CHAPTER VII

A STUDY OF THE CELLULAR STRUCTURE OF THE INTERFACE IN ZINC CRYSTALS USING AN ETCH METHOD

Results have been presented in this chapter, of a successful use of the etch method to study the nature of the cellular structure of the interface. A qualitative agreement is shown to exist between the observations presented here and the earlier work on tin and other metals.

Mention has already been made about the work of Rutter and Chalmers[1] on the cellular interface structure of a metal crystal growing under conditions of supercooling. The crystals were grown by these authors at three different ranges of growth namely ($>$ 13 mm/min) fast, (1 to 13 mm/min) intermediate and ($<$ 1 mm/min) slow ranges, from metal of 99.986% purity. It was observed that the cellular structure exists in the medium speed of growth. Each cell projects into the melt, the cell boundaries being depressions and region of high solute concentration. The cell dimensions in a specimen is not constant and varies considerably. They do not show any preference in orientation. As the growth rate approaches the lower limit of the intermediate range, the corrugation spacing and cell-size become relatively large and do so quite rapidly. Increase in the impurity content increases the all dimensions which are increased also by an increase in the temperature gradient and decreased by an increased growth rate. A steep

gradient can depress this structure altogether. At very low rates the interface remains planar and at high rates it is dendritic.

Rutter and Chalmers have explained this structure as due to the existence of a supercooled region in the melt in the region immediately ahead of the interface. This supercooling is produced by the redistribution of the solute which occurs at the interface and is due to the changes in the composition of the melt. The authors consider that the cell-size is controlled by three factors: (a) the probability of spontaneous solidification occurring at the interface when the liquid adjacent to it below its equilibrium liquidus temperature by a given amount (b) the coefficient of volume diffusion of impurities in the liquid metal and (c) the thermal diffusivities of the liquid and solid metal.

At high speeds of growth the projections increase considerably in length until they become dendrites. Thus variation of growth conditions can lead to a continuous transition at the stable planar intefface into conditions of cellular interface and finally into a solidification under dendritic conditions. Transition from a smooth to a cellular interface has been investigated by Tiller et.al.[2,3]. The cellular structure in tin alloys have been studied by

Plaskett and Winegard[4]. The alloys investigated were made from zone refined tin with additions of lead, bismuth and antimony. For tin in antimony the equilibrium coefficient Ko is greater than unity and it was observed that the cells projected into the liquid, but contrary to the other cases with $k_o < 1$, the cell boundaries contain the pure metal, whereas the projections contain the impurities. This is in accordance with the predictions of Rutter and Chalmers[1] that the solute distribution should be reversed from $k_o < 1$ case. The cellular to dendritic transformations also has been investigated by Tiller and Rutter[3], Morris et.at.[5] and by Plaskett and Winegard[6]. The commencement of the cellular structure is evidenced by the pox-like appearance of the interface. Tiller and Rutter[3] has observed that the long axis of the elongated cells lie along, or nearly along the (111) trace on the interface unless the interface itself is (111) plane, when the cell edges broke up into a range of directions. This disagrees with the observations of Rutter and Chalmers who found no crystallographic significance of the cell boundary. Moreover, Hulme[7] noted that the shape of the cells in zinc single crystals grown in a horizontal boat under conditions of supercooling depends markedly on the orientation of the crystals. He delineated the boundary by electrolytically polishing the crystal surface. When the growth was promoted along the direction in

