

Growth and Perfection of Zinc Single Crystals from the Melt

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Received September 30, 1965

A study was performed with respect to the crystal growth and the perfection of the rod-like single crystals of zinc grown by the Bridgman technique. The substructures in the crystals were examined by optical microscopy and X-ray diffraction techniques. The preferred orientation of the growth direction of unseeded crystals of 99.9% zinc was approximately $[\bar{1}100]$, the preference of which is explained by the survival of the grain having the growth direction of $[\bar{1}100]$ at the cellular interface. The preferred orientations of 99.999% zinc crystals were the orientations parallel to the basal plane, the preference of which is explained by the growth of the grains developed from the nuclei satisfying the minimum surface free energy in the heterogeneous nucleation on the inner wall of a glass crucible. The size and shape of the cell of the impurity-substructure observed in the low purity zinc crystals (99.9%) were related to the crystallographic orientation of the growth direction. Zinc crystals free from subboundaries of larger misorientation than 1 min. of arc were obtained by using a method devised by one of the authors (Maeda). The origin of this misoriented subboundary in zinc was also explained by his conclusion in the case of tin, namely, that mechanical stress due to adhesion between crystal and crucible had been an important factor.

INTRODUCTION

It is well known that every real crystal contains imperfection, and many methods have been investigated for obtaining more perfect crystals. The method in which crystals are obtained from the melt is relatively easy, and preferable to other methods for obtaining large amounts of crystals. Therefore, this method is highly desirable, if good crystals can be obtained from the melt. Although semiconductors with low dislocation densities ($\lesssim 10^2/\text{cm}^2$) can be easily obtained, it is very difficult to obtain metal crystals with dislocation densities below $10^6/\text{cm}^2$. As recently reported by Young^(1,2), however, it has been confirmed that crystals grown from the melt by the Bridgman technique are very nearly perfect. The lack of imperfections is attributed to the use of special crucibles with innerwalls which are very smooth, and to examination of the crystals by using such methods as acid cutting and acid polishing which do not introduce mechanical stress. Young obtained Cu crystals of low dislocation densities ($\approx 10^2/\text{cm}^2$) by this method and observed individual dislocations by transmission X-ray diffraction micrography (Lang's method). A study of the production of zinc single

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crystals with low dislocation densities by the Bridgman technique, and the observation of their degree of perfection by X-ray diffraction micrography without introducing any mechanical stress into them was undertaken. A report of this study is one of the objectives of this paper.

In the growth of metal crystals from the melt, it has been thought that preferred orientations of the growth direction seem to exist, and that the origin of the preference may be related to the growth mechanism. The mechanism of crystal growth has been chiefly discussed with respect to two subjects. One, is the problem of nucleation. Hellawell and Herbert³⁾ indicated that the growth orientations of crystals were determined by the nucleation when crystals were slowly grown from the melt. They pointed out that relatively few nuclei were likely to form and that the resultant crystal, or crystals might have any orientation. Yamamoto and Watanabe⁴⁾ also reported that crystals grown slowly from the melt had no preferred orientation. Intrinsically, however, probability of the nucleation is closely related to the surface energy of the nucleus which is roughly proportional to the product of the surface atomic density times the number of missing bonds per atom on the surface. It is further proposed that even in the process of nucleation some preferred orientation of growth direction may be chosen because of the difference in the surface energy of each atomic plane. This point is investigated in this study by nucleating in glass crucibles with different types of bottoms.

The second subject concerns the survival of crystals having a particular crystallographic orientation. This subject is important in the case of a growth condition where many nuclei are formed, that is, where the crystals are of low purity and grow rather rapidly from the melt. However, it is also involved in the growth of high purity crystals at low growth rate after the nucleation. Interface morphologies between solid and liquid contain a key to the solution of this problem. Freezing interfaces may develop a variety of microstructures depending upon the degree of supercooling which arises from the solute concentration ahead of the advancing interface^{5), 6), 7)}. The interfaces may be classified into the following three types; planar interface, cellular interface and dendritic interface. A planar interface has a preferred orientation of the growth direction in which the planes of close packing (e. g. (111) for Pb) lie close to the plane of the interface^{8), 9)}. A dendritic interface has a preferred orientation of growth direction composed of conjugate close-packed planes (e. g. [100] direction composed of four conjugate {111} planes in the case of Pb). Walton and Chalmers¹⁰⁾ observed the preferred orientation mentioned above in the dendritic interface, but could not find any preferred orientation of growth direction in the cellular interface in Pb. Tiller¹¹⁾, however, pointed out theoretically that a preferred orientation of growth direction in the cellular interface as well as in the other types of interfaces should exist, and this existence was confirmed experimentally by Rosenberg and Tiller⁸⁾ in lead. In order to clarify further the mechanism of the growth of cellular interface, the problem of preferred orientation of zinc crystals is discussed in this paper in relation to the size and shape, which are dependent on the crystallographic orientation of growth direction, of the cellular structure.

