PART II

STUDIES ON ZINC CRYSTALS

CHAPTER V

A STUDY OF THE EFFECT OF GROWTH RATE AND IMPURITIES ON THE ORIENTATION OF UNSEEDED ZINC SINGLE CRYSTALS

Metallic zinc has the h.c.p. structure with $c=4.937^{o}A^{o}$ and $a=2.660\ A^{o}$. The axial ratio $c/a = 1.856$, is larger than that predicted by the theoretical close packing of spheres which is $c/a = 1.633$ indicating an extension in a direction of the hexagonal axis and close packing in the basal plane. The bonds are stronger in the hexagonal layers and this fact is responsible for the anisotropy of the physical properties of the crystals, which show large values of compressibility and coefficient of thermal expansion in the direction of hexagonal axis. The single crystal cleaves along the basal plane and this property is used for the determination of the orientation. The (0001) is the plane of easy glide along $\langle 11\bar{2}0\rangle$ direction and twinning plane is $(10\bar{1}2)$. Under conditions unfavourable for basal glide the other glide systems $\{10\bar{1}0\}$ $\langle 11\bar{2}0\rangle$ at higher temperature and $\{11\bar{2}2\}$ $\langle \bar{1}\bar{1}23\rangle$ at room temperature are operative. It has a high vapour pressure, $\log_{10}p$ being -0.812. The pure metal is very soft and is hardened by the presence of small amounts of impurities. It is highly reactive and is attacked by most acids, alkalis and halogens.

The present chapter deals with the study of orientation of the single crystals grown under different conditions. The earlier work of Goss and Weintroub shows that the temperature gradient, rate of growth, impurities and the state of stress are the controlling factors of the orientation of the unseeded metal crystals. These authors have studied the growth of crystals using a horigontal travelling furnace. The crystals were about 0.5 cms in diameter and 20-30 cms in length. The temperature gradient and rate of growth were varied over a wide range as possible. Their work on zinc can be briefly summarised as follows. The crystals were grown at the rates: 16,5.3,1.5,0.5 mm/min. and the temperature gradient in the above four cases were between the ranges 8-30,2-40,3-45, 8-30°c/cm. In the first case the crystals obtained were polycrystals consisting of a number of strips. At rates 5.3 mm/min. bicrystals were obtained. In the third case most of the crystals were bicrystals and a few single crystals were obtained. Complete single crystal were obtained only at slow rates of 0.5 mm/min. and the orientation was at random. In a subsequent publication Goss[2] observed that for slow rates of growth bismuth, and cadmium ~~and zinc~~ showed preferred orientation while indium and zinc did not. It was explained that at slow rates of growth the heat flow is from the crystallising interface along the specimen, the temperature of which is about the same or lower than that of its surrounding and hence the crystal will grow along that orientation for which the heat is conducted away most easily. For zinc the thermal conductivity changes very little with orientation and hence no preferred orientation is observed. Goss further observed that zinc grown in a vertical position showed a preference for the c axis to be perpendicular to the specimen axis. As a result of these studies Goss concluded that no one factor was responsible for the existence of preferred orientation; but that the thermal conductivity was the main factor for slow rates of growth.

The work of Goss and Weintroub[1] was not mainly concerned with the orientation of the crystals but with the actual process of growth. In this respect it deserves credit in that a number of metals have been studied under different conditions. However, so far as the orientation of the unseeded crystal is concerned the results cannot be conclusive. Even though four different rates of growth has been studied only in one case - the lowest rate, could they obtain single crystals. Therefore one cannot get a definite idea of the effect, the growth rate has on the orientation. Secondly, the effect of the various metallic impurities has not been studied. Moreover, little was unknown at that time about the morphology of interface.

Grinberg[3] has recently studied the effect of growth rate on the orientation of the basal plane of cadmium with respect to the crystal axis. The crystals were grown by Bridgman's method in a vertical furnace at a temperature gradient of 15°C/cm. Various growth rates were tried in the range 2-10 cm/hr. It was observed that as the rate of lowering of the crucible was decreased from 10 cm/hr, the angle between the basal plane and the crystal axis increased linearly until a critical value was reached, at which the orientation became random. When the mould was changed to graphite the nature of the variation remained the same except for a shift in the curve. The results were interpreted as follows: For fast growing crystals the isotherms inside the mould are ellipses elongated in the direction of the mould axis. Therefore, the basal plane is parallel to the major axis of ellipse. When the rate of travel of the mould slows down the ellipse becomes a circumference and the orientation of the basal plane becomes random. The shift in the curve of when graphite mould is used as expected because of the higher conductivity of graphite over that of glass. Grinberg concludes that the anisotropy of thermal conduction has a marked effect on the orientation of the crystals.