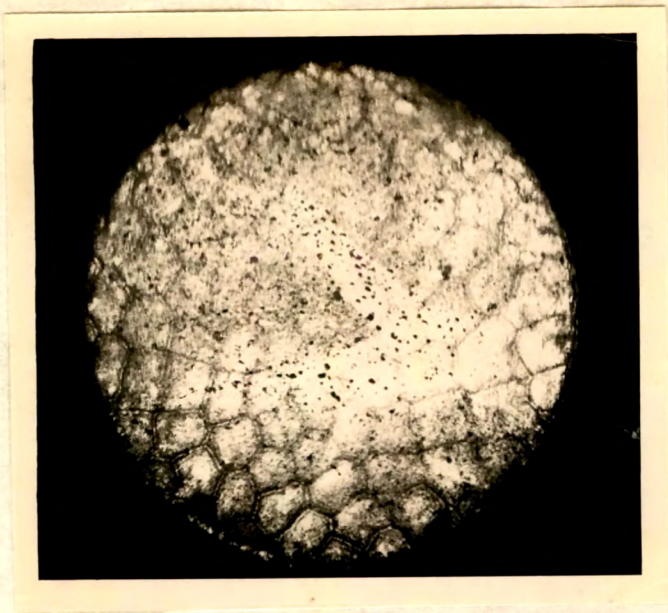

Fig. VII -1 X 10

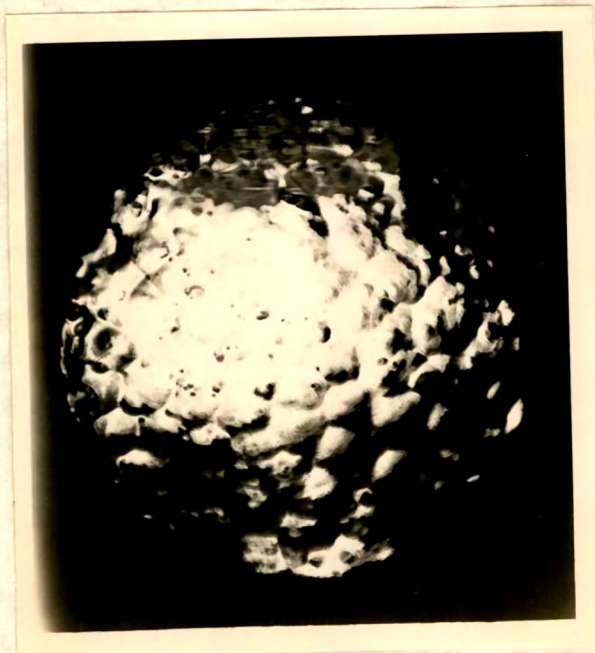

Fig. VII -2 X 10

the basal plane, the cells were greatly elongated and became lamellae parallel to the basal plane.

The theory of Rutter and Chalmers that the transition from planar to cellular interface requires the onset of supercooling produced by the pile-up of solidification of the interface. However, they have observed that no incubation distance is necessary for the onset of cellular structure. This appears to be in error.

In view of the controversial results about the dependence of the cellular structure on the orientation of the crystal and the contradictory results of Chalmers on the incubation distance, it is worthwhile to study the structure in more detail. The results presented in this chapter are therefore the investigation of the cellular structure on zinc crystals. The interest of the author on this problem was provoked by the appearance of a structure shown in fig.V-3 on the top surface of some crystals. Subsequent etching for a long time in a solution containing 20 gms of chromium trioxide, 1.5 grms of sodium sulphate and 5 cc. of concentrated nitric acid, made up to 100 cc. with distilled water, showed that this structure still existed. Fig.VII-1 shows the top surface of a crystal containing 0.02% cadmium grown in a temperature gradient of 10°C/cm and at a rate of 1 cm/hr. Etching for 15 minutes reveals the surface as shown in fig.VII-2. The crystal was

sectioned and etched in the solution mentioned above and observed under the microscope. The appearance of the surface was again similar suggesting that this is a body phenomena and the observed structure indicates the cellular nature of the interface during the crystal growth. The boundaries of these cells were grooved and the cells were projections. This preferential etching at the boundaries is due to the fact that they contain a large excess of solute and hence are preferentially etched with the reagent. The observation suggests that the phenomena of preferential etching at the boundaries can be used to study the cellular structure and the etchant described above can be used for the purpose.

