Studies on Line Structures in Tin Single Crystals. (II)

Hideo TAKAKI, Masashige KOYAMA and Hidekiyo FUJIHIRA*

(H.Takaki Laboratory)

Received July 30, 1955

In this study, a microscopic observation was performed with single crystals of tin whose [100] direction was parallel to the direction of growth. Further examination was carried out with respect to the specimens grown in the directions which inclined from [110] to [100] direction, fixing the [001] direction, at the angles of 10, 15, 20, 30 and 45 degrees respectively.

A "partial dendrite structure" in which the secondary skeleton developed on the side of the growth direction alone, was observed on the (001) plane of specimens, whose [100] directions were parallel to the direction of the temperature gradient, probably owing to the low purity. Two kinds of cell structure (one was large and the other smaller) were also observed on both the top free surface and the sectional one of specimens having the above-mentioned structure. This structure is inferred to be an intermediate structure, when the corrugation changes to the dendrite.

I. INTRODUCTION

A relation between one of the line structures, that is, the corrugation structure and the lowering speed has already been reported in the first report[1] with respect to tin single crystals grown in the [110] direction (direction of easy growth in tin) by the Bridgman method.

In this report, an experimental result will be described with respect to the case, in which the direction of crystal growth (direction of specimen axis) was changed in various angles from the [110] to the [100] direction.

II. EXPERIMENTAL PROCEDURES

The purity of tin was 99.87 percent as in the first report,[1] but a different material was used since the same material as in the first report[1] could not be obtained.

The electric furnace and the methods for growing crystals and for taking out specimens from the glass moulds were all similar to those in the first report.[1]

Rod crystals, oriented in the desired crystallographic directions, were prepared using the technique described by Takaki et al.[2] In this case, tin single crystals whose directions of rod axes were parallel to the [110] direction, were used as seeds, and crystals were grown varying the direction of rod axis at 10, 15, 20, 30 and 45 degrees from the [110] to the [100] direction respectively by making the [001] direction a rotation axis.

* 高木 秀夫, 小山 昌重, 藤平 秀清

The corrugation structure and others were observed on the free surface and the surface etched electrolytically under the same conditions as in the first report.[1]

III. EXPERIMENTAL RESULTS

A. Results of Observations on the Surfaces of Rod Specimens Grown in the [100] Direction

1. Result of observation in unetched state.

Grooves corresponding to the boundaries of the corrugations in the first report,[1] were observed only on the (001) plane in the side surface near the top of specimens, and the direction of the grooves was near the <110> direction. The microstructure on the (001) plane of the specimen grown at the lowering speed of 1 mm/min is given in Fig. 1, in which the shorter grooves nearly normal to the above-mentioned grooves are arranged at a narrower distance. This new structure, not observed in the first report,[1] was also observed even on the specimen grown at the lowest speed possible in the apparatus used (0.7 mm/min). This new structure in which the side arms develop on the side of the growth direction alone, is termed

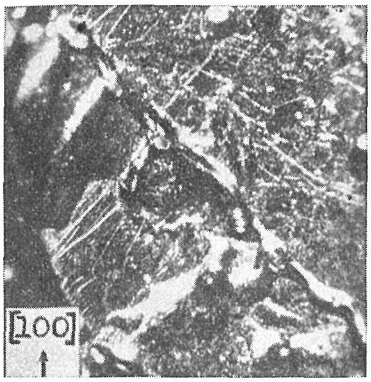


Fig. 1. Microstructure of side free surface of the specimen grown in the [100] direction, (001). Lowering speed, 1 mm/min.

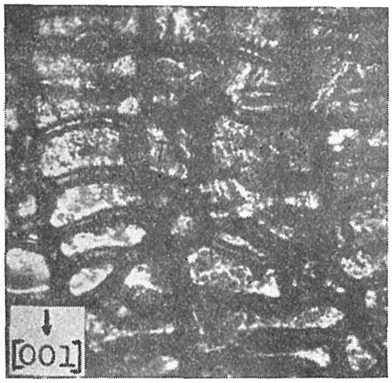


Fig. 2. Microstructure of top free surface of the specimen shown in Fig. 1, (100). Lowering speed, 1mm/min.