The observations are significant, for the fact that by the proper choice of the mould, gradient and rate of growth, the crystal orientation can be controlled. Properly oriented single crystals are essential for the investigation of plastic deformation of metal and hence if it is possible to obtain crystals of any orientation without seeding, it is possible to avoid all the disadvantages of using the seed crystal. No report of the systematic investigation has been reported on the orientation of single crystals of zinc eventhough a few publications on this topic are available. Bridgman[4,5] observed that in crystals grown in a temperature gradient furnace the angle between the c axis and the specimen axis was not random but was usually quite large exceeding 65°. Jillson[6] using moulds with blunt bottom and temperature gradient with a lateral as well as vertical component obtained random distribution. He suggested that preferred orientation might be the result of small amounts of impurities present in the metal used by the previous worker and that zinc of 99.999% purity would give a random distribution. Slifkin and Kaufman[7], prepared single crystals of zinc of same purity as those of Jillson and yet obtained usually large angle. It appeared that the unique observation of Jillson may be due to some other factor. Slifkin[8] using a mould, the capullary end of which was pulled into a flat bottomed fish-hook found that the angle between the direction of the horizontal section of the capullary hook and the basal plane of the crystal was very small in every case. The results suggested that the Geometry of the crucible can have some influence on the orientation. However, none of these observations were systematic and the contradictory nature of the results suggests that the problem requires careful investigation.

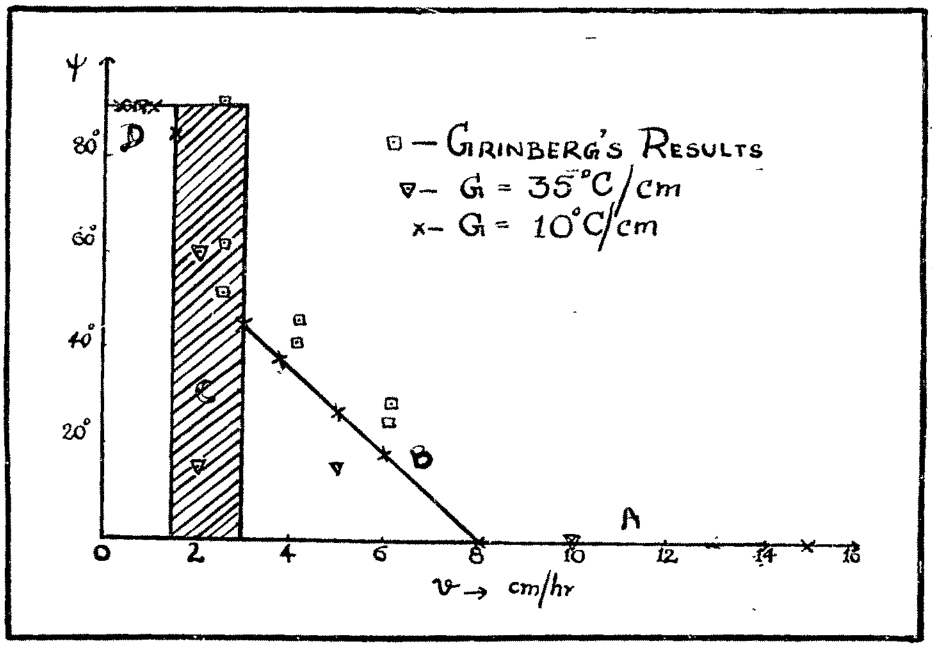
It was therefore decided to make a detailed study of the factors controlling orientation of the unseeded zinc crystal. Simultaneous variation of all factors cannot be expected to give the desired information. Accordingly, the method of growth, the nature and dimensions of the comtainer was kept throughout the work the same. Bridgman's method has the advantage that the growing crystal has the temperature decreasing from top to bottom and hence the no convection currents are set up in the molten metal. The only manner in which the heat is removed from the interface is by conduction down the solid. Therefore one anticipates that the small anisotropy in thermal conduction may have a significant effect. The arrangement described in Chapter IV has been used for the growth. Experiments have been conducted at two different temperature gradients. Mould velocity has been varied in the range 0.3 cm/hr - 15 cm/hr. Metal of different purities have been used in this work. Pyrex mould of 6 m.m. diameter and 5 cms long with a capillary end of 1 mm diameter and 2 cms long was used throughout. In this way, the effect of the mould on the orientation was eliminated. Moulds of other dimensions were also used in some cases to find whether these have any influence on the orientation of the crystal. The junction of a thermocouple was kept in contact with the outer surface of the mould and temperature was recorded at regular intervals to observe any fluctuations in the temperature. The melt temperature was kept initially at 470°c in all cases and the mould is maintained at this temperature for about 12 hrs. In this way by keeping all external conditions constant and varying only the mould velocity, whatever change in orientation that is observed, can be safely attributed to the growth velocity. To determine the orientation the crystal was cooled to liquid nitrogen temperature and cleaved with a knife-edge in the conventional way. The angle between the basal plane and the axis of crystal could be determined either by tracing the boundaries on a paper or by using a goniometer. At each rate about 8-10 crystals were grown, and when all of them do not have the orientation, the most favoured orientation has been quoted in the data. However when zone refined material was used, the number of observations in each case was limited to two or three, unless results vary very largely, in which case a number of observations have been recorded. This is in view of the limited stock of zone refined material.