EXPERIMENTAL

1. Materials

The analyses of the zinc used are as follows :

99.9% Zn		96.999% Zn	
Pb	0.01%	Pb	0.0000%
Fe	0.01%	Fe	0.00015%
Cu	0.005%	Cu	0.00006%
Cd	0.05%	Cd	0.0007%
As	0.00005%		
S and P compounds	Small		

2. Crucibles

Molton zinc was sucked up into glass crucibles of 5 mm in diameter carefully so as not to produce any cavity. The glass crucibles used in this way were cone shaped at one end. Though the glass crucibles were often cracked by thermal stress, they were preferable to other kinds of the crucibles since they could be dissolved away by hydrofluoric acid without introducing any mechanical stress into the metal crystals. Various shapes of glass crucibles used are shown in Fig. 1. Type (a) is the most simple shape of glass crucibles for

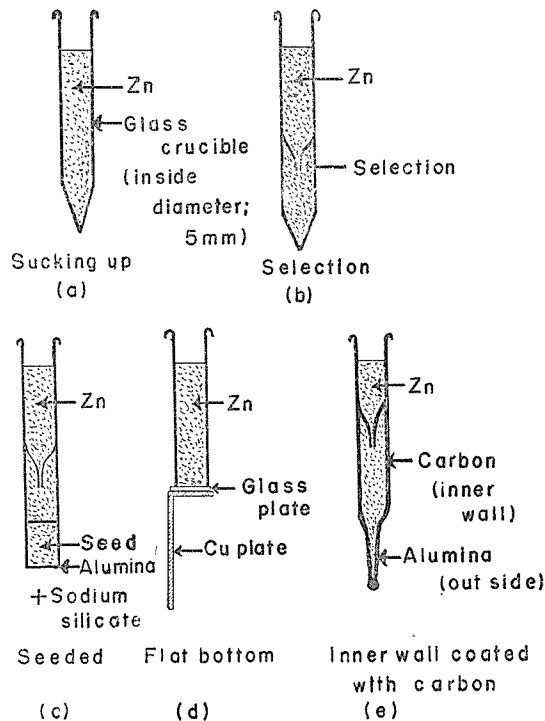


Fig. 1. Crucibles.

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producing single crystals. Since zinc specimens grown in glass crucibles of type (a) were not always single crystals, glass crucibles of type (b) devised by Maeda¹²⁾ were used to obtain single crystals by selecting one of 2 or 3 grains formed in the lower part of glass crucibles. When crystals of specific orientations were required, glass crucibles of type (c) having a seed crystal at the lower end were used. In this case the selection* was used to remove subboundaries from the seed. To investigate the problem of the nucleation, the crucibles of type (d) were used, where the flat bottoms were attached to copper plates to freeze specimens from the bottom along the crucible axis. As all the crucibles mentioned above were always cracked when high purity zinc was sucked up, the glass crucibles of type (e) were used, following the technique used by Maeda¹²⁾ in the growth of tin crystals. The inner walls of these crucibles were coated with carbon, generated by the imperfect combustion of fuel gas, to avoid the generation of stress induced by adhesion between the glass crucible and the crystal surface. In this case the tips of the crucibles were sealed with alumina slip mixed with sodium silicate, because the carbon coating was oxidized in the process of fusing the crucible tips by heating.

3. Procedures

A vertical type of vacuum furnace was used, the temperature gradient of which was 20°C/cm at 419°C as shown in Fig. 2. The glass crucibles filled with zinc were suspended in the furnace in which the pressure was $10^{-3} \sim 10^{-4}$ mm of Hg and lowered at a constant rate by a synchronous motor. The growth rates adopted were 0.3, 1.7 and 6.7 mm/min.

The glass crucibles were immersed in hydrofluoric acid after growing the crystals and removed from the specimens without introducing any mechanical

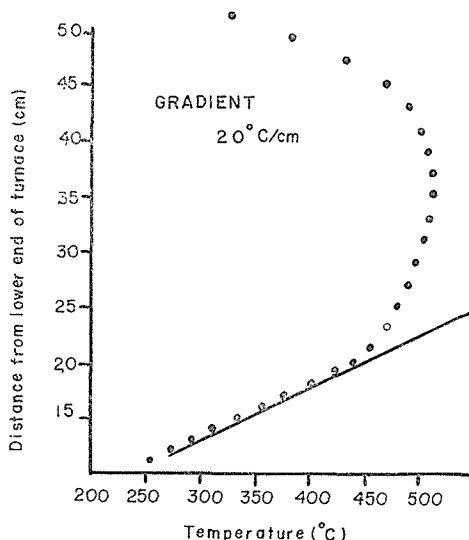


Fig. 2. Temperature *vs* distance along inside of furnace.