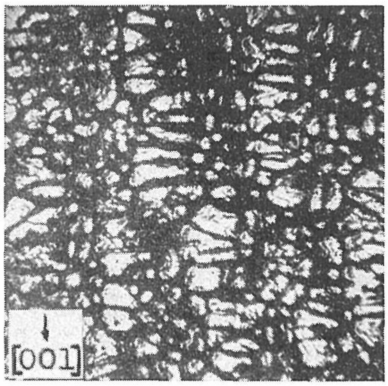
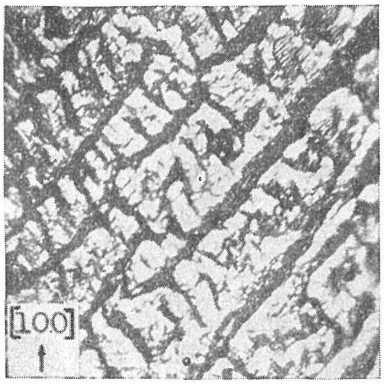


Fig. 3. Microstructure of top free surface, (100). Lowering speed, 3 mm/min.

the "partial dendrite structure" by the authors.

Two kinds of complex cell structure (one is large and the other smaller) are observed in Figs. 2 and 3, showing the top free surfaces of the specimens grown at the speeds of 1 and 3 mm/min respectively. The larger cells and the smaller cells in these figures show the transversal appearances of the primary skeletons of partial dendrite crystals and of the top parts of the side arms of the primary skeletons respectively, obliquely cut by the top surface of the specimens.

2. Result of observation in the state etched electrolytically.



×50

Fig. 4. Microstructure of side surface, (001). Lowering speed, 5 mm/min.

×50

Fig. 5. Microstructure of side surface, (001). showing the cross partial dendrite structure. Lowering speed, 14 mm/min.

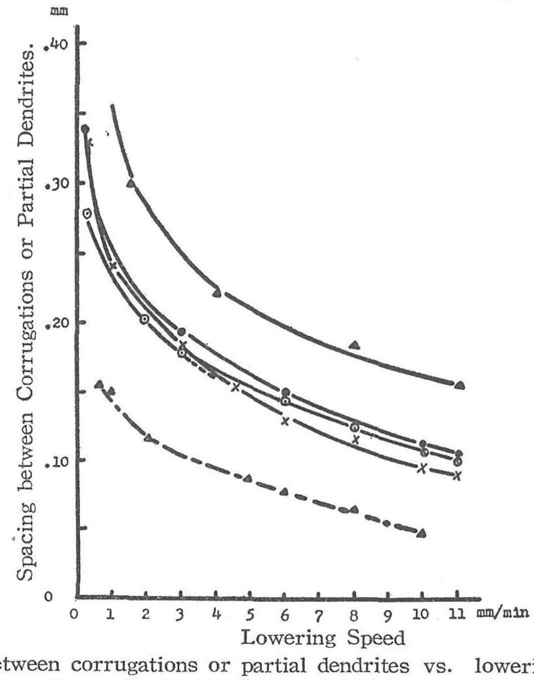


Fig. 6. Spacing between corrugations or partial dendrites vs. lowering speed. ▲, Direction of growth is parallel to [100]; ●, inclines at 30° from [110] to [100]; ⊙, inclines at 20° from [110] to [100]; ×, inclines at 10° from [110] to [100]. Chain line corresponds to side arms.