The observations presented in this work correspond to the lowest range quoted in the work of Goss and others. This has been chosen so, because good single crystals are obtained only for low rates of growth. The growth rate has been assumed to be the same as the rate of travel of the mould in the furnace. This assumption is justified by the earlier work[2].

TABLE V-1

ORIENTATION OF ZONE REFINED METAL

Temp. Grad. G°c/cm	Mould velocity v c/hr	No.of crystals grown	No.of single crystal	Most favourable ψ	No.of crystals in correct orientation	Other orientations
10	15	2	2	0	2	-
"	10	2	2	0	2	-
"	8	2	2	0	2	-
"	6	2	2	15°	2	-
"	5	2	2	25-30°	2	-
"	4	3	3	35°	2	42°
"	3	2	2	45°	2	-
"	2	6	6	-	-	60°-45°-30°
"	1.5	4	4	85°-90°	2	60°
"	1.0	2	2	90°	2	-
"	0.8	2	2	90°	2	-
"	0.5	2	2	90°	2	-
"	0.3	2	2	90°	2	-
35	10	2	2	0	2	-
"	5	2	2	15°	2	-
"	2	2	2	-	-	60°,15°
"	0.8	2	2	90°	-	-



ψ
80°
60°
40°
20°
D
C
B
A
0
2
4
6
8
10
12
14
16
v → cm/hr
□ — Grinberg's Results
▽ — G = 35°C/cm
× — G = 10°C/cm

Fig. V -1

The first set of observations were carried out using zone refined material. The ingot was cast from A.R.quality metal in the form of a rod 1 cm. diameter in a pyrex tube 15 cms long and refined in the unit described in Chapter IV. The number of passes were about 30 and visible seggregation of impurities could be observed at the end. The ends of the rod were cut off and the metal was moulded as usual and crystals were grown. The results are presented in Table V-1. Fig.V-1 shows the plot of $\Psi \rightarrow v$ Results of Grinberg are also shown for comparision.

Four distinct ranges can be observed. For velocities in the range 15 cms/hr to about 8 cms/hr the basal plane of the crystal remains parallel to the crystal axis within about 1^{o} to 2^{o}. The last range is characterised by the basal plane tending to be normal to the crystal axis. The four regions are marked A,B,C & D.

