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

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Line structures termed "corrugations" and "striations" by Chalmers et al. were studied microscopically with single crystals of tin (purity of 99.87 percent) grown from the melt, in which the [110] directions were parallel to the direction of the temperature gradient.

The same line structure as the corrugation was observed on the side surface of specimens, and the so-called cell structure was also observed on both the top free surface and the transversal surface etched. However, it is noticeable that the line structure observed on the $(1\bar{1}0)$ plane of specimens was irregular despite its regularity on the (001) plane, and further that a tortoise-shell pattern was observed on the (110) plane, probably owing to the low purity of specimens. It was also found that the striation boundaries always coincided with the corrugation boundaries on the (001) plane in single crystals.

I. INTRODUCTION

It has been well known that the substructures called "line structures" appear in single crystals of metals. In 1934, Buerger[1] observed a substructure with a difference of crystallographic orientation of about one degree in zinc single crystals grown from the melt and called it "lineage structure". Hence, studies on the line structures were carried out with various metals** by many investigators[2] and it was assumed by most of the investigators that the generation of line structures was attributable to the segregation of a slight quantity of impurities. However, Pond et al.[2] alone thought that the line structure would be observed even in perfectly pure metals. Recently, a systematic study in tin was carried out by Chalmers et al.[3] and each ridge of the corrugated structure observed on the top free surface of the specimen was called "corrugations" whose generation was attributable to the segregation of a slight quantity of impurities. The corrugation structure corresponds to the side surface of the bundle of columnar cells. As to the case where impurities were perfectly soluble in base metal, they[3] explained that the generation of the corrugation structure was attributable to the segregation and the diffusion of impurities in the liquid phase immediately before the beginning of freezing.

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** This structure has been observed in tin, lead, zinc, aluminium, nickel, silver, copper, indium, bismuth and antimony.

Besides the corrugation structure mentioned above, Chalmers et al. reported another line structure termed "striation"⁴⁾; e.g. as for tin, this structure reveals itself when etched in the mixed solution of ferric chloride and hydrochloric acid. They have explained anyhow that the generation of the striation structure would be attributed to a special arrangement of edge dislocations originating in the vacancy disk. It seems that some of the investigators mentioned above have observed the corrugation structure and other investigators the striation structure as the line structure. The relation between the corrugation and striation structures has not yet been completely clarified.

The authors have already reported that the line structure (corrugation) is observed in tin single crystals grown from the melt by the Bridgman method and that the crystallographic orientation and the spacing of corrugations greatly depend on the lowering speed and the purity of specimens.⁵⁾ In order to perform more detailed studies, a microscopic observation was carried out, in this investigation, with the specimens whose [110] directions were parallel to the direction of crystal growth (direction of specimen axis). A relation between the corrugation and striation structures was also examined.

II. EXPERIMENTAL PROCEDURES

The purity of tin was 99.87 percent. The slender tip of glass tube (inner diameter of 5 mm) was pushed into the crucible holding the molten tin and the molten tin was frozen after being sucked into the glass mould. After a part of the polycrystal tin was replaced with a seed of tin single crystal crystallographically analysed at a part of the slender tip, the glass mould was sealed at this end. The another end of the glass mould was also sealed in vacuum of 10^{-2} mm Hg in order to prevent the oxidation of specimens in the course of growing and to facilitate an observation on the unetched free surface of specimens. An elliptic glass tube shown in Fig. 1 was used for the investigation of the relation between the corrugation and striation structures i. e., the specimen was grown from a seed which was set so that the direction of specimen axis was parallel to the [110] direction and the shorter diameter of the elliptic glass tube was normal to the (001) plane.* The glass mould holding polycrystal tin was lowered at a constant speed after being hung on a fine molybdenium wire in the nichrom electric furnace held at the tem-

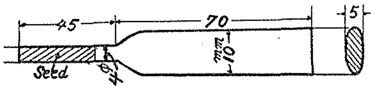

Fig. 1. Glass tube mould of special design for investigation of the striation.