Figs. 4 and 5 show the microstructures of the (001) planes of the specimens grown at the speeds of 5 and 14 mm/min respectively, in which the same partial dendrite structures as in 1 are observed. As the lowering speeds increased, the spacings of the partial dendrite crystals corresponding to the spacings of corrugations and also those of side arms decreased (Fig. 6). Further, the directions of

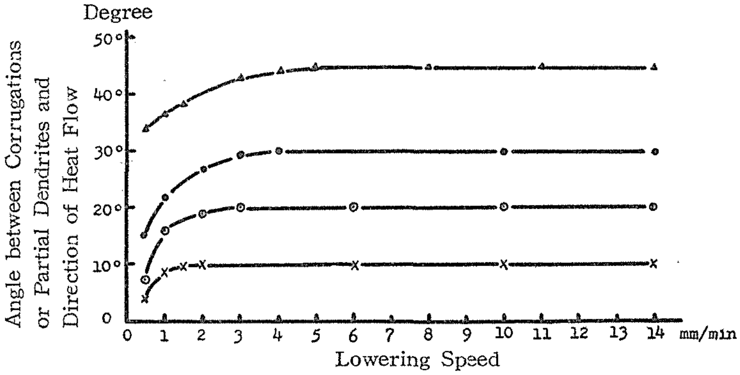


Fig. 7. Direction of corrugations or partial dendrites vs. lowering speed. ▲, Direction of growth is parallel to [100]; ●, inclines at 30° from [110] to [100]; ⊙, inclines at 20°; ×, inclines at 10°.

growth of both the primary skeleton and the side arms of partial dendrite crystals were always parallel to the <110> direction at a higher speed than 5 mm/min, while at a lower speed the directions gradually inclined from the <110> direction to that of the specimen axis (Fig. 7). These tendencies are qualitatively similar to the relation between the corrugation structure and the lowering speed in the first report.[1]

As the photograph in Fig. 4 was taken on the side plane (001) of the rod specimen, only a part of the (001) plane is obviously shown. If a surface perfectly parallel to the (001) plane is obtained by cutting the specimen as in the surface A

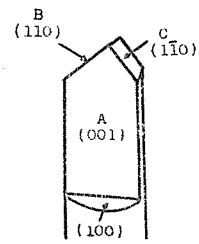
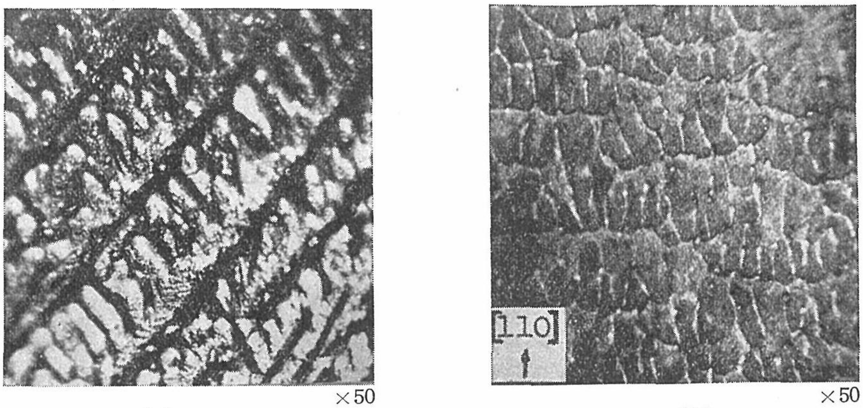


Fig. 8. Model picture.

in Fig. 8, a more detailed appearance of growth of the partial dendrite structure may be made clear (Fig. 9a). When the surface B, cut in parallel to the primary skeleton of each partial dendrite crystal and at the same time perpendicularly to the surface A in Fig. 8, was etched electrolytically as well as the surface C, cut perpendicularly to the surfaces A and B, then a cell structure corresponding to the



×50 (a) ×50 (b)

Fig. 9. Microstructures of the sectional surfaces of the specimen shown in Fig. 4.
(a) (001) plane etched electrolytically.
(b) $(1\bar{1}0)$ plane etched electrolytically.

transversal surface of each side arm of partial dendrite crystals was revealed on the surface B, while another cell structure corresponding to the transversal surface of each partial dendrite crystal was observed on the surface C (Fig. 9b shows the result on the surface C). That is, it may be found that single crystals are made of assembles of partial dendrite crystals, whose transversal surfaces are shorter in the $\langle 001 \rangle$ direction and longer in the $\langle 110 \rangle$ direction and also whose side arms are parallel to the $\langle 110 \rangle$ direction.