Crystals were grown at rates 10 cm/hr, 5 cm/hr, 2 cm/hr and 0.8 cm/hr with zone refined metal in a temperature gradient of $35^{o}C/cm$. The values are shown in Table V-2 and the observations as triangular points in fig.1. The results remain same in regions A & D but the region C shows a value of smaller than the corresponding rate in the previous case. In view of the fact that the number of observations are limited the implications of the results are not known. It was therefore, decided to study in more detail the

TABLE V-2(a)

ORIENTATION OF A.R. QUALITY METAL

Temp. Grad. $G^{o}c/cm$	Mould velocity v cm/hr	No.of crystals grown	No.of single crystals	Most favourable ψ	No.of crystals in correct orientation	Other orientation
10	15	18	13	0	13	-
"	10	8	8	0	8	-
"	8	8	8	0	6	15^{o}
"	6	8	8	15^{o}	5	$0-5^{o}$
"	5	8	8	25^{o}	6	15^{o}
"	4	8	8	35^{o}	5	30^{o}, 45^{o}
"	3	12	8	45^{o}	5	60^{o}
						50^{o}(2)
						30^{o}(2)
						45^{o}(3)
"	1	10	10	90^{o}	7	60^{o}, 75^{o}
"	0.8	8	8	90^{o}	7	75^{o}
"	0.3	6	6	90^{o}	5	55^{o}

TABLE V-2(b)

ORIENTATION OF A.R.QUALITY METAL

Temp. Grad. $G^{o}c/cm$	Mould velocity v cm/hr	No.of crystals grown	No.of single crystals	Most favourable ψ	No.of crystals in correct orientation	Other orientations
35	15	10	6	0	15	-
"	10	5	5	$0-5^{o}$	5	-
"	8	5	5	$0-5^{o}$	5	-
"	6	5	5	5^{o}	4	0^{o}
"	5	5	5	15^{o}	4	-
"	5	5	5	15^{o}	4	-
"	4	5	5	25^{o}	4	15^{o}
"	2	5	5	-	-	45^{o},15^{o}
"	1	5	5	90^{o}	5	-
"	0.3	5	5	90^{o}	5	-

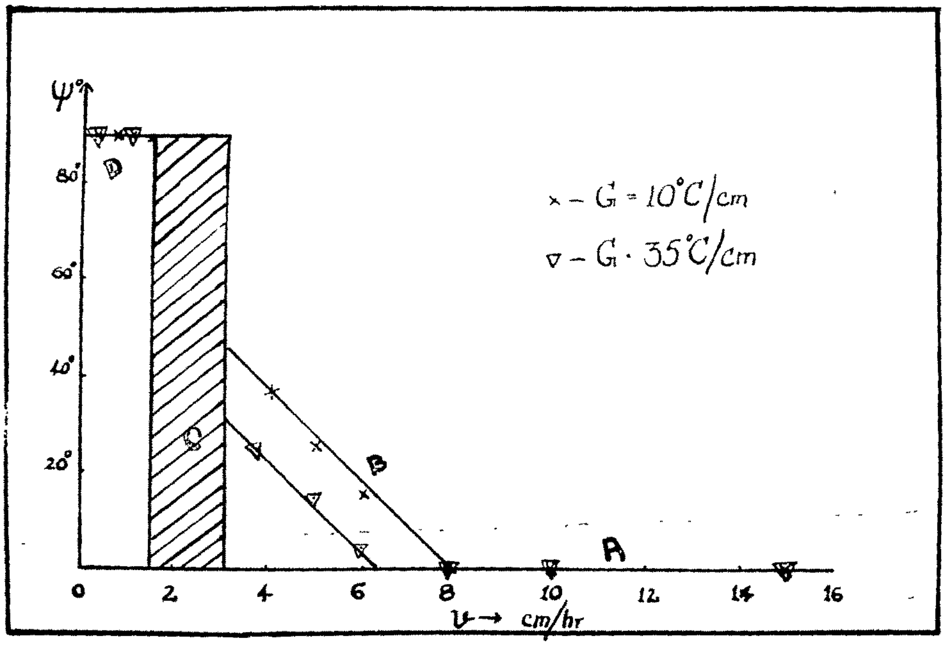


Fig. V -2

growth using A.R.quality metal containing 0.002% lead, 0.002% iron and 0.00001% Arsenic. The observations are presented in Table V-2 (a) and (b). The plot of ψ versas v is shown for the temperature gradients 10°C/cms and 35°C/cm in figure V-2. The general nature of the graph remains the same. Comparision of the results obtained for the zone refined metal and for the A.R.quality metal shows that the curves do coincide. The results with 35°C/cm gradient shows a small shift towards the a axis at higher temperature. Comparision of the orientation for the zone refined metal and for A.R.quality metal at larger temperature gradient was also found to be coincident. However the results are found to fluctuate in some cases. To illustrate the particular case, at the rate of 5 cm/hr the orientation of crystals of both A.R. and of zone refined metal were 25° for the smaller temperature gradient and 15° for the larger gradient, indicating that the small impurities do not affect the orienta-tion. The results will be discussed later.