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* The striation structure is easily revealed on the (001) plane.

perature which was about 70°C higher than the melting point of tin. In this case, the temperature gradient at 232°C was 13°C/cm. As for the observation in etched state, glass moulds were immersed into hydrofluoric acid for taking out tin crystals, as in the previous investigation⁵⁾*. In unetched state, however, specimens were taken out by breaking glass moulds carefully.

The following methods were adopted for the observation of specimens.

A. Observations of Corrugation Structures

1. Observation in unetched state.

An observation in unetched free state was carried out at the upper part of rod crystals where a space was always formed between the inner wall of glass mould and the specimen.

2. Observation in the state etched in 50 percent nitric acid.

The corrugation structure was examined by etching in 50 percent nitric acid, because the structure was difficult to observe in unetch free state at the part where a space was not formed between the inner wall of glass mould and the specimen.

B. Simulaneous Observation of Corrugation and Striation Structures

1. Surface observation.

The corrugation and striation structures were revealed by etching in nitric acid and in the mixed solution of ferric chloride and hydrochloric acid** after polishing electrolytically at the room temperature (about 15°C) under the conditions that the composition of the electrolyte was perchloric acid of 50 cc and glacial acetic acid of 80 cc and that the cathode was a cylindrical lead tube.

2. X-ray analysis.

Differences of crystallographic orientation in the corrugation structure and the striation structure, were X-ray analysed by using the pin hole of a thermometer graduated at 0.1°C for slit. A part of the specimen was polished electrolytically again, in which both structures were revealed by the method mentioned in B-1, and this part was used for the incident position of X-rays. The part not polished electrolytically was used for determining the incident position. The distance between the specimen and the plate was 50 mm.

III. EXPERIMENTAL RESULTS

A. Results of Observations Concerning the Corrugation Structure

1. Result of observation in unetched state.

The corrugation boundaries parallel to the specimen axis were observed on the

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* In this study, the range of lowering speed was from 0.7mm/min to 35mm/min.

** This mixed solution was used by Chalmers et al. for revealing the striation structure in tin, and its composition was 10 percent ferric chloride, 10 percent hydrochloric acid and 80 percent water.

side surface of specimens (Figs. 2, 3). The higher the lowering speed, the narrower became the spacing of corrugations and this tendency is qualitatively similar to the result of Chalmers et al. However, the spacings of corrugations became wider than in the case of Chalmers et al., owing to the lower purity of specimens used by the authors. The mean values of the spacings of corrugations measured on the (001) plane are given in Fig. 4.

Fig. 2. Microstructure of side free surface, (001). Lowering speed, 0.7mm/min.

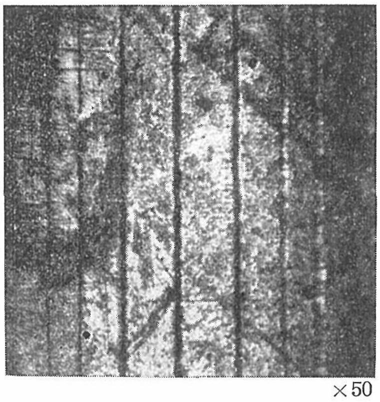

Fig. 3. Microstructure of side free surface, (001). Lowering speed, 6.2mm/min.

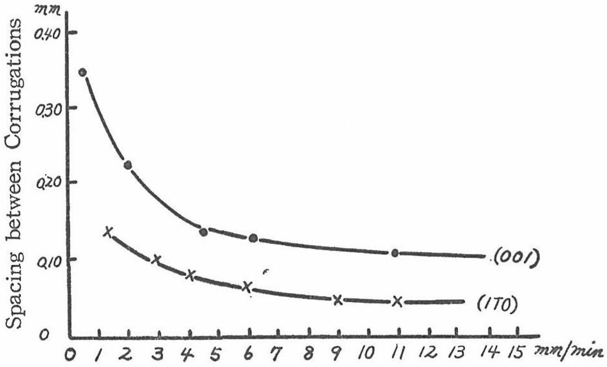

Fig. 4. Corrugation spacings observed on (001) and $(1\bar{1}0)$ planes vs. lowering speed.