* Henceforth, the word "selection" means the method of type (b) of Fig. 1.

stress. At the same time the specimens were etched by this solution. In this case, if the surfaces were dirty, the specimens were chemically polished with nitric acid and etched by dilute HCl solution. The orientations of single crystals were determined by the Laue-Back Reflection method. The single crystals were chemically cut by an acid saw and polished by an acid polisher when flat surface of the crystals was required. For the observation of the cellular structure, about 15 sec-etching by dilute HCl was effective. This structure was also observed by electro-etching with 20% CrO₃ aqueous solution using small currents. In order to observe the substructures in the crystals (mainly striation), the Berg-Barrett X-ray diffraction method was used. The source of X-rays was a line focus of 0.2×15 mm² and the distance from focus to specimen was 40 cm. Therefore its resolving power was ~6μ and the sensitivity was 1 min. of arc. The crystals having two typical orientations of growth direction of $[\bar{1}100]$ and $[0001]$ were studied with respect to the observation of the striations and the cellular structures.

RESULTS

1. Preferred Orientations

Many specimens were produced by the method described above. The orientations of growth direction of about 60 crystals composed of less than three grains were studied, in these specimens. The lower part of glass crucibles for unseeded crystals was not exactly the same shape although they were glass tubes 5 mm in diameter, tapering off to a tip in a distance of approximately 1.5 cm.

The orientations of growth direction of unseeded crystals of 99.9% zinc grown at the rate of 1.7 mm/min by using the crucibles of types (a) and (b) are shown in Fig. 3. Though a considerable number of specimens of 99.9% zinc were polycrystals at the growth rate of 1.7 mm/min, the orientation of each grain of single or bi-crystals in the specimens was plotted in Fig. 3. At the growth rate of 6.7 mm/min neither single nor bi-crystals were obtained.

Fig. 4 shows the orientations of growth direction of the crystals after the selection of some specimens shown in Fig. 3 by using the crucibles of type (b). If a specimen of Fig. 3 is a bi-crystal, the orientation of that crystal making up

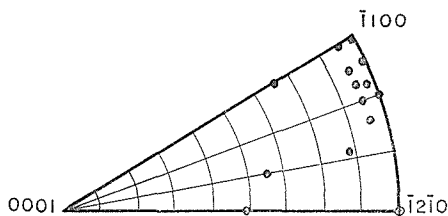


Fig. 3. Orientations of growth direction of unseeded crystals of 99.9% Zn grown at the rate of 1.7 mm/min by using the crucibles of types (a) and (b).

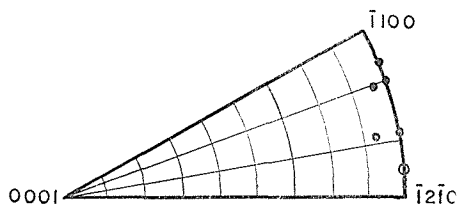


Fig. 4. Orientations of growth direction of the crystals after the selection of some specimens shown in Fig. 3 by using the crucibles of type (b).

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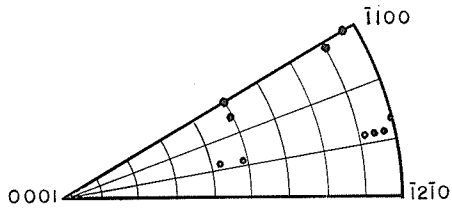


Fig. 5. Orientations of growth direction of unseeded crystals of 99.9% Zn grown at the rate of 0.3 mm/min by using the crucibles of type (a).

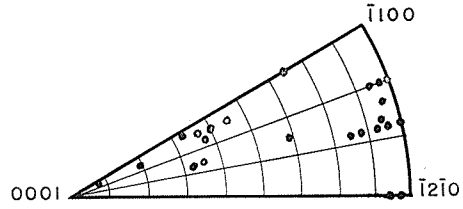


Fig. 6. Orientations of growth direction of unseeded crystals of 99.999% Zn grown at the rate of 1.7 mm/min by using the crucibles of type (e).

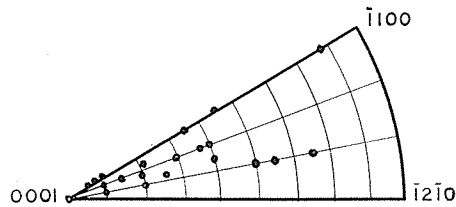


Fig. 7. Orientations of growth direction of unseeded crystals of 99.999% Zn grown at the rate of 1.7 mm/min by using the crucibles of type (d).

the larger part will be probably shown by this method. The orientations making $30^\circ \sim 40^\circ$ with the basal plane in Fig. 3 are not seen in Fig. 4. These two figures seem to indicate that the orientations of growth direction parallel to the basal plane are predominant. This predominancy is clearly shown by the experimental result that no crystal of the $[0001]$ orientation was obtained even by growing from the seed crystal of high purity zinc of that orientation. In addition, $[\bar{1}100]$ may be more predominant than $[\bar{1}2\bar{1}0]$, but this predominancy is not so remarkable. In these figures the specimens indicated with open circles were especially grown by initially setting the tip of the crucible at the maximum point of the furnace temperature.

Fig. 5 shows the orientations of growth direction of unseeded crystals of 99.9% zinc grown at the rate of 0.3 mm/min by using the crucibles of type (a). One of the preferred orientations of growth direction is similar to those of Fig. 3 and Fig. 4, while the predominancy of the $[\bar{1}100]$ orientation is weak compared with that of Fig. 3. Another preferred orientation is that making an angle of $40^\circ \sim 50^\circ$ with the basal plane.