Crystals grown from L.R.quality metals also behave similarly in region A & B. However for rates of growth above 10 cm/hr single crystals were difficult to grow. The crystals were in the form of a number of strips of basal planes parallel to the axis. No detailed study has been made in the slowest range D.

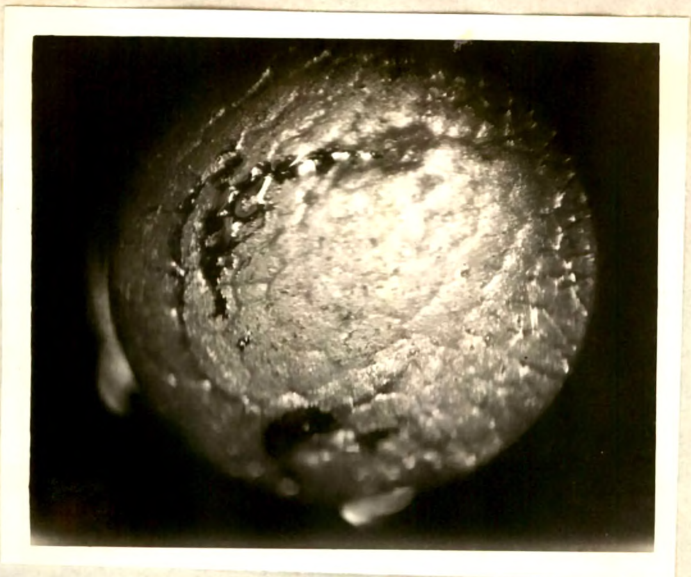


Fig. V -3

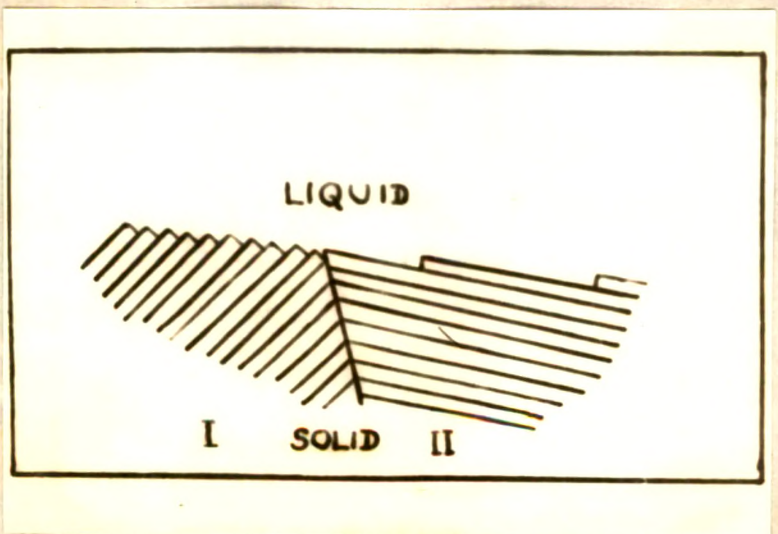


Fig. V -4

TABLE V-3

EFFECT OF IMPURITIES ON ORIENTATION

Impurity	Temp. Grad. °C/cm	% of impurity	No. of crystals grown	Rate of growth	Most favourable ψ
Cd	35	0.2	4	10	0°
Sn	35	0.02	2	10	0°
Pb	35	0.1	2	10	0°
Cd	35	1.0	2	10	0°
Cd	35	3.0	2	10	-
Sn	35	0.02	2	5	15°
Sn	35	0.02	2	1	90°
Sn	10	0.02	2	10	0°
Sn	10	0.02	2	5	25°
Sn	10	0.02	6	1	
Cd	10	0.02	2	½	60°

During the investigation it was observed that the orientation of the capillary end was different from that of the crystal. In certain cases it was found that in the region A the crystal initially starts growing by two different nuclei and the nuclei in the correct orientation occludes the other one as the growth proceeds and subsequently the final portions of the crystal contained only one orientation. Crystals grown in tubes of larger diameter and length were also oriented in the same way as those of standard dimensions used in this investigation.