Fig. 5 shows two partial dendrite structures developing in the [110] and $[1\bar{1}0]$ direction respectively and this complex structure is termed the "cross partial dendrite structure" by the authors. Each direction of the cross partial dendrite structure was alternately varied at any interval and the side arms of each partial dendrite crystal always developed only in the direction of crystal growth (inverse direction to the temperature gradient).

Stray crystals developed from a higher speed than 15 mm/min. The partial dendrite structure was observed only on the (001) plane and on some planes nearer to this, whereas on the $(0\bar{1}1)$ plane a cell structure began to appear, and a complex cell structure was observed on the $(0\bar{1}0)$ plane.

Two kinds of cell structure (one was large and the other smaller) were observed by etching electrolytically the transversal surface of specimens, similarly to those observed on the top free surface of specimens in 1, and it was found that these sizes decreased as the lowering speed increased. A model picture is given in Fig. 10, showing the relation between the cross partial dendrite structure observed on the (001) plane and the cell structure on the (100) plane: Large cells always appear on the upper side of each boundary of the partial dendrite crystals corresponding to the corrugation boundary, and smaller ones correspond to the side arms of the partial dendrite crystals.

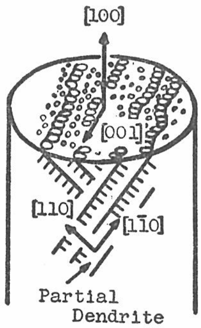


Fig. 10. Model picture of the cross partial dendrite and cell structures.

B. Results of Observations on the Surfaces of Rod Specimens Grown in the Directions Inclined from the [110] to the [100] Direction at the Angles of 10, 15, 20 and 30 Degrees Respectively

The following observations were chiefly carried out in the state etched electrolytically on the side surface of specimens and also in the top free state on the transversal surface of specimens. From the experimental results in the first report[1)] and in A in this report, the following facts were made clear : at the lowering speeds from 0.7 to 35 mm/min, as the lowering speed increased, in the former result, the corrugation structure, then the dendrite structure and lastly the stray crystal developed successively, while in the latter the partial dendrite structure firstly developed and was succeeded by the stray crystal.

Therefore, when grown in the various directions between the [110] and [100] directions at the above-mentioned region of lowering speeds, relations among various structures observed on the specimens should be made clear.

1. Result of observation on the side surface of specimens.

In the case inclined at 10°, the same corrugation structure was observed (Fig.

×50

Fig. 11. Microstructure of side surface of the specimen, (001), which was grown in the direction inclined at 10° from [110] to [100]. Lowering speed, 0.7 mm/min.

×50

Fig. 12. Microstructure of side surface of the specimen, (001), which was grown in the direction inclined at 20° from [110] to [100]. Lowering speed, 0.7 mm/min.

11*) as in the first report,[1] and as the lowering speed increased, the width of corrugations decreased, while the direction of corrugations inclined from the direction of specimen axis to the [110] direction (Figs. 6 and 7). At a higher speed, the perfect dendrite structure firstly developed and was succeeded by the stray crystals without generating the partial dendrite structure.

In the case inclined at 20°, the corrugation structure was observed at a lowering speed slower than 4 mm/min (Fig. 12*), while at one faster than 4 mm/min the partial dendrite structure was observed on the (001) plane of specimens and further the perfect dendrite structure developed over 8 mm/min. A transition appearance from the partial dendrite structure to the perfect dendrite structure is shown in Fig. 13,* that is, it was found that the direction of side arms inclined rather to the

×50

Fig. 13. Microstructure of side surface of the specimen which was grown in the direction inclined at 20° from [110] to [100]. Lowering speed, 14 mm/min.

inverse direction of the temperature gradient than to another direction of easy growth in tin, the [1$\bar{1}$0] direction. Figs. 6 and 7 show the relations of the spacings of corrugations and partial dendrite crystals and of the directions of these two structures with respect to the lowering speeds.**

In the case inclined at 30°, the partial dendrite structure was already observed on the (001) plane from 0.7 mm/min as in A. The relations of both the spacings between the partial dendrite crystals and those directions to the lowering speeds are given in Figs. 6 and 7 respectively. In this case, as the lowering speed increased, the perfect dendrite structure, in which the side arms developed on both sides of primary skeletons, developed before the generation of stray crystals.