Fig. 6 shows the orientations of growth direction of unseeded crystals of 99.999% zinc grown at the rate of 1.7 mm/min by using the crucibles of type (e) in Fig. 1. In this circumstance almost all specimens were single crystals. One of the preferred orientations of growth direction is near the middle between $[\bar{1}100]$ and $[\bar{1}2\bar{1}0]$ and another is the orientations at about 50° from the basal plane.

Fig. 7 shows the orientations of growth direction of unseeded crystals of 99.999% zinc grown at the rate of 1.7 mm/min by using the crucibles of type (d) in Fig. 1. The greater part of crystals grown with these conditions were composed of 2~3 grains. The orientations near $[0001]$ are predominant in this case.

This result suggests the predominancy of the formation of the nuclei, (0001) planes of which are parallel to the crucible flat end cooled by the copper plate. All low purity zinc specimens grown at these conditions became polycrystals.

2. Cellular Structure

Cellular structures were observed by an optical microscope after 15 sec-etching by dil. -HCl. As the surfaces of the etched crystals are oxidized in air, the observation must be made immediately after etching. Impurity-subboundaries were observed both on the transversal section and on the side surface. Impurity

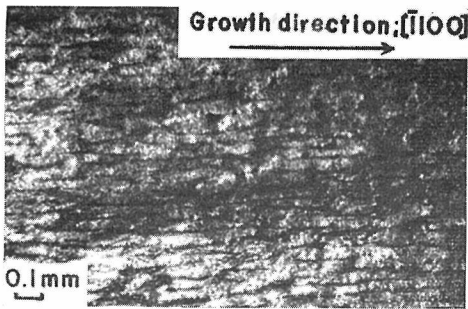


Fig. 8. Corrugations of a 99.9% Zn single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min.

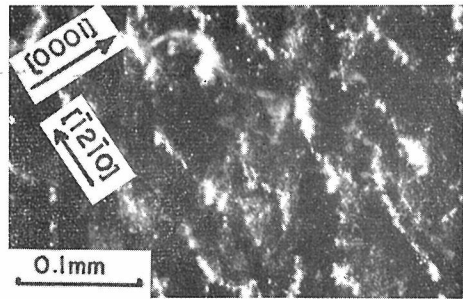


Fig. 9. Cellular structure of a 99.9% Zn single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min.

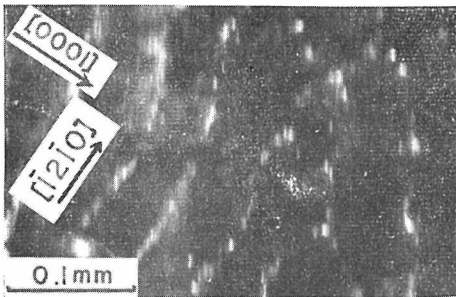


Fig. 10. Out of-focused figure of Fig. 9.

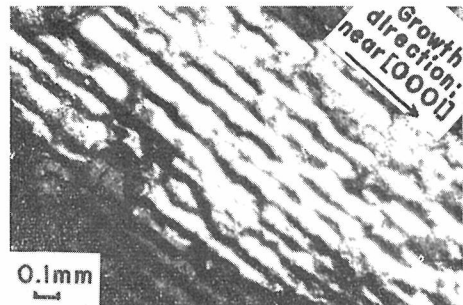


Fig. 11. Corrugations of a 99.9% Zn single crystal grown in the direction nearly parallel to $[0001]$ at the rate of 1.7 mm/min.

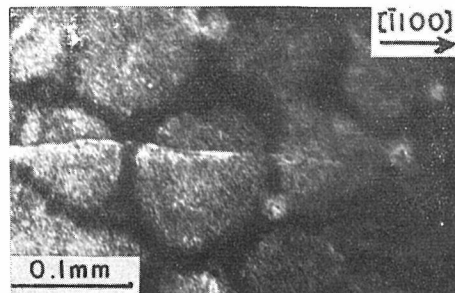


Fig. 12. Cellular structure of a 99.9% Zn single crystal grown in the direction nearly parallel to $[0001]$ at the rate of 1.7 mm/min.

substructure of the section is called cell structure, and that of the side, corrugation.

Fig. 8 shows the corrugations of the side surface of a 99.9% zinc crystal grown parallel to $[\bar{1}100]$ at the rate of 1.7 mm/min. The corrugations of 0.05mm in width are seen parallel to the growth direction. On the transversal section of this crystal the cellular structure corresponding to the section of the corrugation is observed as shown in Fig. 9. Fig. 10 shows the photograph taken by bringing Fig. 9 slightly out of focus. The elongated cells^{13,14,15,16)} which extend to $[\bar{1}2\bar{1}0]$ along the basal plane are clearly seen in Fig. 10. This means that impurities are likely to segregate along the basal plane.

