CHAPTER VI

MICROTOPOGRAPHIC STUDIES ON ZINC CRYSTALS

This chapter deals with a study of the various surface features observed on the crystals grown from melt by Bridgman's method. Each of the crystals discussed in the previous chapter have been examined under the microscope and the various features observed on the top surfaces, cylindrical surfaces and the cleavage planes have been studied in detail. Many interesting features, which have not been reported earlier, have been observed and their significance and origin have been discussed. Only a limited number of photographs have been included in this thesis. The study has been classified under three heads:- (1) The free surface at the top, (2) the cylindrical surface which is in contact with the glass during the growth and (3) the basal surfaces resulting from the cleavage of the specimen.

(1) FREE SURFACE AT THE TOP:

The microstructure of the free surface depends on the conditions of growth. In general, the surface becomes dull when small amounts of impurities are present and when the crystal is grown at low speeds. This seggegration of the impurities is characteristic of the'normal freezing'of metals. The surface remains convex at the top for fast rates but tends to be plane at slow speeds of growth.

When the A.R.quality metal or zone refined metal is used and the crystal is grown at fast rates of about 10 cm/hr,

Fig. VI -1   X 35

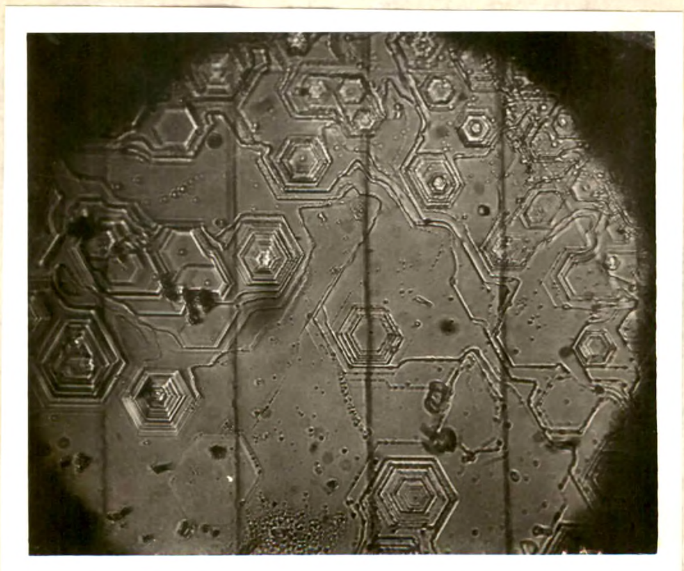

Fig. VI -2   X 170

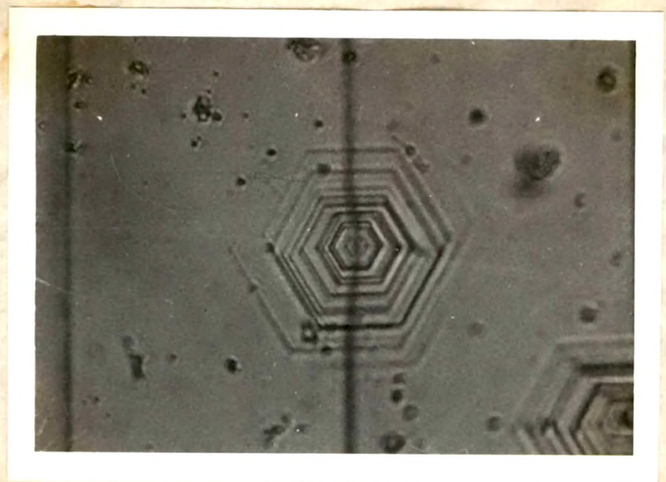

Fig. VI -3 X360

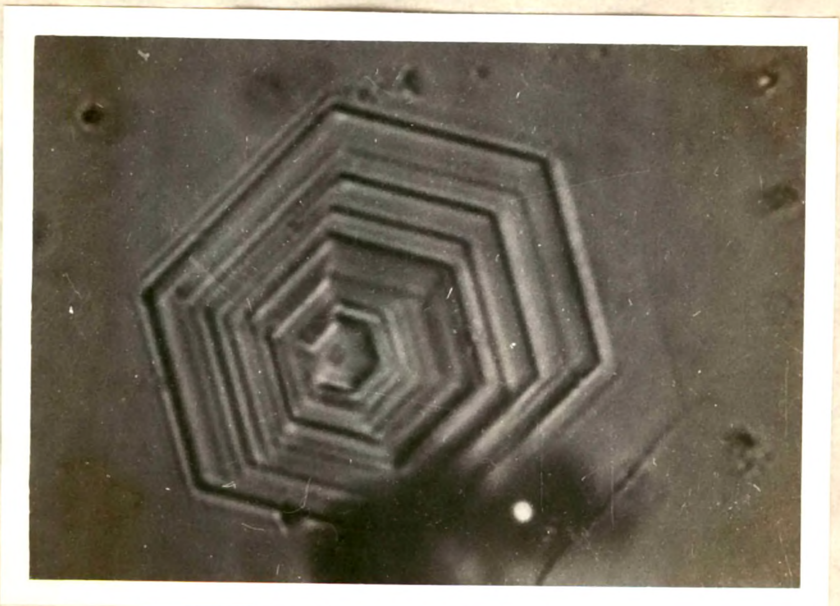

Fig. VI -4 X 720

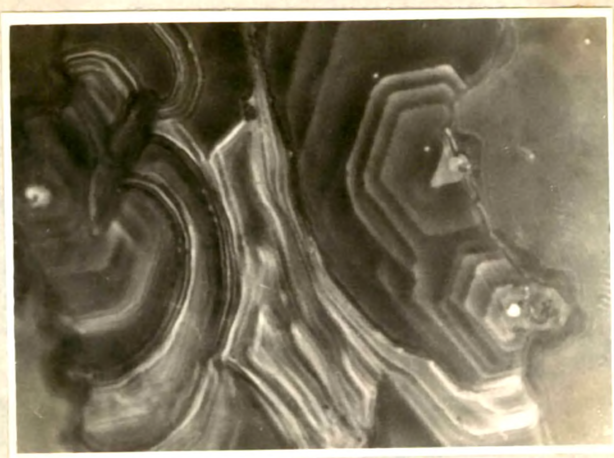

Fig. VI -5   X 170

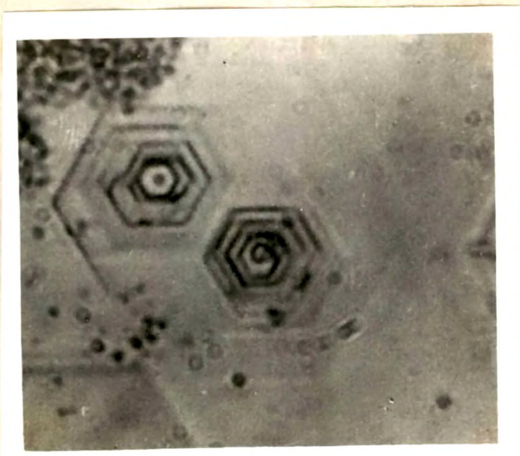