* Lines crossing the photographs are the slip bands introduced through a careless treatment.

** The curve corresponding to the case inclined at 20° from the [110] direction in Fig. 6 steeply decreased in its inclination from 3 mm/min. This is due to the fact that the spacings become wider than those of corrugations owing to the generation of the partial dendrite structure from 4 mm/min. Accordingly, the spacings should become as in the dotted line, should crystals grow as the corrugation structure.

The results in the first report[1] and in A and B-1 in this study are summarized in Fig. 14, showing the speeds in which corrugation structures become parallel

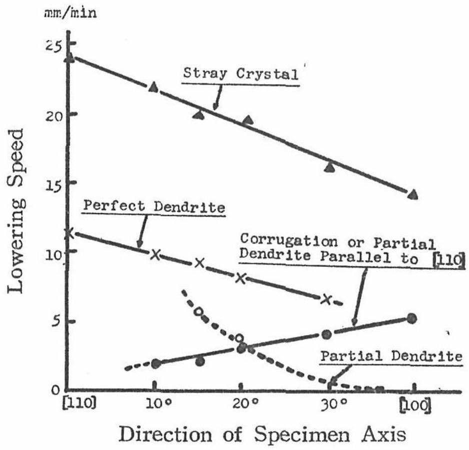
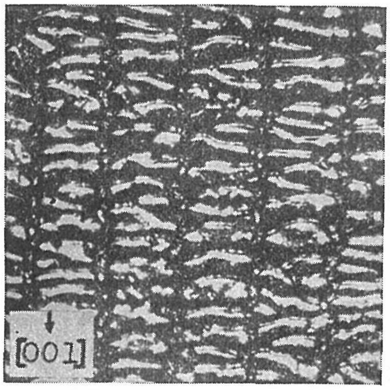


Fig. 14. Relation between direction of crystal growth and lowering speed.

to the [110] direction, and also the speeds at which partial dendrite structures, perfect dendrite structures and stray crystals begin to develop respectively. The manner in which corrugation structures, partial dendrite structures, perfect dendrite structures and stray crystals develop successively, as the lowering speed increases, can be understood from this figure very well.

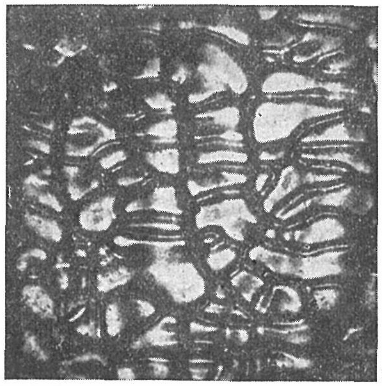
2. Result of observation on the top free surface of specimens.

An example of the microstructures of specimens inclined at 10° is given in Fig. 15, showing that the tortoise-shell pattern is not observed so clear as in the first report[1] but the deep grooves parallel to the [001] direction are vividly observed. The relation between the size of cells and the lowering speed was similar to the result in the first report.[1]



×50

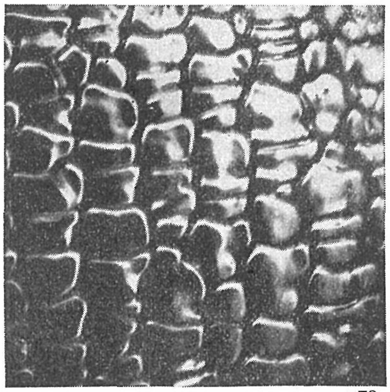
Fig. 15. Microstructure of top free surface of the specimen which was grown in the direction inclined at 10° from [110] to [100]. Lowering speed, 3 mm/min.