Fig. 11 and Fig. 12 show the corrugation structure and the cellular one, respectively in a 99.9% zinc small crystal in which the growth direction is nearly parallel to $[0001]$ (this was formed occasionally in the specimen grown at the rate of 1.7 mm/min). In this case, the corrugations are parallel to the growth direction and the cells are hexagonal, indicating the existence of bundles of hexagonal rods whose axes are parallel to the growth direction. The width of the cell or corrugation is 0.1 mm, that is, about twice that of the crystal of $[\bar{1}100]$ growth direction. Impurity substructures are also observed in single crystals of 99.9% zinc grown at the rate of 0.3 mm/min but the width of the cell (or corrugation) becomes larger. In crystals of 99.999% purity no impurity substructure was observed even at the growth rate of 1.7 mm/min. From these experimental results it is found that the shape and size of impurity substructure are dependent on the orientation of growth direction.

3. Striation

The misorientation which arises from an arrangement of dislocations (striation) was observed by Berg-Barrett X-ray diffraction micrography. Side surfaces of rod crystals were examined but the transversal sections were not observed. The interior parts of some crystals were also investigated after polishing with nitric acid.

Fig. 13 shows an X-ray diffraction photograph from the $(12\bar{3}5)$ reflection plane of a 99.9% zinc single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are removed by the selection. The growth direction is from the left to the right in the figure. The crack (indicated by an arrow) was produced accidentally in electro-polishing and not in the growth. This photograph was taken from the surface after removal of the outer layer of 2 mm in thickness. The white and black lines correspond to the overlapped subboundaries and the separated ones respectively in the sense of misorientation. Since the crystal shown in Fig. 13 is of low purity and was grown fairly rapidly, many subboundaries of small misorientations are seen.

Fig. 14 shows an X-ray diffraction photograph from the $(10\bar{1}4)$ reflection plane of a 99.999% zinc single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are not removed. In this photograph the left image is due to the diffraction of $\text{Cu } K\alpha_1$ and the right one is due to that of $\text{Cu } K\alpha_2$ because the X-ray source is sharply focused by the use of a

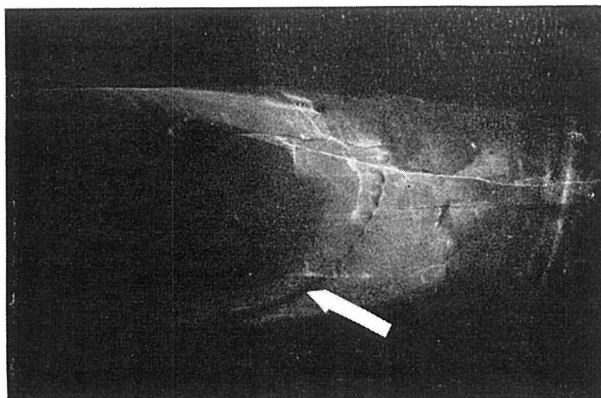


Fig. 13. Berg-Barrett photograph of the side of a 99.9% Zn single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are removed by the selection. The diffraction plane is $(12\bar{3}5)$. $\times 7$.



Fig. 14. Berg-Barrett photograph of the side of a 99.999% Zn single crystal grown in $[1100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are not removed. The diffraction plane is $(10\bar{1}4)$. $\times 7$,

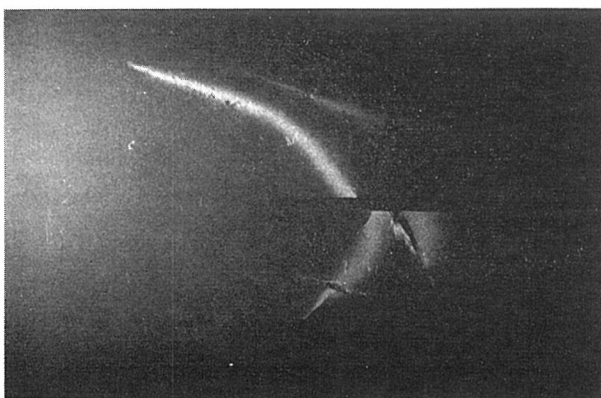


Fig. 15. Berg-Barrett photograph of the side of the slightly interior part of a 99.999% Zn single crystal grown in $[\bar{1}100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are not removed. The diffraction plane is $(10\bar{1}4)$. $\times 7$.

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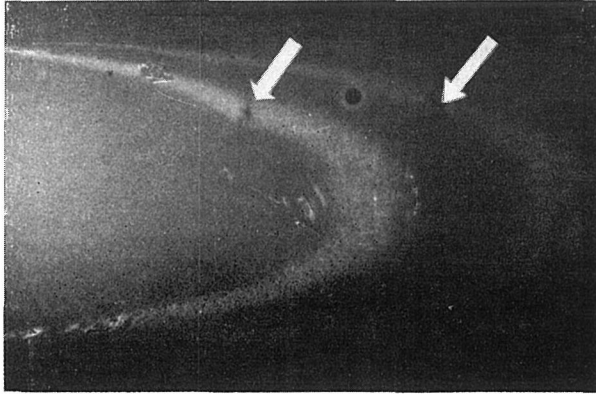


Fig. 16. Berg-Barrett photograph of the side of a 99.999% Zn single crystal grown in $[1100]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are removed by the selection. The diffraction plane is $(10\bar{1}4)$. $\times 7$.