Fig. VI -6   X 940

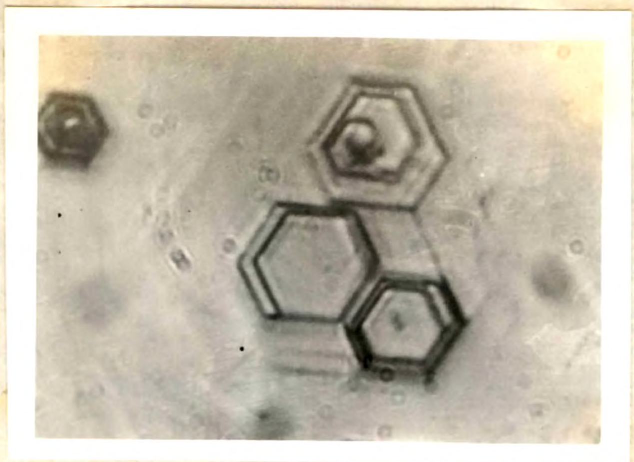

Fig. VI -7 X940

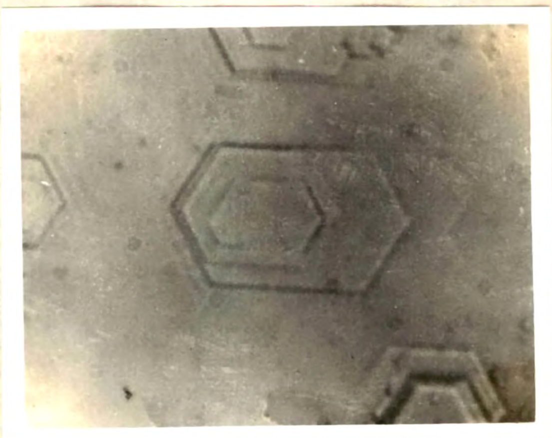

Fig. VI -8 X 940

the free surface solidifies in the form of a number of flat facets. Usually at this rate one observes the basal plane to be parallel to the crystal axis. But when the basal plane is slightly inclined to the vertical axis by a few degrees the facets are larger. The conditions under which such faces are developed, have not been conclusively established, but in general, a high purity metal and a fast growth are essential for this to occur. Detailed examination of these facets have been carried out by the author. A typical facet is shown in fig. VI-1. The plane facets are very bright and bear many growth features. There are a number ~~few spirals~~ of hexagonal closed loops and also few spirals. Fig.VI-2 shows the region containing these features with light profiles running across. The profiles suggest the smoothness of the facet at places other than where loops are present. Fig.VI-3 shows a hexagonal closed loop, under higher magnification. The profiles show a well defined shift indicating large step height, between the ledges amounting to 1-2 microns. These could be seen to be elevated terraces and not depressions. Hexagonal loops which are eccentric are also seen as in fig.VI-4. Fig.VI-5 is a phase contrast photograph of a complex loop pattern of low step height. A few spirals have been also observed. Fig.VI-6 is one such case and Fig.VI-7 shows another where the ledges shift after one rotation and subsequent ledges form close loops. An elongated hexagonal spiral is shown in fig.VI-8. A complex