The so-called cell structure corresponding to the top of the bundle of columnar cells was observed on the top free surface of specimens, but the shape of each cell was irregular and most of the cells were transversely long. It is noticeable that a tortoise-shell pattern made of the groups of several irregular cells was observed and each group was surrounded by the deep groove. This abnormal cell structure has not yet been reported. The higher the lowering speed, the smaller became the size of each tortoise-shell as in the small cells (Figs. 5, 6). It was

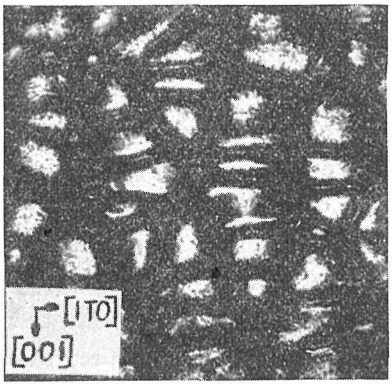

Fig. 5. Microstructure of top free surface, (110). Lowering speed, 0.7mm/min.

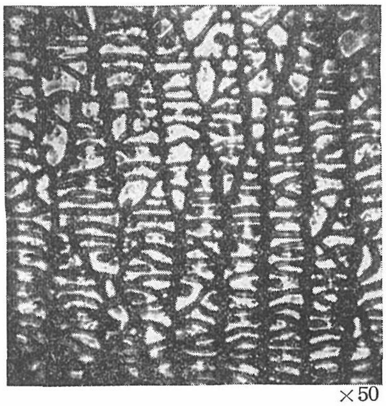

Fig. 6. Microstructure of top free surface, (110). Lowering speed, 4.5 mm/min.

found from the X-ray analysis that the longitudinal direction of the tortoise-shell pattern was parallel to the [001] direction and the transversely long direction of each small cell was parallel to the [1$\bar{1}$0] direction.

The corrugations observed on the side surface of the [001] direction were parallel to each other and relatively regular (Figs. 2, 3), while those on the side surface of the [1$\bar{1}$0] direction were tolerably parallel but irregular and the spacings of corrugations were narrower than those in the [001] direction. The above-mentioned tendency was observed in all the lowering speeds adopted in this study (Fig. 4).

2. Result of observation in the state etched with nitric acid.

The same corrugation structure as in 1 was clearly observed on the whole side surface of specimens. In addition, the relation between the spacing of corrugation and the lowering speed and further the relation of regularity between the [001] and [1$\bar{1}$0] directions on the side surface of specimens were quite similar to the result in 1 (Fig. 7 shows the irregularity of the corrugation structure on the

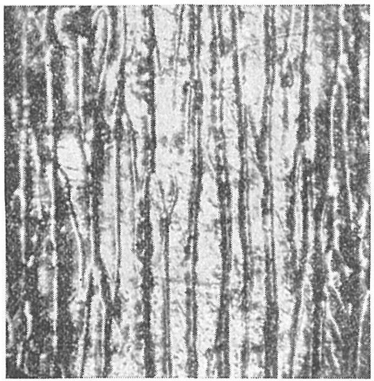

Fig. 7. Microstructure of side free surface, (1$\bar{1}$0). Lowering speed, 6.2mm/min.

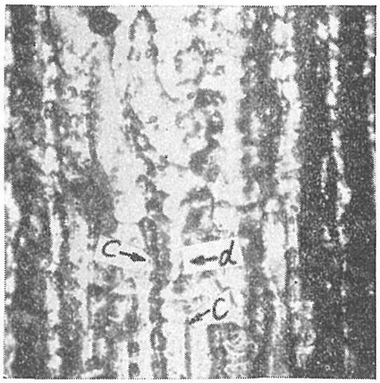

Fig. 8. Microstructure of the side surface etched in nitric acid.