Accordingly, crystals grown under different growth rates, impurity contents, and temperature gradient were studied. The crystals were cut with a fine jewellers' saw taking care to avoid plastic deformation and etched in the solution mentioned above for about 15 minutes, so that the cold worked layer is completely removed and the surface shows minimum deformation lines. The surface is then observed under the microscope and the cell dimensions, direction of cell boundaries etc. where studied in detail. The cell dimensions and other characteristics were found to depend on the temperature gradient, impurities and the rate of growth. The average cell size increases with a decrease in the rate of lowering of the capsule, increase in the temperature

gradient and an increase in the impurity content. In general, the cell dimensions on a particular surface is not constant. It has been observed that an impurity content of 0.1% cadmium produced no cellular structure when the temperature gradient inside the furnace was maintained at 35°C/cm. when the rate of lowering was 1 cm/hr. The same growth rate and impurity content produces a cellular structure when the temperature gradient is lowered to 10°C/cm.

To study the effect of the crystal orientation on the nature of the cells, a tricrystal was cut perpendicular to the crystal axis so that three different planes were exposed. The crystal was etched and the structure was studied. In this case, since all these three planes are grown under identical conditions, it is reasonable to assume that whatever difference in the nature of the cells are observed, they can be attributed to the orientation of the crystal. Fig.VII-3 shows the surface. The grain A is the basal plane and the hexagonal cells are very regular. The grain B is perpendicular to the basal plane and in this case the cells are elongated. The grain C is making an angle of about 45° with crystal axis and it can be seen that the structure is less regular than that of the basal plane. This observation shows that the orientation of the crystal has a striking effect on the cell boundaries. To investigate whether this is a bulk-property

Fig. VII -3 X 10

Fig. VII -4 X 10

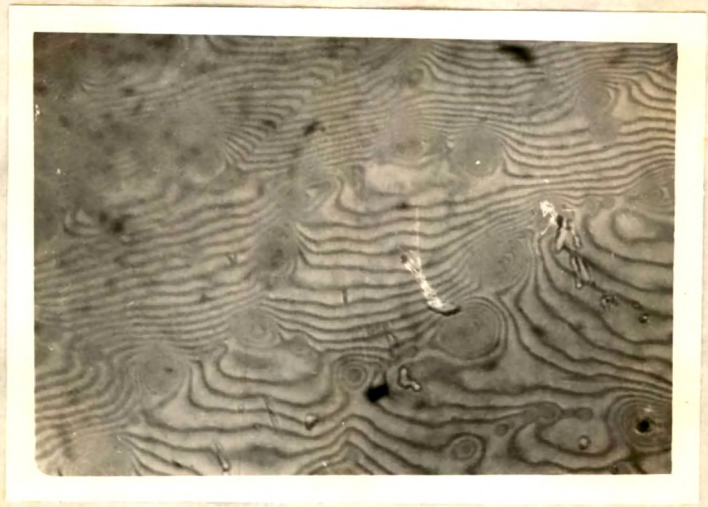

Fig. VII -5 X 90

or not, the counter parts of the specimen obtained after sectioning were also treated in the same manner and observed under the microscope. The amount of material removed during polishing was estimated to be more than 2 mm. in length. The counterpart photograph is shown in fig.VII-4. The striking one to one correspondance between the photographs VII-3 and VII-4, in spite of the large amount of material removed, except for the deformation bands, implies that the structure repeats itself over a large length of the crystal and is quite stable. The observations are in excellent agreement with the results of Hulme[7] that the shape of the cell boundaries depends markedly on the orientation of the crystal. Another interesting observation is that in no case the cell boundary is seen crossing the grain boundary which implies that each grain tries to maintain its own cells.

Fig.VII-5 shows the multiple beam interferogram taken over a surface showing the cellular structure. Pits are formed at the intersection of the cell walls and the fringes form concentric rings at these points. The curvature of the fringes and the regularity of the pattern are self explanatory.