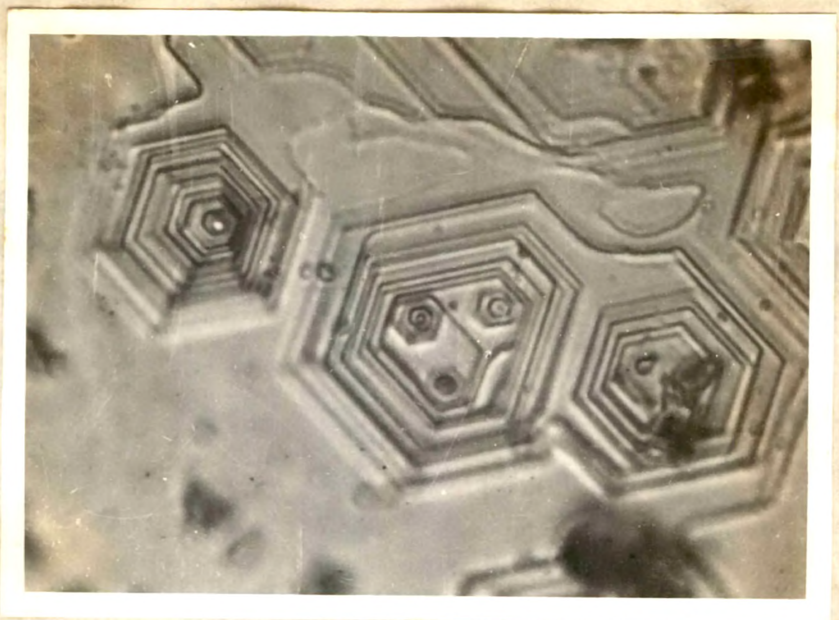

Fig. VI -9 X170

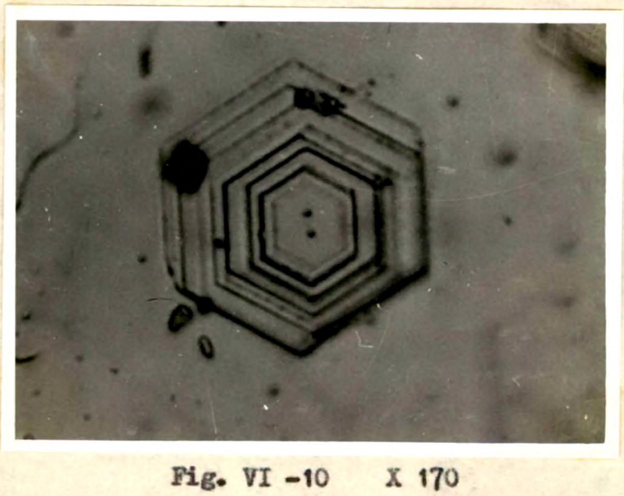

Fig. VI -10 X 170

spiral system arising out of three spiral layers is shown in fig.VI-9. Further it is seen that the spirals and the loop pattern are seen only on facets which are nearly parallel to the basal plane of the single crystal.

Spirals and closed loops are known from the theory of crystal growth. The development of the theory of crystal growth, its implications and experimental evidences have already been discussed in chapter II. The works of Forty[1] and George[2] on crystals of zinc grown from vapour have already been mentioned. A number of crystals have been grown by Forty in the form of flat hexagonal plates and subsequent examination have shown a large number of growth hills. Yet no spirals have been reported. Forty has analysed his results and observes that the crystals are probably formed by two dimensional nucleation of the monolayers which is catalysed by crystalline overgrowths of zinc oxide. Zinc oxide also has the same structure as zinc and is known to sublime easily when heated with the metal. The stock metal might contain traces of oxide and this evaporates along with the metal. This can serve as an active nucleus for the monolayers of zinc if it has a stable size and ensures coincidences of a hexagonal network after a 'vernier repeat'. Since the spacing of zinc oxide exceeds that of zinc by 6% one zinc oxide crystal can initiate 17 monolayers of zinc. If several zinc oxide crystals are active at the same time, the growth can proceed with periodic incoherence between the structures of oxide crystals and metals. However, one cannot explain why such a process is active only in case of zinc and not in other hexagonal metals like cadmium and Magnisium.

The growth pattern presented in the figures are unique, in the sense, they have been observed on the facets of the melt grown crystals. The spirals shown in fig.VI-6-9, constitute the first direct observation of growth spirals on zinc crystals. No measurements could be made, of the step heights because of the presence of other faces nearby which makes it difficult to match the optical flats on these surfaces However, examination at the highest possible magnification with light profiles could not resolve the steps indicating that they may be of monomolecular height. However the complex spiral (fig.VI-9) could be resolved and gives a step height of about 0.1 micron at the outer loops. The closed loops shown in fig.VI-3 etc. have very large step heights of the order of microns. Any explanation to be offered for the existence of the loops should also explain this feature. One cannot assume large Burgers' vector for the dislocation, since theory shows that dislocations with large Burgers' vector are unstable and dissociate. If the growth spirals observed are to be attributed to the screw dislocation, it should be explained as to how such a feature can be observed on the melt grown crystals. So far as the growth of metal crystals from melt is concerned, the screw dislocation is not necessary to provide the sites for the addition of atoms. It can be shown however that these features can be explained on the basis of the screw dislocation mechanism as follows:

The facets are developed due to rapid growth, and is quite likely that these facets contain screw dislocation terminating at their surface. If the growth of crystal proceed from the vapour phase under low supersaturation over these facets then the growth spirals can be developed on these faces. Such a vapour phase growth occurs as follows. While the mould is prepared under vacuum, it is customary to leave some space above the metal to account for the expansion of the metal at high temperature and the metal vapourises into this evacuated space because of its high vapour pressure. On cooling down the metal solidifies first, as the temperature is less at the bottom, and the facets develop. As the capsule is lowered further the vapour also cools and condenses on the facets and develop the spirals on these facets. The shrinkage of spirals in fig.VI-6 and 7 can be attributed to the motion of dislocation during the growth. Such motion of dislocation might be possible during the solidification of the melt due to the different thermal expansion of glass and metal and consequent stress developed inside the crystal. Dislocation multiplication, dissociation and movement due to such stresses have been reported recently[3] on cadmium. The closed loops might have been the result of a double spiral growth mechanism, analogous to the so called Frank-Read source. The large step height can be explained if one assumes a mechanism proposed by Henschke[4] to explain similar pattern of large step height observed on cathode-sputtered copper films. Henschke has shown that, in a strained lattice, two alternately acting double spiral mechanism can produce closed loops with large step height. Such a mechanism might be possible in this case also. It is not possible, however, to rule out other mechanisms being active in the development of these growth terraces. For example, the crystals of zinc oxide forming monolayers on the growing steps can produce large steps on the surface of the growing crystals. To study this in detail, the crystals were etched in a solution containing 20 gms CrO_3, 1.5 gms of Na_2SO_4, 5 c.c of concentrated HNO_3 and made up to 100 c.c. Such a reagent has been used by Servi to reveal dislocation sites. It was observed on etching, that two pits were formed at the centre of the loops as shown in fig.VI-10. This is a clear demonstration of the presence of dislocations and lends ~~leads~~ support to the idea of a double spiral mechanism, analogous to Frank-Read source. These observations clearly indicate that the

Fig. VI -11   X 10

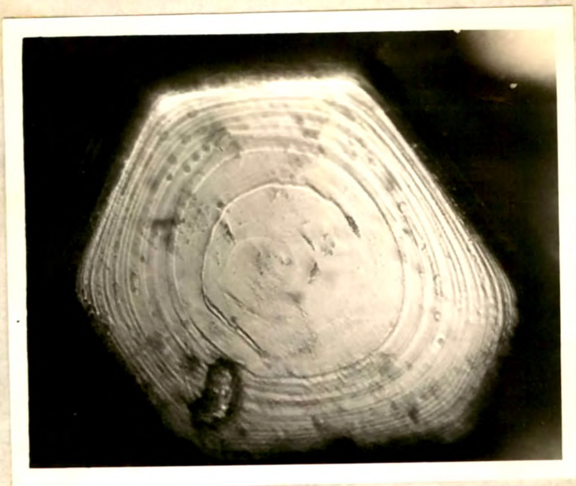

Fig. VI -12 X 170

Fig. VI -13 X 170

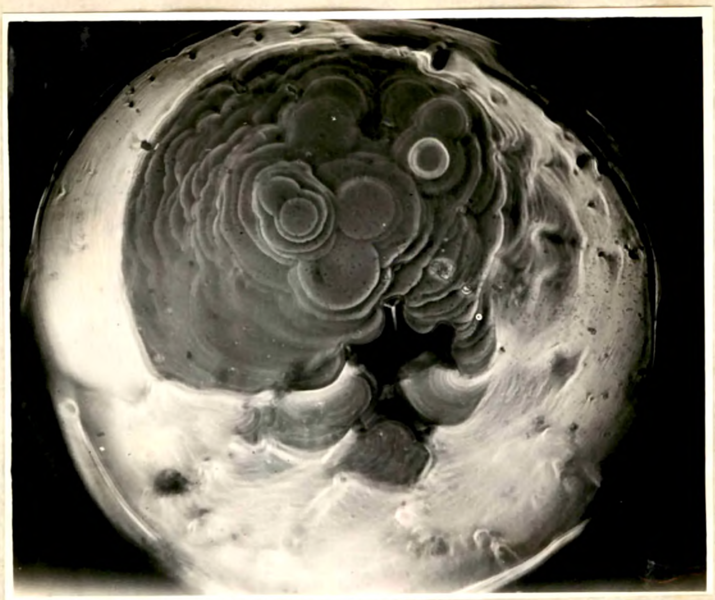

Fig. VI -14 X 170

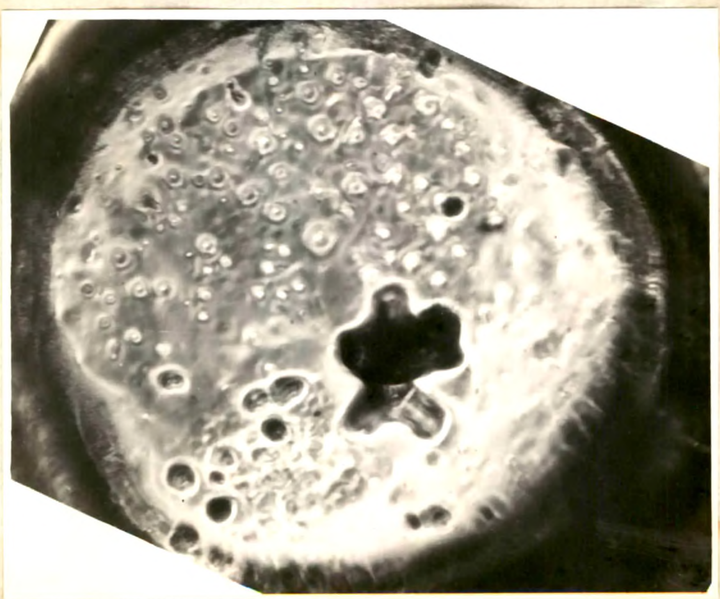

Fig. VI -15 X 170

dislocations are active in the growth of zinc crystals also.