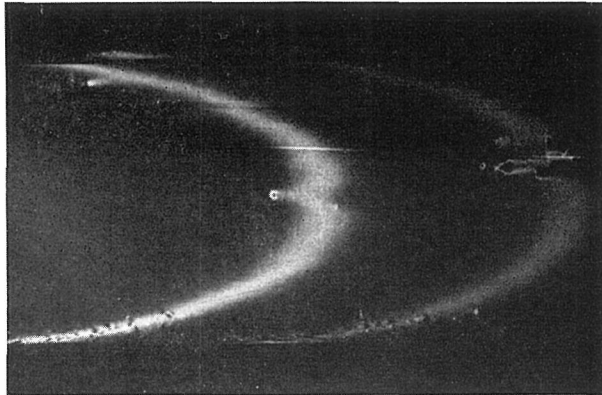


Fig. 17. Berg-Barrett photograph of the side of a 99.999% Zn single crystal grown in the direction nearly parallel to $[0001]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are not removed. The diffraction plane is $(20\bar{2}1)$. $\times 7$.

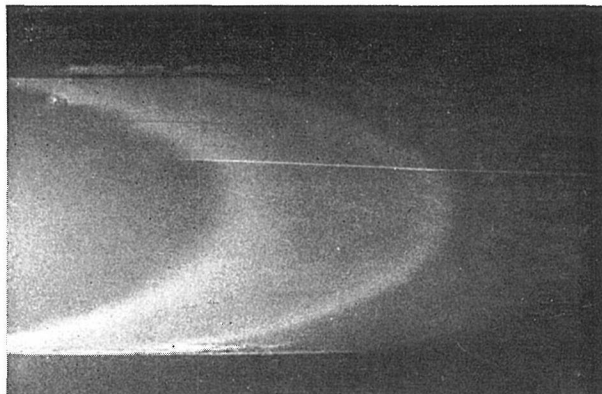


Fig. 18. Berg-Barrett photograph taken from the same crystal as shown in Fig. 17 by using the X-ray source of a non-biased Wherelt tube. The diffraction plane is $(20\bar{2}1)$. $\times 7$.

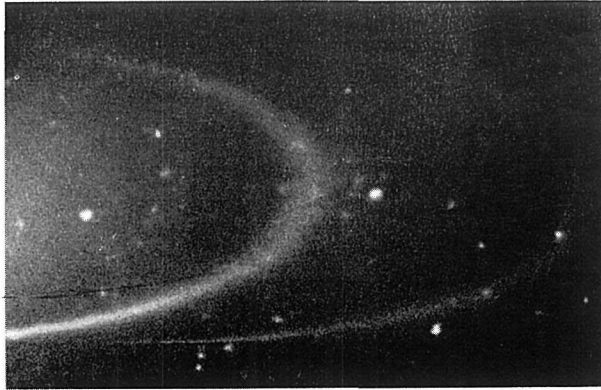


Fig. 19. Berg-Barrett photograph of the side of a 99.999% Zn single crystal grown in $[\bar{1}100]$ at the rate of 0.3 mm/min, in which subboundaries developed from the seed are removed by the selection. The diffraction plane is $(10\bar{1}4)$. $\times 7$.

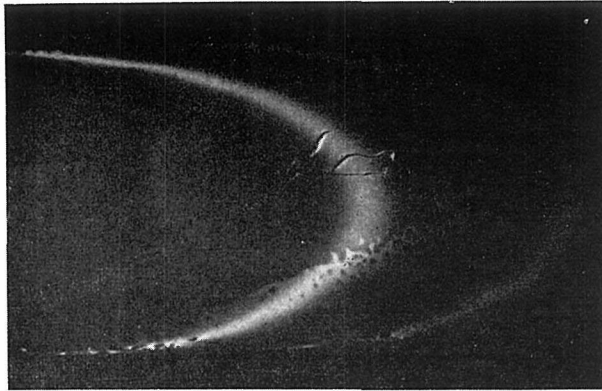


Fig. 20. Berg-Barrett photograph of the side of a 99.999% Zn single crystal grown in the direction nearly parallel to $[0001]$, in which subboundaries developed from the seed are removed by the selection. The diffraction plane is $(20\bar{2}1)$. $\times 7$.



Fig. 21. A easily-deformed-crystal of high pure zinc grown in the direction nearly parallel to $[0001]$ at the rate of 0.3 mm/min. The slip plane is nearly perpendicular to the specimen axis.

biased Whenelt tube. Since this crystal was not selected and may have contained subboundaries developed from the seed, a considerable number of subboundaries are seen in this figure. At the center of the figure there is a very wide black line having a misorientation of about 20 min. and about 90 min. of arc around the horizontal and vertical axes, respectively. After polishing the surface, the photograph from a slightly interior part of this crystal is shown in Fig. 15, where the small misoriented subboundaries seen in Fig. 14 are not observed but where the large misorientated subboundary at the center still remains and deviates slightly from the specimen axis. A comparison of these two figures with respect to the number of subboundaries suggests the effect of the stress induced by the adhesion between the crystal surface and the glass crucible.