To study how far this structure manifests itself in the longitudanal direction, the cells are cut along the growth axis and the counterparts are treated as usual to

Fig. VII -6 X 10

reveal the inner structure. A number of ridges can be seen in the counterparts reproduced in fig.VII-6 running parallel to the axis of the crystal. This is in agreement with the Tillers view that a single crystal growing under conditions of low supercooling can be considered as being comprised of a bundle of pencils stacked together. The ends of the pencils represent the cellular interface and the axis of the pencils, the crystal axis.

Fig.VII-7 and VII-8 are two crystals having same orientation, with basal planes parallel to the axis of the crystal, grown in a temperature gradient of $10^{\circ}C/cm$. The crystals have been cleaved and hence the cross section is semi circular. Both the crystals were grown at 8 cm/hr. Crystal shown in fig.VII-7 has an impurity content of 0.02% cadmium, while that in fig.VII -8 has a higher impurity content. It can be seen that while in the former the cells are regular and elongated along the [0001] direction, fig.VII-8 has an irregular cell structure, the cell size being larger. One can conclude that the cell dimensions increase and the regularity is lost when the seggregation of impurity is more. This is also in agreement with the observations of Rutter and Chalmers.

The effect of growth rate on the cell dimensions is evident when fig.VII-1 and fig.VII-7 are compared. The cell

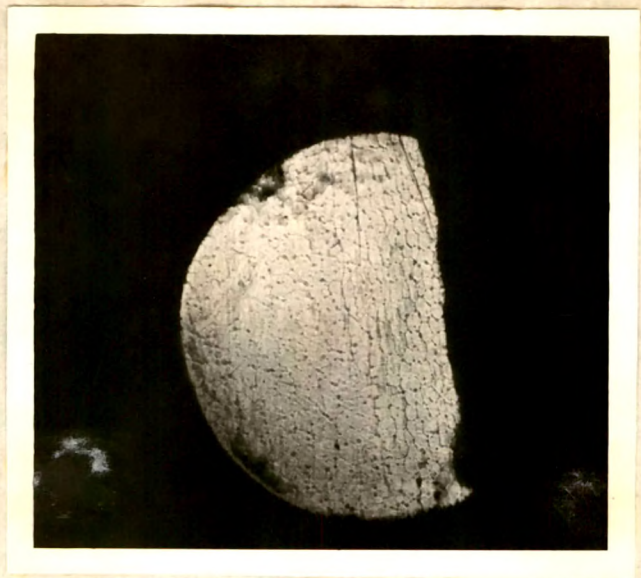

Fig. VII -7 X 10

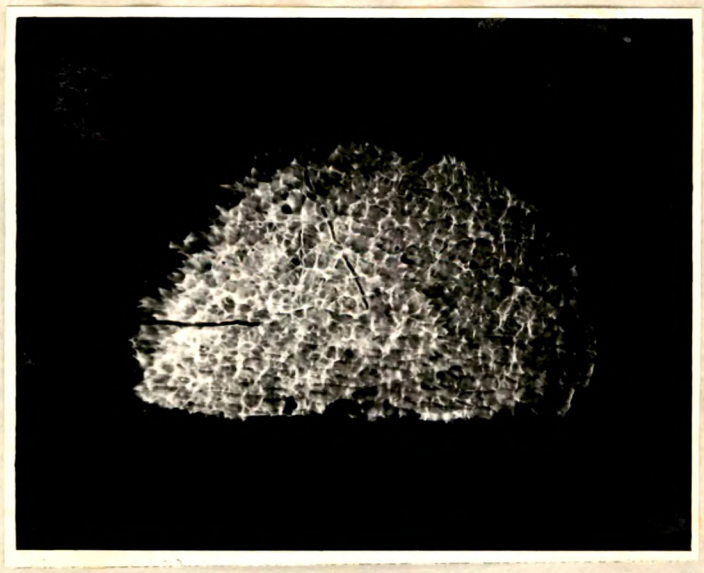

Fig. VII -8 X 10

dimensions become extremely larger as the growth rate becomes smaller.

