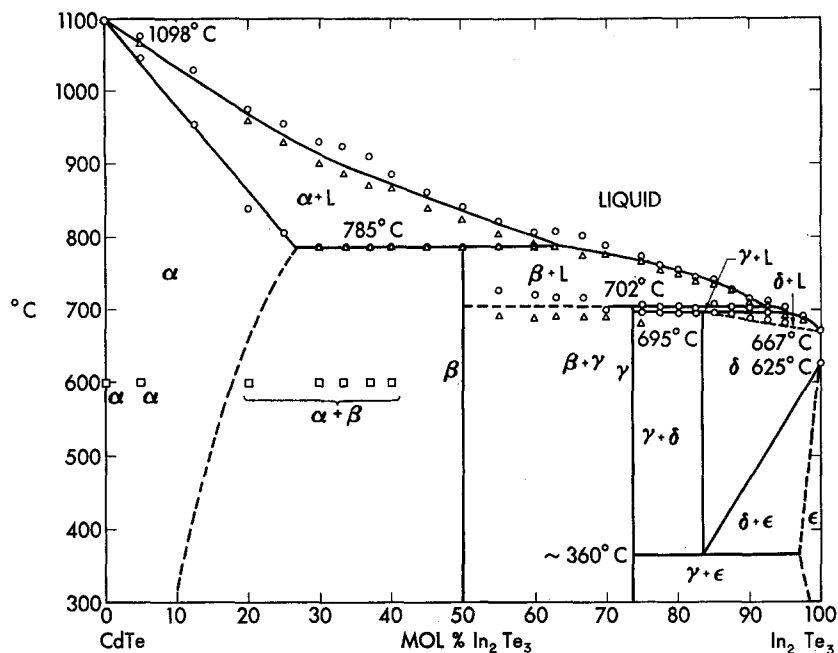


Fig. 1. Phase diagram for the pseudobinary system CdTe-In<sub>2</sub>Te<sub>3</sub>.

a sample which has, initially, a uniform composition. The initial composition must be determined from the desired material balance in the final state, based on the phase diagram and the fraction of the zone leveling ingot which is normally molten. In order to obtain a sample like that discussed under mode I, complete homogenization of the charge would give a composition of about 53 mol % In<sub>2</sub>Te<sub>3</sub>. This composition has been found to be satisfactory.

In this procedure the sample is fused from the elements and zone refined inside the same tube. After pyrosynthesis, a molten zone of this composition can

then be established at one end and transported through the ingot. From the phase diagram in Fig. 1, it can be seen that the solid which is the first to freeze would be  $\alpha$ -phase saturated with In<sub>2</sub>Te<sub>3</sub>. The  $\alpha$  phase would continue to precipitate until the composition of the liquid region had increased to 63 mol % In<sub>2</sub>Te<sub>3</sub>, whereupon the  $\beta$  phase would start to precipitate. The liquid composition would continue to increase, since 53 mol % In<sub>2</sub>Te<sub>3</sub> is used as feed material. At the end of the first pass, the zone travel direction is reversed. At the end of the second pass, the concentration of In<sub>2</sub>Te<sub>3</sub> in the liquid zone would be decreased as the originally precipitated  $\alpha$  phase is dissolved. On reversing the zone travel direction for a third pass, the amount of precipitating  $\alpha$  phase diminishes or disappears. After several passes, the system is essentially equilibrated and homogeneous samples of the 50 mol % In<sub>2</sub>Te<sub>3</sub> are obtained.

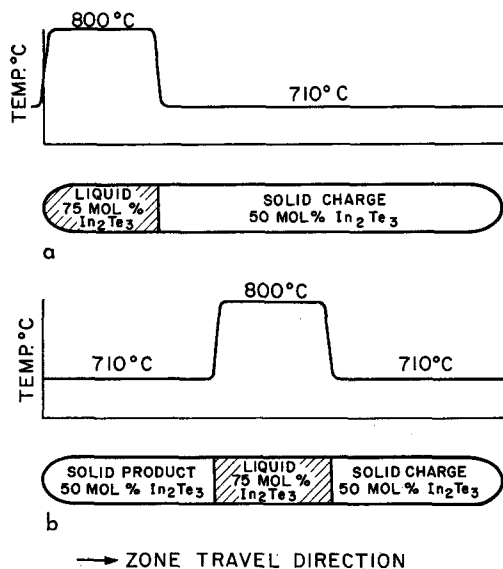


Fig. 2. Compositions and temperature distributions in a typical peritectic zone refining operation.

### Effect of Zone Travel Rate

The preceding discussion presupposes that the precipitation of the  $\beta$  phase from the melt occurs under equilibrium conditions, whereas Burton *et al.*<sup>4</sup> and Tiller *et al.*<sup>5</sup> have shown that this is seldom realized in practice. As the excess In<sub>2</sub>Te<sub>3</sub> is rejected from the solid at the solidifying interface, there is a buildup of In<sub>2</sub>Te<sub>3</sub> in the liquid film and a lowering of the liquidus saturation temperature. At the same time, the dissolution of the 50% compound at the opposite end of the liquid zone causes a decrease in the In<sub>2</sub>Te<sub>3</sub> concentration at

<sup>4</sup> J. A. Burton, R. C. Prim, and W. P. Slichter (Part I), *J. Chem. Phys.* **21**, 1987 (1953); J. A. Burton, E. D. Kolb, W. P. Slichter, and J. D. Struthers (Part II), *ibid.* **21**, 1991 (1953).