To investigate whether the spiral growth takes place when the supersaturation of the vapour above the surface is more, a small amount of metal was allowed to solidify on the top portion of the glass mould. This is not difficult and as the crystal grows this stock metal at the top can provide a regular supply of vapour as it is at the highest temperature. In such cases profuse whisker growth in the form of hexagonal platelets more or less parallel to the axis of the crystal takes place. Fig.VI-11 shows a typical case. A large number of hexagonal plates are available, their size being a few millimeters. These platelets are extremely small in thickness and of high reflectivity. Many of them show a characteristic circular feature as shown in fig.VI-12. No complete spiral has been observed so far on these crystals. Some contain parallel striations also. Circular growth layers have been observed on the top surface of the crystal. Fig.VI-13 and 14 are the phase contrast pictures of these layers, the former being on the top of a crystal having the basal plane parallel to the crystal axis and the latter being on a surface in which the basal plane perpendicular to the crystal axis. The apparent resemblance of the features indicate that they are not dependent on the crystallographic nature of the surface. Fig.VI-15 shows the surface after etching. Superimposing the two photographs it could be seen that the pits are developed at the centre of these growth layers and remains evenafter the layers have been completely etched away, indicating thereby the presence of dislocations at these points and that the growth layers are formed on these.

It is possible to compare the growth features observed in the two cases described above at this stage. The hexagonal features are observed on surface parallel or nearly so, to the basal planes of the crystals and these have been observed under low vapour pressure and hence probably under low supersaturation. In the second case the supersaturation is definitely more and the features are not dependent on the crystallographic nature of the surface. One can conclude that the growth under high supersaturation is not sensitive to the crystallographic nature of the surface, while under low supersaturation spiral growth around the screw dislocation is seen only on the basal plane. Also, the supersaturation affects the shapes of the growth features.

Crystals grown under conditions of constitutional supercooling develop cellular structure and sometimes this structure manifests itself on the top of the crystal as is shown in fig.VI-3. The details of this structure has been studied and will form the matter for discussion in the next chapter.

Fig. VI -16   X 10

Fig. VI -17   X 10

(2) CYLINDRICAL SURFACES:

The nature of the microstructure appearing on the cylindrical surfaces is dependent on the growth conditions and the nature and amount of impurities. No detailed study of the cylindrical surface has been reported so far. A detailed study of these surfaces was undertaken. The surface is in general smooth and plane. However if the metal contains a small amount of cadmium about 0.1% some fine lines are seen developing on the surfaces. These are parallel to the crystal axis at fast rates. When a larger amount of cadmium (6%) is added, these lines form a network as shown in fig.VI-16. These lines are ridges projecting out of the surface. Fig.VI-17, shows the top portion of a crystal containing 0.1% of cadmium. The spacing between these ridges are dependent on the amount of impurities present, being larger when the impurity content is small. The direction of these corrugations are not dependent on the rate of growth. When the amount of cadmium present is extremely small, (less than 0.1%) and the growth rate is low, no ridges are seen in the lower portion of these crystal, but develop at the upper portions. This suggests that these lines are the results of a build up of concentration gradient in the liquid metal and the impurities have been pushed away to the sides of the tube which solidify dendritically. These