Fig. 16 shows an X-ray diffraction photograph from the upper part of the crystal after the selection of the specimen shown in Fig. 15. The large misoriented subboundary seen at the center in Figs. 14 and 15 is not seen in this figure. The crystal is fairly perfect in comparison with that of Fig. 14 but the strain of the crystal is observed in the upper part of the photograph (indicated by arrows in the figure).

Fig. 17 shows an X-ray diffraction photograph from the $(20\bar{2}1)$ plane of a 99.999% zinc single crystal grown in the direction nearly parallel to $[0001]$ at the rate of 1.7 mm/min, in which subboundaries developed from the seed are not removed.

Fig. 18 shows the photograph taken from the same crystal as shown in Fig. 17 by using the X-ray source of a non-biased Whenelt tube. Striations parallel to the specimen axis were observed.

Fig. 19 shows an X-ray diffraction photograph from the $(10\bar{1}4)$ reflection plane of a 99.999% zinc single crystal grown in $[\bar{1}100]$ at the rate of 0.3mm/min, in which subboundaries developed from the seed are removed by the selection. No subboundary is seen and the reflection image is sharper in comparison with that in Fig. 16.

Fig. 20 shows an X-ray diffraction photograph from the $(20\bar{2}1)$ reflection plane of a 99.999% zinc single crystal grown in the direction nearly parallel to $[0001]$ at the rate of 0.3mm/min, in which subboundaries developed from the seed are removed by the selection. The dirty region of the lower part is the result of a mistake in the fixing process of the photograph. The cracks at the center were made by accident. The sharp diffraction image indicates that the crystal is fairly perfect. Since the other part of the crystal showed the same pattern, it is concluded that the crystal having no subboundary (larger than ~ 1 min) can be made easily by using the crucibles of type (e).

From these experimental results any difference in perfection between the crystals of the growth direction of $[0001]$ and those of $[\bar{1}100]$ could not be found. To investigate this difference individual dislocations must be observed. It can be said, at least, that 99.999% zinc single crystals of the growth direction of $[0001]$ are easily deformed as shown in Fig. 21, because the slip plane (0001) lies perpendicular to the specimen axis. From the softness of the crystals used in these experiments, dislocation densities of these crystals seem to be fairly low.

DISCUSSION

1. Preferred Orientation and Cell Structure

The reasons why the cellular structure has such shapes and sizes depending on the orientations of growth direction, and why a crystal grown from the melt has such preferred orientations of growth direction depending on the degree of purity of the metal, growth rates and shapes of the crucible bottom as mentioned in the experimental results, are explained as follows. In the platelet growth of the planar interface which is attained only when high purity metal is grown very slowly, one of the planes of close packing becomes close to the plane of the interface as pointed out by Tiller⁹⁾. In the case of zinc this results in the preferred growth orientation of $[0001]$ as observed by Hellawell and Herbert⁹⁾. In the cellular interface there is no planar interface between solid and liquid but a series of small projections convex to the liquid are formed over the interface. It can be said, however, that the growth in cells is explained by the platelet growth mechanism, since the traces of the platelet growth are seen in each cell as shown by Tiller¹¹⁾. Interface morphologies of the cells of unseeded crystals of 99.9% zinc grown at 1.7 mm/min will be discussed with reference to the schematic representation in Fig. 22.

In this case planes of (0001) and $(\bar{1}100)$ are considered as the growth planes. When the growth direction is near $[\bar{1}100]$, the platelet growth advances with the platelet planes; $(\bar{1}100)$ nearly parallel to the interface and (0001) nearly perpendicular to the interface as shown in Fig. 22 (a') which is developed from Fig. 22 (a) by the lateral sweeping of impurities because the (0001) plane completes a flat surface rapidly. Hence, steep platelet planes relative to the average plane of the interface are formed. On the other hand, when the growth direction is $[hkl]$, shallow platelet planes relative to the average plane of the interface com-

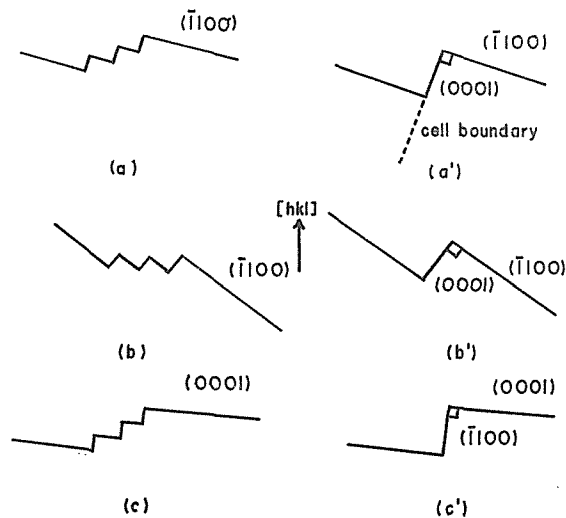


Fig. 22. Interface morphologies.