To study the effect of metallic impurities small amounts of metals like cadmium, tin and lead were added and the resulting orientations were measured. The behaviour was found to be similar in the regions A and B. In region D a very peculiar phenomena was observed. The orientation of the crystal at higher gradient were with the basal plane perpendicular to the crystal axis as usual, whereas, when the gradient was small ($10^{o}C/cm$) basal plane was not perpendicular to the crystal axis. A number of crystals were tried and the orientation was at random. The examination of the top free surface showed a cellular structure on some crystals as shown in fig.V-3. Subsequent chemical polishing proved that this was an inherent structure and could be identified to be due to the cellular interface structure. The results indicate that the cellular structure has an influence on the orientation of the crystal.

Detailed studies indicated that cellular structure existed on all crystals grown at lower gradient and containing impurities 0.02%. However only when the rate of growth was small < 1cm/hr could they have any influence on the orientation.

The experimental observations can be summarised as follows. When the rate of growth is in the range 8-15 cm/hr the crystal grows with their basal planes parallel to the crystal axis. This preference is shown by metal of highest purity as well as metal containing 1% impurities. However the impure metal do not give single crystals at fast rates, but shows a strip like structure. Neither the temperature gradient nor the rate of growth has any control over the orientation. Also the morphology of the interface do not change the orientation.

Below 8 cm/hr the orientation of the basal plane is dependent on the rate of growth as well as on the temperature gradient. As the mould velocity decreases the basal planes deviates away from the crystal axis and this deviation being more when the temperature gradient is small. This variation is not sensitive to impurities upto 1%, nor to the morphology of the interface.

When the velocity of growth is in the range 1.5 cm/hr to 3.0 cm/hr the orientation of the crystal is at random. The transition to this range is not well defined and fluctuations are often observed.

For slower rates of growth in the range 0-1.5 cm/hr, the basal plane tends to be perpendicular to the crystal axis. This preference is not dependent on the purity nor on the temperature gradient, but is sensitive to the morphology of the interface. When the interface is cellular the preferred orientation does not exist.

The experimental results can be interpreted as follows. Since the crystals are grown under an externally imposed temperature gradient inside a closed tube, heat flow by convection currents and other means are not available. The heat produced at the interface during solidification has to be removed by conduction only. Hence in order to reduce the free energy at the interface the heat has to be conducted away and atoms will align in a manner such that the direction of maximum thermal conductivity will lie along the direction of heat flow. The thermal conductivity along the basal plane being slightly more than that perpendicular to it (1.03:1) the basal plane tends to be along the crystal axis. The isothermal surfaces in this case will be ellipsoids with their major axis parallel to the specimen.

The observations in the region B correspond to those on cadmium reported by Grinberg. In view of striking similarity between the results in the two cases a similar interpretation can be given to this case also. Due to the anisotropy of thermal conduction the direction of heat flow does not coincide with the direction of temperature gradient but makes small angle with it. Also the isotherms are elongated ellipses and the basal planes tend to lie along the major axis of these ellipses. This has been mentioned earlier. The fluctuations observed may be due to the fact that the small anisotropy being not so prominent, orientation can be affected by other fluctuations. When a large temperature gradient is maintained, the flow of heat is more and hence the basal plane makes smaller angles with crystal axis. This observation is in agreement with the expectations and lends support to the explanation offered. The results agree with those obtained by Grinberg on ceadmium using graphite as mould and this has a higher conductivity than that of glass and hence the basal planes make smaller angle with the mould.

No satisfactory explanation can be offered for the random orientation observed in the range C. It has not yet been possible to study this region in more detail, because no systematic variation has been observed. However the collapse of the isothermal ellipses[3] into circles may be one of the reasons. It is possible that other factors like thermal fluctuations, interface morphology and temperature gradient may have some effect on the orientation.