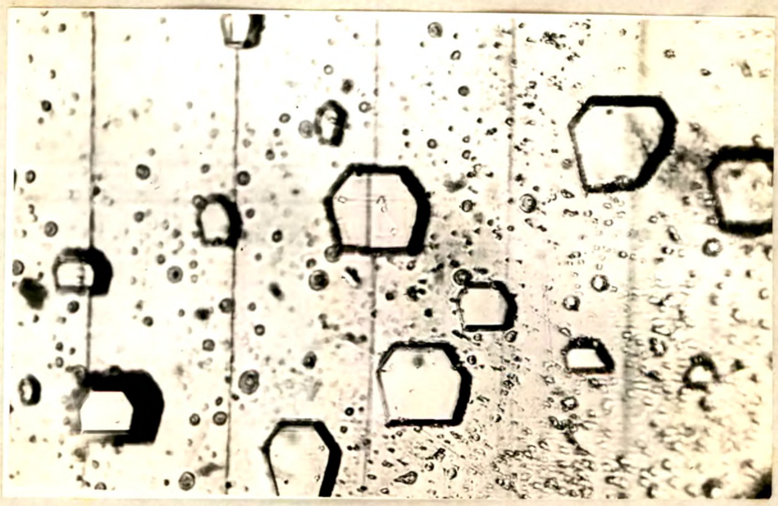

Fig. VI -18   X 360

Fig. VI -19   X 170

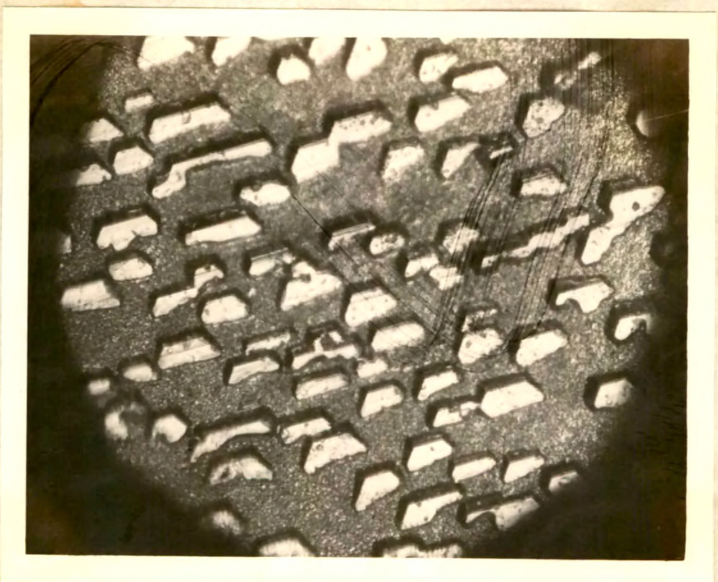

Fig. VI -20   X 270

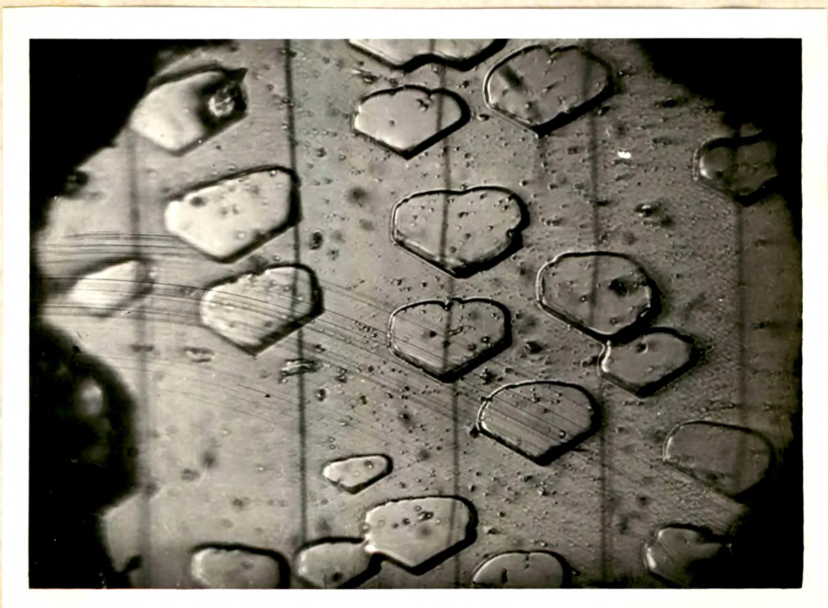

Fig. VI -21   X 360

Fig. VI -22   X 360

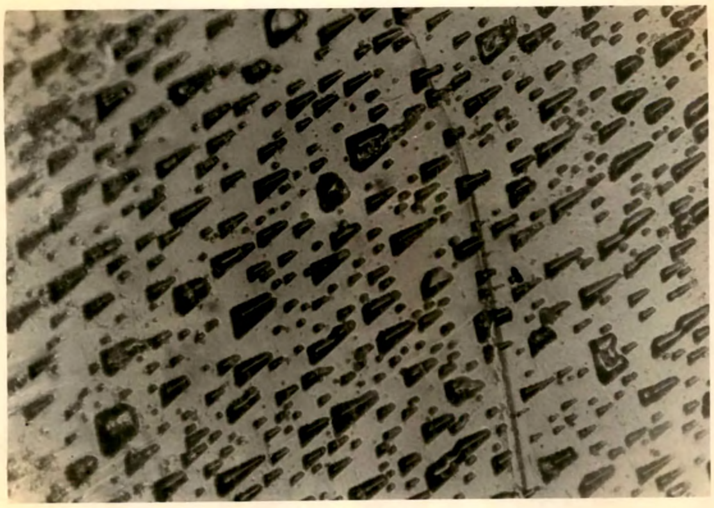

Fig. VI -23   X 170

Fig. VI -24   X 170

Fig. VI -25   X 170

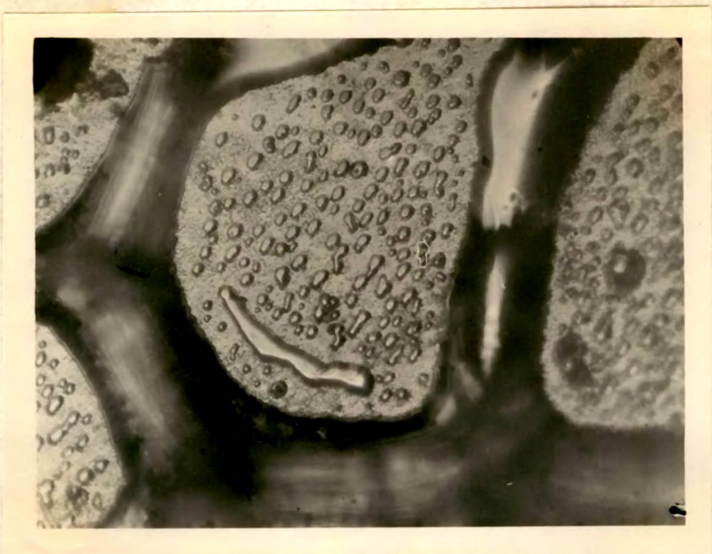

Fig. VI -26 X 360

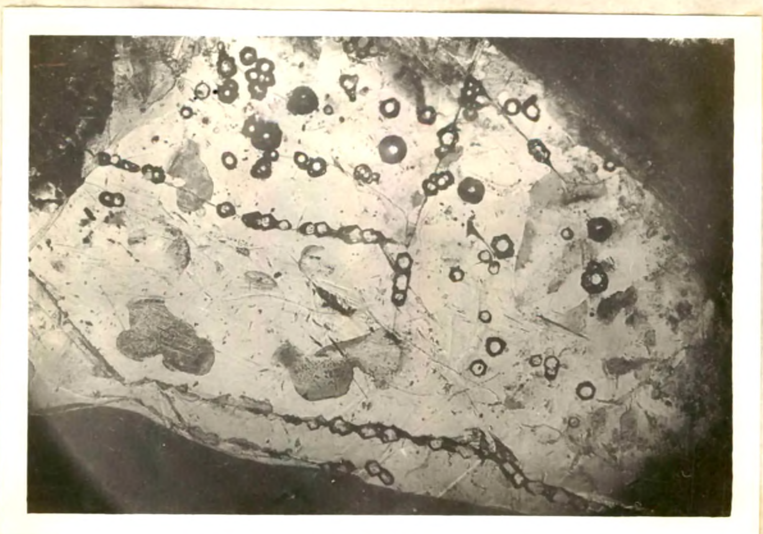

Fig. VI -27 X 90

observations are consistent with the results of Hillawell and Robert[5] and Weinberg and Chalmers[6], that dendrites of zinc and cadmium are formed as ridges parallel to the basal plane.

Another interesting feature observed on the cylindrical surface of the crystal is the well defined rows of etchpits of various form aligned along the axis of the crystal. The pits have been studied in detail. Fig.VI-18 shows a hexagonal row with profiles running across, while fig.VI-19 shows rectangular pits and fig.20 is a phase contrast picture of half hexagons. A variety of other shapes are shown in figs.VI-21 to 24. The variation of shape is observed around the cylindrical surface. To study the variation in shape of the pits, a crystal with basal plane parallel to the axis was taken and mounted horizontally on a Wollaston's goniometer and studied under the microscope. The hexagonal pits are produced when the direction of observation is perpendicular to the basal plane. From this position a rotation of 45° produces the half hexagonal pits and 90° produce the rectangular pits. The triangular shapes are seen at angles of about 60° and 30°. In regions where pits are not seen, the surface shows a corroded appearance shown in fig.VI-25. The distribution of these pits are not affected by the presence of the dendritic ridges formed when crystal contains cadmium. This can be seen from fig.VI-26. When the basal planes are oriented at definite angles to the crystal axis, the pits shape is found to vary along the surface of the crystal also. In all cases the distribution of these pits is along the axis of the crystal. The size of the pits is larger at slow rates of growth and the edges of the pits are rounded as shown in fig.VI-21. The depth is found to be of the order of microns, as can be seen from the profile shift and density $\approx 10^4/cm^2$. The results suggest that these pits are produced by evaporation from the surface. The various shapes seen are projection of the hexagonal basal plane at different angles. These pits are produced by evaporation possibly at dislocation sites. Due to the difference in the thermal expansion of glass and the metal the crystal shrinks as it cools down and the evaporation takes place from the surface of the crystal into the space between surface and the walls of the glass due to the high vapour pressure of the metal and the low pressure inside the capsule. To verify whether such evaporation is possible, a cleaved specimen is sealed in a glass tube under vacuum, placed inside a furnace at 300°C for a few hours, cooled slowly and observed under a microscope. A number of hexagonal pits are produced and these are shown in fig.VI-27. These observations imply that the evaporation of zinc crystals proceeds anisotropically. By careful study and standardisation this property can be used to determine the orientation of the basal plane and for checking the planes of the crystals.

(3) CLEAVAGE SURFACES:

There has been considerable work reported on the examination of the cleavage faces of the metals. Generally the appearance of the faces is complicated and many types of surface markings are visible, some clearly associated with the crystallography of the metal. Of the crystallographic type most prominent are twins, with associated accommodation kinks or other kink bands and slips. The surface topography associated with twins have been extensively studied by Pradt et. al.[7,8]. Holden[9] has used the interferometric techniques to study the plastic deformation features on the cleavage surface of metals. A brief account of the application of multiple-beam interferometry to study metallic surfaces has been described by Tolansky[10]. Deruyttere and Greenough[11] have carried out systematic study of zinc crystals of different orientation cleaved by Tension. The resultant basal surfaces have been compared and the results on the twin bands were shown to conform to the theory of Bilby and Bullough[12].

The interest of the present authors was not directly related to the mechanism of cleavage and twinning. Hence the observation has been restricted to the study of the