To study the structure in more detail a crystal with basal plane perpendicular to the axis and showing a cellular structure on the free surface at the top, as shown in fig.VII-1 was cleaved at different lengths from the capillary end and were examined after etching. While the upper portions show regular hexagonal cells, the lower region was extremely plane. At a distance of about 1.3 cms from the capillary end, a few projections, similar to the pox-like structure was observed. This is shown in fig.VII-9. In a region about 3 mm. away from this surface the structure is as shown in fig.VII-10. One can see that a number of cells have been developed, but the structure is not complete. This suggests that the transition from the planar to cellular structure is not abrupt but it takes place gradually. These results are contradictory to the observations of Chalmers that no incubation distance is necessary for the development of the cellular structure. However, they are in complete agreement with the theory, which requires the build up of a supercooled region ahead of the interface. The reason for this difference in observation lies in the high purity metal and the slow rate of growth employed in this case.

In a crystal containing a larger amount of impurity grown at a faster rate, the chemical treatment

Fig. VII -9 X 10

Fig. VII -10 X 10

described before to reveal the cells, also reveals a structure which resembles the dendrites as shown in fig.VII-11. Whether this represents the dendrites or not, is not yet conclusively established; but judging from the conditions of the experiment, it appears to be so.

When the basal planes are perpendicular to the crystal axis, a 0.5% solution of Bromine in Methenol may be used to study the cellular structure with the advantage that small pits produced along the boundary of the cells can be correlated with the dislocations. However bromine is not effective in planes other than the basal plane as the surface presents a corroded appearance.

The general pattern described above compares well with the results of Rutter and Chalmers. However the range of growth rates used in this investigation corresponds to the lowest range in the earlier studies where the authors have observed planar interface. The reason for this difference lies primarily in the thermal distribution inside the furnaces used for growth. The method used by Rutter and Chalmers was to move a horizontal furnace over the boat containing the metal. In this case the transfer of heat by conduction and radiation are prominent. The vertical gradient furnace used by the present author the ends of the tube were completely closed both at top and bottom and the gradient was quite small

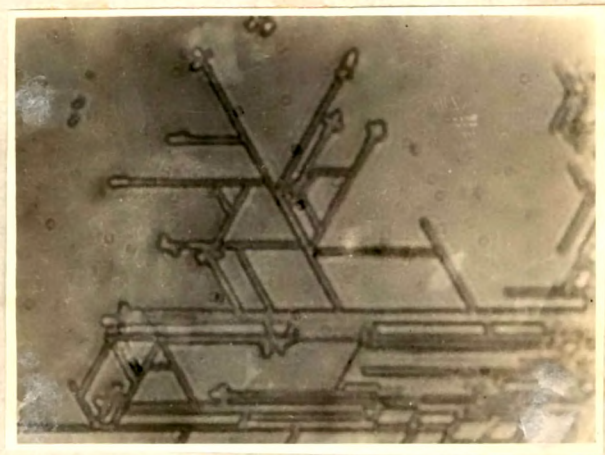

Fig. VII -11 X 170

$10^{o}C/cm$. This difference in thermal distribution in furnace might be responsible for the observed features. This is justified when referring back to chapter V, we find that the same effect is seen on the orientation of the crystals also.

CONCLUSIONS:

(1) The chemical etching and polishing of the crystal on a surface perpendicular to the axis reveals the cellular structure of the interface.

(2) This method can be successfully used to study the cell dimensions and orientation.

(3) Crystal orientation has a marked effect on the shape and direction of the cell boundaries.

(4) It has been possible using a slow rate of growth and high purity of metal to show that the development of the cellular structure is not abrupt but takes place gradually. An incubation distance is indeed necessary as required by theory.

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