The behaviour of the crystals in the region D is consistent with the idea that in a crystal growing under near-equilibrium conditions, the most closely packed planes tend to make small angles with the interface. The interface in the case of the slow rates of growth is nearly planar in the absence of supercooling. The development of an orientation with the basal plane nearly parallel to the interface can be explained on the basis of Tiller's theory.[10] Considering the interface to be rough, an accordance with the theory of Burton et.al.[11] Consider two grains growing as shown in fig.V-4. In grain of type I the planes of close packing are shown making relatively large angles with the plane of the interface. The grain of this type should be able to grow forward into the liquid because of the presence of a large number of sites for the atom arriving from the liquid. On the other hand the grain of this type have a small velocity of growth laterally when compared with the grains of type II, in which the basal planes lie almost in the plane of the interface. Since there is a positive temperature gradient the grain of type I is unable to advance ahead of grain of type II despite the potential sites available, so that the growth rate and the ultimate texture are determined by grains of type II, and as the growth proceeds, the slower grains expand and occlude the other grains, so that there evolves a texture in which the planes of close packing lie in or make small angles with the interface. This is exactly what has been observed in the experiments. The observations that the crystal exhibiting a cellular structure has a different orientation in the lower range of velocities is also consistent with the above theory and with the observations of Rosenberg and Tiller[12], that in columnar castings the orientation is dependent on the interface morphology.

The results presented above can at this stage be compared with the earlier data. The results are consistent with the observations of Goss and Weintroub that zinc shows a preference for the c axis to be normal to the specimen at high rates. The linear part of the fig.I & II are similar to those observed by Grinberg. Slifkin[8] observes that the basal plane develops an orientation perpendicular to specimen axis if capillary end is bent into a flat hook. He has grown the crystal at a temperature gradient of 15°c/cm at a rate of about 1 cm/hr. In the observation presented in this chapter this rate falls into lowest range where the orientation of the basal plane is normal to the axis in the absence of supercooling. However the competitive growth observed in this case and explained on the basis of the Tillers theory exclude the possibility of the geometry of the crucible influencing the orientation. In the recent studies on the development of preferred orientation in high purity metal and alloys, Hellawell and Herbert[13] observe that cellular structure do not favour any particular orientation. The fact that a random orientation is observed at slow rates when the interface is cellular is consistent with this result also. The observation agrees well with the theory that the fundamental growth process at slow rates is an edgewise extension of close packed planes or an atomically rough surface rather than a growth normal to any particular lattice plane.

<u>CONCLUSIONS</u>: The following conclusions can be drawn from results presented in this chapter:

(1) Zinc single crystals do exibit a preferred orientation when grown in an externally imposed temperature gradient. The preferred orientation is dependent on the velocity of growth.

(2) Impurities do not influence the orientation of the crystal by themselves.

(3) The morphology of the interface affects the orientation when the growth rate is small or approximately 1 cm/hr.

(4) Temperature gradient as well as growth rate have influence when the growth rate is in the range 3.0-6 cm.

(5) By proper choice of the temperature gradient and growth rate it is possible to grow single crystals of any desired orientation.

(6) There exists a region where the crystals are oriented at random, which has not been completely understood.

(7) The observations presented are consistent with the idea that the fundamental growth process is an edgewise movement of these packed planes.

The data presented in the chapter and the coInclucions drawn are the result of a systematic study of over 300 single crystals grown by the author.

REFERENCES

1.	Goss A.J. & Weintroub S.	(1952)	Proc.Phy.Soc.(Lond) B-65,561
2.	Goss A.J.	(1953)	Proc.Phy.Soc.(Lond) B-66,525
3.	Grinberg D.K.	(1961)	Canad.J.Phy.39,1919
4.	Bridgman P.W.	(1923)	Proc.Am.Acad.Sc.58,165
5.	Bridgman P.W.	(1925)	Proc.Am.Acad.Sc.60,305
6.	Jillson D.C.	(1950)	Trans.Am.Inst.Min. Engrs.188,1005
7.	Slifkin L.M. & Kaufman W.	(	Private Communication.
8.	Slifkin L.M.	(1951)	J.Appl.Phy.22,1216
9.	Nye J.F.	(1953)	Acta.Met.I,153
10.	Tiller W.A.	(1958)	J.Appl.Phy.29,611
11.	Burton W.K., Cabrera N. & Frank F.C.	(1951)	Phil.Trans.Roy.Soc. A-243,299
12.	Rosenberg A. & Tiller W.A.	(1957)	Acta.Met.5,565
13.	A.Hellawell & Herbert P.M.	(1962)	Proc.Roy.Soc.A-269,560