<sup>5</sup> W. A. Tiller, K. A. Jackson, J. W. Rutter, and B. Chalmers, *Acta Met.* **1**, 428 (1953).

the melting interface and a corresponding increase in the liquidus saturation temperature.

The stability of the solidifying interface depends on the relative temperature gradient within the sample and the equilibrium liquidus temperature gradient at the interface. As long as the temperature gradient in the melt is greater than the equilibrium liquidus temperature gradient as shown in Fig. 3(a), the system is stable.

On the other hand, if the furnace temperature gradient is lower than the equilibrium liquidus temperature gradient established by the concentration gradient as shown in Fig. 3(b), then unstable dendritic growth can occur, and occlusions are formed in the ingot.<sup>5a</sup>

### EXPERIMENTAL RESULTS

Several ingots of  $\text{CdIn}_2\text{Te}_4$  have been prepared with these techniques, using zone travel rates of between  $\frac{1}{8}$  in. hr and  $1/20$  in. hr.

Ingots have been made by starting with two separate charge regions, as well as by starting with an original charge ingot having a nominal composition of 53 mol %  $\text{In}_2\text{Te}_3$  along the length of the bar.

Some of the ingots have been sectioned, polished, and etched, and were found to be remarkably uniform in appearance. The uniformity was also checked by making microhardness tests; these agreed well not only with themselves but also with other samples of  $\text{CdIn}_2\text{Te}_4$  that had been prepared by quenching and annealing. The grain sizes were large, on the order of a mm in width, and extended several mm in length. In a few instances the grain boundaries of an ingot made by mode I were decorated with discrete particles of two different phases, thus indicating that some small dendrites were present and capable of generating occlusions. This was about 1–2% of the total material. An ingot made by mode II showed only small amounts of one additional phase at the grain boundaries, apparently reflecting the effect of a lower equilibrium concentration of  $\text{In}_2\text{Te}_3$  in the liquid zone.

This technique also has been used to prepare homogeneous ingots of the  $\delta$  phase in Fig. 1, starting with an ingot with an average composition of 90 mol %  $\text{In}_2\text{Te}_3$  and 10 mol %  $\text{CdTe}$ .

Up to the present time, attempts to form specimens of the  $\gamma$  phase have been unsuccessful because of the narrow temperature and composition range of the corresponding liquidus line. The zone refining conditions and the compositions of the charges are very difficult to control satisfactorily in order to obtain a homogeneous sample.

<sup>5a</sup> See also G. F. Bolling and W. A. Tiller, *J. Appl. Phys.* **31**, 2040 (1960).

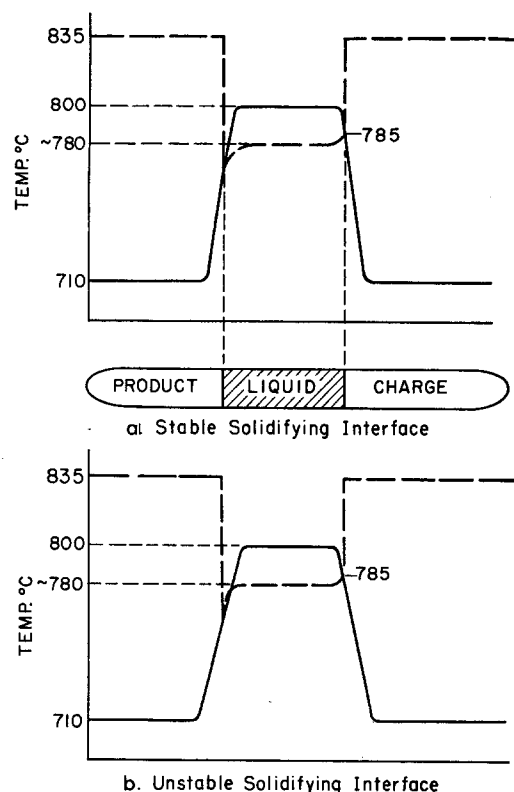


FIG. 3. Stability criteria for a solidifying interface of  $\text{CdIn}_2\text{Te}_4$ .

Electrical and optical measurements of  $\text{CdIn}_2\text{Te}_4$  prepared in this work have been measured and reported by Edwards and O'Kane.<sup>6</sup>

In the indium-tellurium system<sup>7</sup> the peritectic compounds  $\text{In}_2\text{Te}$  and  $\text{In}_2\text{Te}_5$ , as well as a previously unreported peritectic compound with composition  $\text{In}_4\text{Te}_7$ ,<sup>8</sup> have been prepared. The compound  $\text{ZnIn}_2\text{Te}_4$  has also been prepared.

This technique has a considerable advantage over Czochralski-grown or normally frozen ingots. Ingots produced by zone leveling have substantially a uniform composition, whereas the normally frozen crystals contain concentration gradients.

### ACKNOWLEDGMENTS

The assistance of several students who prepared the samples is acknowledged. John C. Sarace performed the microscopic examinations.

<sup>6</sup> D. F. Edwards and D. F. O'Kane, *Bull. Am. Phys. Soc. Ser. II* **5**, 78 (1960).

<sup>7</sup> M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed., p. 863.

<sup>8</sup> This work will be reported at a later date.