$(1\bar{1}0)$ plane). In a higher speed than 11 mm/min, the dendrite structure which was not observed in unetched state was revealed by etching in nitric acid (Fig. 8). It was observed that the primary skeleton of dendrite crystals developed from the centre of the corrugation (the arrows c in Fig. 8 show the end points of the corrugation boundaries and also the arrow d shows the starting point of the primary skeleton of the dendrite crystal). The corrugations near each side of the primary skeleton were gradually suppressed by the side arms of the primary skeleton and these side arms developed widely in the obliquely upper direction. As the lowering speed increased, the number of dendrite crystals increased but the width became rather wider. The stray crystals developed from a higher lowering speed than 24 mm/min. The same cell structure as in 1 was observed on the transversal plane by etching in nitric acid after cutting the specimen and etching away the strained region, but the tortoise-shell pattern was more obviously revealed than the small cells. The corrugation structure on the side surface was scarcely observed by etching in the solution used for revealing the striation structure by Chalmers et al., while on the transversal plane the tortois-shell pattern was observed though indistinctly but the striation boundaries were not.

B. Results of Simultaneous Observations of Corrugation and Striation Structures

1. Result of surface observation.

Examples of the macrostructure on the (001) plane of the specimens grown from the melt at the lowering speed of 1 mm/min, are given in Figs. 9a, 9b*, and

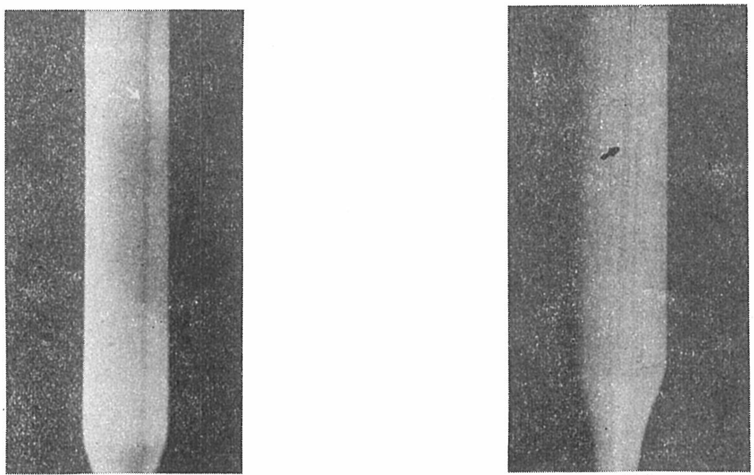
(a) ×1 (b) ×1

Fig. 9. Macrostructures of the corrugation and striation structures revealed by etching in nitric acid and mixed solution.

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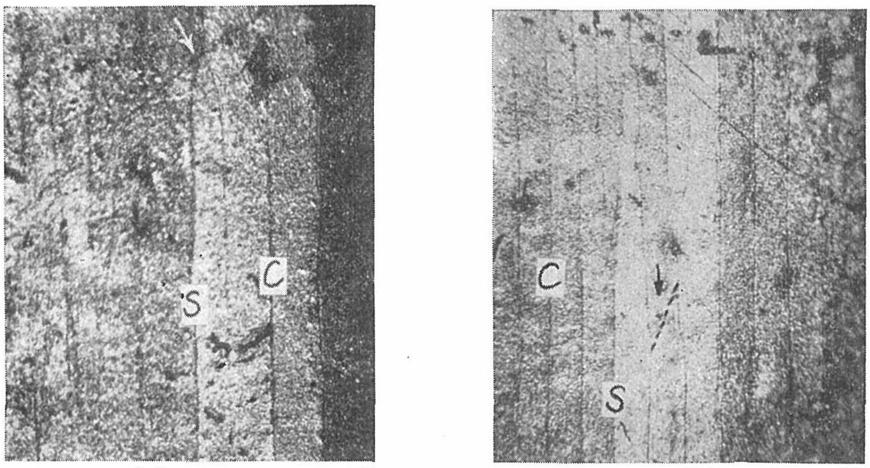
* The [110] direction of the specimen shown in Fig. 9b slightly inclines to the right to the specimen axis.