×50

Fig. 16. Microstructure of top free surface of the specimen which was grown in the direction inclined at 20° from [110] to [100]. Lowering speed, 1 mm/min.

In the case inclined at 20°, a cell structure as in Fig. 16 was observed on the top surfae of specimens grown at a speed within the region in which the corrugation structure developed. It was also found that the shape of cells was more complex than in the first report[1] and as the lowering speed increased the size of cells decreased, while on the specimen having the partial dendrite structure, the same ppattern as in Fig. 17, showing the result in the case inclined at 30°, was observed.



×50

Fig. 17. Microstructure of top free surface of the specimen which was grown in the direction inclined at 30° from [110] to [100]. Lowering speed, 3 mm/min.

Two kinds of cell structure are similarly observed in Fig. 17 as in Fig. 3, but the structure is simpler and the number of small cells smaller than in the latter.

In the case inclined at 30°, the cell pattern as shown in Fig. 17 was already observed from the lowering speed of 0.7 mm/min and the relation of the size of cells to the lowering speed was qualitatively similar to the result in A.

IV. DISCUSSION

The phenomenon in which when grown in the [100] direction, the partial dendrite structure develops, whose primary skeletons are near the [110] or the [$1\bar{1}0$] direction, may be explained as follows. It may be supposed that the actual plane of growth is (110) or ($1\bar{1}0$) plane. Further, it may be supposed that when the direction of primary skeletons is parallel to the [110] direction, the actual plane of growth is (110) plane and the growth on the ($1\bar{1}0$) plane is suppressed. In the course of growing, it may be considered that the solid tips are formed on each (110) plane and the impurities segregated to the liquid phase are diffused away around the solid tips and the growth on the ($1\bar{1}0$) plane is suppressed, as shown in Fig. 18. After the forming of supercooled places between the primary skeletons arranged side by side, at a suitable lowering speed, side tips would be formed on the ($1\bar{1}0$) plane of each primary skeleton and would become side arms. However, these side arms would not develop strongly owing to the developing of the nearest pri-

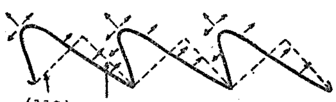


Fig. 18. Model picture.

mary skeleton. If the difference introduced by the effect of temperature in the diffusion rate of impurities in the [$\bar{1}$10] and [1$\bar{1}$0] direction on the (110) plane, as well as the difference in the advancing rate of steps in both directions mentioned above, is taken into consideration, the phenomenon that the direction of the partial dendrite structure slightly inclines from the [110] direction to that of the specimen axis (the [100] direction) may be explained. The phenomena that when the directions of growth are inclined at various angles from the [110] to the [100] direciton, the direction of the corrugation structure or the partial dendrite structure deviates from the [110] direction and further the grade of deviation is a function of lowering speeds, may also be explained similarly as before. In the theory mentioned above, it is a daring supposition that the actual plane of growth is considered to be the {110} plane alone, but this is not inconsistent with the discussion in the first report.[1]

It has been inferred that a feature of the dendrite growth is in the regularity in the crystallographic orientation.[3] However, it was found in this study that the direction of primary skeletons in the partial dendrite structure in single crystals grown at a slower speed, especially the directions of those side arms as well as of the side arms of perfect dendrite crystals (Fig. 13), deviated from the characteristic direction (the <110> direction in tin). This implies that the partial dendrite structure is a transition structure from the corrugation structure to the perfect dendrite structure. This abnormal phenomenon was also observed in another study carried out by the authors.[4]

The expense of this research has been chiefly defrayed by the Scientific Research Expenditure of the Ministry of Education.

REFERENCES

(1) H.Takaki, M.Koyama and H.Fujihira, This Bulletin, **33**, 177 (1955).
(2) H.Takaki et al., *J. Phys. Soc. Japan*, **9**, 204 (1954).
(3) L.Northcott and D.E.Thomas, *J. Inst. Metals*, **65**, 205 (1939).
(4) H.Takaki and M.Koyama, This Bulletin, **33**, 153 (1955).