Fig. VI -28 X 10

Fig. VI -29(a) X 20

Fig. VI -29(b) X 20

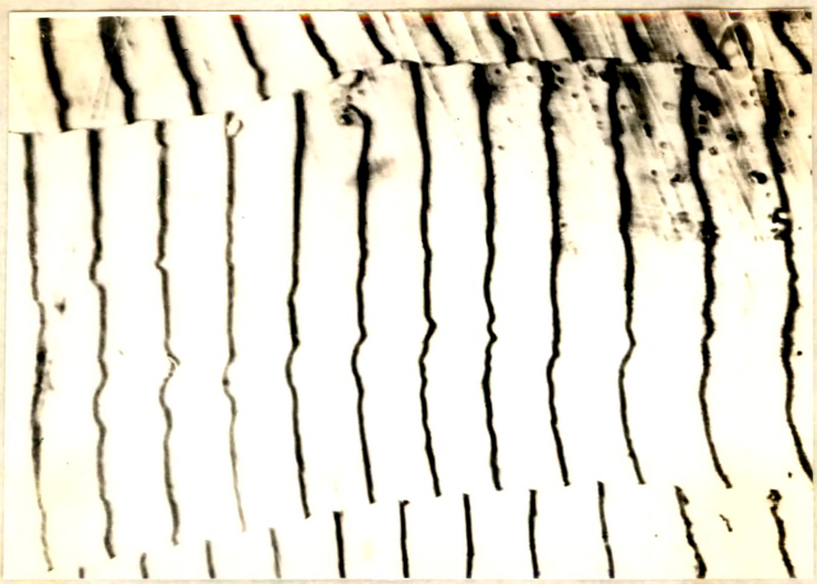

Fig. VI -30   X 90

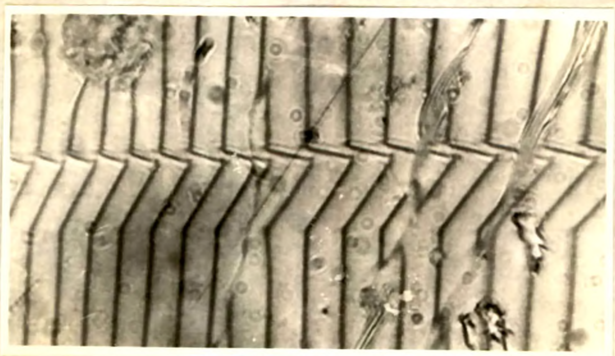

Fig. VI -31   X 90

surface cleaved by a sharp blow on a knife edge oriented roughly along the basal plane. The results conform to those obtained by Holden[9] and others[11], and hence only a brief discussion is presented here. The crystals of different orientation and impurities were cleaved at liquid air temperature. The two faces of the cleavages were examined and compared. Fig.VI-28 is cleaved surface. Fig.VI-29(a) and (b) are the cleavage counterparts of another specimen. The surfaces contain the cleavage lines. These lines show perfect matching on the counter parts and are non-crystallographic in nature. The step heights of a number of such lines have been measured and it was observed that the step heights are not constant, and vary widely from 500 A.U. Fig.VI-30 shows the interference fringes on a series of cleavage lines. A number of twin bands was observed on the cleavage surfaces. In no case, in all the crystals examined were the twin bands found in both faces in matching positions. Accommodation kinks associated with the twins are usually visible. Fig.VI-31 shows the multiple-beam interference fringes on the twin band and the accommodation bend. The measurements on a number of twin bands show that the angular distortion on these twins were in agreement with the results of Holden. Cleavage by impact may result in compressive stress along the basal plane of the crystal. Orowan[13] has shown that this condition, on a macroscopic scale, will lead to formation of kink bands.

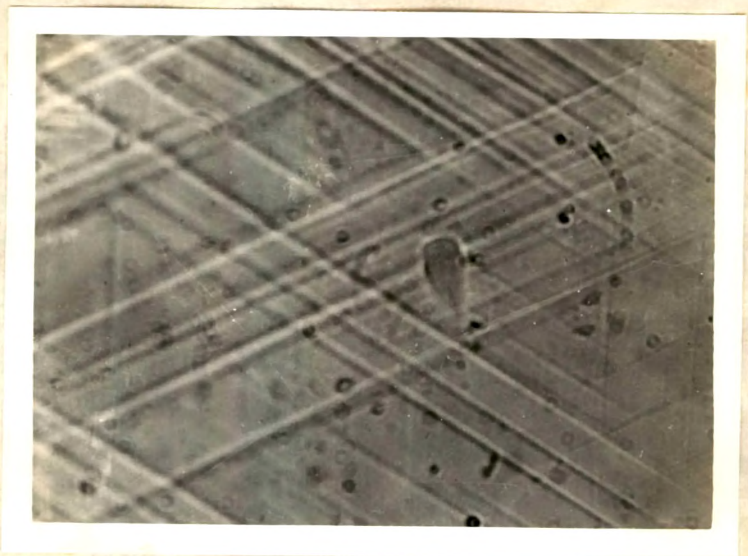

Fig. VI -32 X 170

Such bands are formed during the cleavage of zinc. In fig.VI-32 are shown the typical bands which are very similar to those observed by Holden. The results presented here correspond to the observation of the earlier workers of the field and provide the experimental confirmation of the earlier work.

SUMMARY AND CONCLUSIONS:

(1) The study of the free surface at the top of the crystals have revealed a number of growth features. These have been analysed and interpreted in terms of the dislocation theory of crystal growth.

(2) The first direct evidence has been presented of the growth spirals and closed loops on zinc crystals.

(3) The supersaturation has influence on the shape of the growth layers.

(4) Under high supersaturation the shape of the growth layers are not sensitive to the crystallographic orientation.

(5) Cylindrical surface containing impurities like cadmium show dendritic corrugations parallel to the basal plene.

(6) The cylindrical surfaces show a variety of evaporation pits and these have been analysed and interpreted as sites of dislocations. It has been suggested that the shape of the pits can be used to determine the orientation of the crystals.

(7) The surface features observed on the cleavage planes of the crystal confirm to the results of Holden and others.

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