also the microstructures of Fig. 9a are given in Figs. 10a, 10b*. The arrows c and s show the corrugation boundary and the striation boundary respectively. The striation was from one to several times as wide as the corrugation, and the striation boundaries always coincided with the corrugation boundaries within the region observed in this study.** The width of the striation varied with the place, but there the striation boundary always curved along the branching points of corrugations (see the arrow shown in Fig. 10a), while complex boundaries were also seen as in Fig. 10b. The striation boundaries on the transversal plane were not observed even by polishing and etching electrolytically. This result implies that on the (110) plane the slight difference of the crystallographic orientation can not be revealed by etching.



(a) ×20 (b) ×20

Fig. 10. Microstructures of Fig. 9a.

2. Result of X-ray analysis.

Several X-ray back reflection photographs were taken at the striation and its both sides in the specimen in Fig. 9a, and the results on the corrugation and the striation boundaries are given in Fig. 11 and Fig. 12 respectively. The size of X-

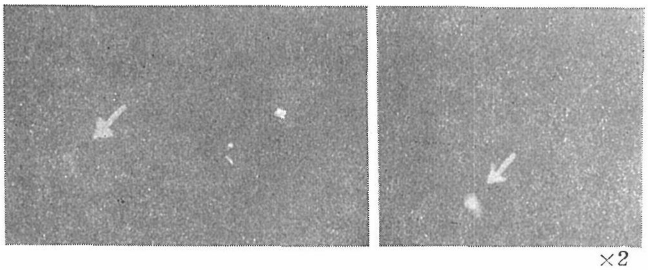

×2

Fig. 11. X-ray back reflection pattern from the corrugation boundary.

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* Each photograph shows the different portions in Fig. 9a.

** Hulme[5] has recently reported the same result on the transversal plane of zinc single crystals by the X-ray microscopy method as in this study.

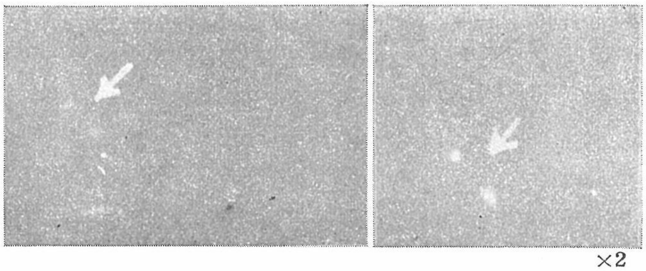

Fig. 12. X-ray back reflection pattern from the striation boundary.

ray beam on the surface of the specimen was about 0.4 mm ϕ, and as the widths of the striation and the corrugations of the specimen in Fig. 9a were 0.8 mm and from 0.25 mm to 0.27 mm respectively, it is assumed that X-rays always fell on the corrugation boundary in each photograph. The same photograph as in Fig. 12 was obtained from each boundary of the striation in Fig. 9a, while the same ones as in Fig. 11 were obtained from the left side, the centre and the right side of the striation in Fig. 9a respectively. The orientation difference in Fig. 11 was within half degree and that in Fig. 12 also about two degrees, and both sides of each boundary of the striation were related by the rotation around the [100] direction and the direction of the rotation was inverse but the orientation difference was equal on each boundary.

IV. DISCUSSION

The generation mechanism of the corrugation structure (columnar cells) has been explained as follows; The parts which later become the centres of columnar cells, may freeze at a higher temperature than the outer rounds which afterward become the boundaries, owing to the lowering of freezing point attributable to the segregation of impurities. Accordingly, impurities segregated to the liquid side may be diffused towards the outer rounds. The outer rounds having a higher concentration of impurities will freeze later than the centres, producing the columnar cells containing many impurities in boundaries. It is assumed that each cell centre is projecting into the liquid side at the actual interface between the liquid and solid phases in the course of freezing.