pared with Fig. 22 (a') are formed as shown in Fig. 22 (b') which is developed from Fig. 22 (b). The steeper the platelet planes are relative to the average plane of the interface, the more solute they can trap in the cell boundaries. Thus steep platelets lower the solute concentration ahead of the interface to a greater extent than do those which make only small angles. Therefore, the freezing temperature of the melt just ahead of cells with steep platelets is higher than that just ahead of cells whose platelets make a small angle with the plane of the interface and hence the former will be able to grow ahead of the latter as pointed out by Tiller¹¹. Then $[\bar{1}100]$ becomes a preferred orientation of growth direction in the cellular interface. When the (0001) plane lies close to the interface as shown in Fig. 22 (c), which developed into Fig. 22 (c'), the crystal in the $[0001]$ growth direction will be suppressed by the crystal of another growth direction, e. g. $[\bar{1}100]$, because the growth rate of the most close-packed plane, (0001), may be slower by nature, and in addition the impurities swept out by the fast lateral growth of the $(\bar{1}100)$ plane will delay the growth of the (0001) plane.

Shapes and sizes of the cell can be explained by the same figure. The platelet planes of Fig. 22 (a') are very steep relative to the average plane of the interface so that they trap many impurities. Hence long steep cell boundaries along the basal plane will be formed as shown in Fig. 10. In this case (the growth direction of $[\bar{1}100]$), the conjugate $\{\bar{1}100\}$ planes other than the $(\bar{1}100)$ plane which lies close to the interface must become the platelet planes paired with the latter at the cell boundaries perpendicular to those of Fig. 22 (a'). Since these conjugate platelet planes, making an angle of 120° with each other, are shallow relative to the average plane of the interface, the short and faint cell boundaries perpendicular to the (0001) plane are formed as shown in Fig. 10. The crystal of the $[0001]$ growth direction has the hexagonal cell which seems to be produced by the (0001) and six $\{\bar{1}100\}$ platelet growth planes.

When the growth direction is $[0001]$, impurities causing large supercooling ahead of the interface diffuse faster laterally than in the case of other growth directions because of the rapid platelet growth of the $(\bar{1}100)$ plane. The (0001) platelet plane covers a large area and hence the cell of the crystal with (0001) growth direction becomes larger. Then the cell size of the (0001) plane is larger than that of the $(\bar{1}100)$ plane, which is consistent with the result of lead observed by Rosenberg and Tiller⁸.

With decreasing growth rate and impurity content of the metal as shown in Fig. 5 and Fig. 6, such a competition among grains as mentioned above seems to decrease and the nucleation seems to determine mainly the growth orientation, though it was observed that the crystal of the growth direction parallel to the basal plane still survived among grains having the degree of purity and the growth rate described in these figures. In the case of the heterogeneous nucleation which seems to occur in this experiment, it is considered that the (0001) plane of the nucleus is likely to adhere to the wall of the tip of the glass crucible which is almost parallel to the growth direction, because it seems to be most stable in energy. This nucleation gives the preferred orientations of growth

direction parallel to the basal plane. The orientations of growth direction making an angle of $40^{\circ}\sim 50^{\circ}$ with the basal plane which are observed in considerable numbers in Fig. 5 and Fig. 6 may be caused by the irregularity of the tip shape of the glass crucible, but the true reason is really not known yet. If the nucleation mechanism mentioned above is correct, the orientation of growth direction of the crystals grown by using the crucible with the flat bottom at which the nucleation starts, should be the $[0001]$ direction. This conclusion is confirmed by the result shown in Fig. 7.

2. Striation and Perfection of Crystals

From the experimental results described above concerning the striation, the higher the purity of metal and the lower the growth rate, the more perfect the crystal becomes. The fact that the width of striations decreases with increasing growth rate and solute concentration suggests that the diffusion time of dislocations is connected with the formation of striations. Maeda¹²⁾ used the crucible of type (b) for removing the misoriented subboundaries in the growth of single crystals of tin and emphasized that this was a useful method for this purpose. At the same time he studied the effect of stress on the origin of misoriented substructures by using the crucibles of type (e) which were devised by him, and concluded that the mechanical stress caused by adhesion of growing crystals to the crucible wall had been an important factor in the formation of the striation. Thus, the results of the present experiments seems to support his conclusions for tin. In fact, the observed result that all glass crucibles are cracked when pure metal is sucked up without using a coating of carbon, and that no subboundary is found in the crystals grown by using the crucible of Fig. 1 (e), indicates how violent the stress is which is induced between crystal surface and glass crucible. The fact that more striations are observed at the surfaces of crystals than in their interiors may support this conclusion. This is consistent with the result of Young and Savage¹⁾ that Cu crystals of low dislocation densities with no subboundaries were obtained when the surface of a crucible was made smooth.

The difference in perfection between the crystals of $[0001]$ growth direction and $[1100]$ could not be found by using the Berg-Barrett X-ray diffraction method, although Young *et al.*¹⁾ have found such difference for copper.

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