Further, the formation mechanism of the slender cell structure and the tortoise-shell pattern on the top free surface and the transversal surface of specimens will be considered. It should be explained in the light of the anisotropy in crystals that the transversely long direction of slender small cells is parallel to the $[1\bar{1}0]$ direction and the longitudinal direction of the tortoise-shell pattern is parallel to the [001] direction. Now, as the mechanism of crystal growth, it will be supposed that the low index plane (110) is the actual plane of growth. Therefore, the normal growth of the (110) plane may take place as one atomic layer after another stacks on this plane. In this case, for forming one atomic layer on the plane it is necessary to consider the advancing rate of one atmic step from a growing nucleus on the plane. It will be also supposed in this study that the advancing rate in the [1$\bar{1}$0] direction is higher than that in the [001] . Impurities segregated from the tip on the interface may be inferred to be uniformly diffused around it. Accordingly, the solid part nearest to the tip centre may unifomly freeze slightly after the freezing of top centre, but the acutual shape of the island of one atomic layer may become slender in the [1$\bar{1}$0] direction if the advancing rate in the [001] direction is very slow. If so, a new tip may develop at the supercooled region generated in the liquid side in the [001] direction, and the assembly of slender cells may be formed. Since impurities diffused in the [1$\bar{1}$0] direction may be widely diffused around the [1$\bar{1}$0] direction, each step of slender cells arranged each other in the [001] direction may stop to advance in the [1$\bar{1}$0] direction at some places. Therefore, the advancing heads of slender cells in the [1$\bar{1}$0] direction may be put in order and the tortoise-shell pattern may form. On the other hand, in high purity specimens, the regular hexagon cell structure is observed as there is probably no differece in the advancing rate between the [1$\bar{1}$0] and [001] directions. In conclusion, it may be supposed that the advancing rate of step in the [001] direction is strongly lowered by impurities.

From the experimental result that the striation boundaries always coincide with the corrugation boundaries, it is assumed that each structure mentioned above has its characteristic columnar cells respectively (in this case, one columnar cell of striation is made of several columnar cells of corrugations). So, it is an interesting problem whether both structures were simultaneously formed in freezing or the striation structure was formed after the formation of the corrugation structure. Chalmers et al. and Hulme have proposed the latter consideration: as the temperature is lowered from the melting point, the vacancies, lacking other suitable sites to eliminate themselves, will form into aggregates. In this case, the most stable form for such an aggregate is in the shape of a flat disk on a special crystal plane. Tendency of vacant lattice sites into flat disks would continue so that, as the temperature decreases, the disks would grow in size. When a critical size is reached, collapse of the lattice across the disks occurs, producing a general ring dislocation (i.e. pair of edge dislocations). At the relatively high temperatures directly behind the interface where these dislocation pairs are formed, the dislocations would be fairly mobile and would have a tendency to form into transition surfaces consisting of arrays of dislocations of one signs. In this case, these disloca tions would be easily caught at the corrugation boundaries containing many impurities.7)

However, it seems to be unfavourable to the consideration of Chalmers et al. that firstly one striation containes several columnar cells of corrugations and secondly a few striations are observed only in one portion of the surface of the specimens studied by the authors.

The incubation period in the generation of striation reported by Chalmers et al. was not observed in the experimental result of the authors. However, from the fact that the striation structure is narrower at the beginning of its generation as in the result of Chalmers et al., it may also be assumed that the gradual increase of a corrugation having a great orientation difference generated occasionally (two degrees) results in making up a bundle of several corrugations. Further detailed examinations must be carried out with respect to the problem consisting of a pure rotation of striations around a common axis.

An X-ray examination is now being performed concerning the striation boundaries on the transversal plane (110) not revealed by etching.

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