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On the Structure of Inter-crystalline Boundaries of Metals. II

By

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§ **V.** *The Groove formed at the Inter-crystalline Boundary.* As stated already, when a metal is heated to a temperature lower by less than $10^0 \sim 20^0$C below its melting point, the liquid layer is formed at the inter-crystalline boundary, and it manifests as a groove when the test piece is cooled to the room temperature. However, the cooling is not necessary to form the groove. When the surface of the test piece in the furnace is looked with a magnifying glass through a glass window set on the wall of the furnace, we can detect that the groove is formed suddenly when the temperature reached to the lowest temperature above which the fluidification of the inter-crystalline boundary has been found to take place. Thus, the formation of the inter-crystalline groove does not require any long continued heating, but only a few seconds heating at the required temperature is sufficient to form it. A prolonged heating and a gradual cooling have only the effect to broaden the groove, and for the formation itself of the groove the heating even for a very short time at the required temperature, as was stated before, is sufficient.

Prof. U. Yoshida and Mr. K. Koyanagi supposed that the inter-crystalline groove is formed by the enhanced evaporation of the inter-crystalline liquid layer. But, the present observation that the inter-crystalline groove is formed by the heating at the required temperature only for a very short time denies their supposition. Further, when a metal is heated in the air, as in the present experiments, it must be considered to be covered by a comparatively thick oxide film which hinders a rapid evaporation of the inter-crystalline liquid layer. This fact is also unfavourable for the evaporation theory. Actually, the formation of the inter-crystalline groove does not depend upon whether the metal is heated in the air or in vacuum.

Another reason for the formation of the inter-crystalline groove, which is next to be considered, is the expansion (contraction with Bi) caused by the thickening of the inter-crystalline liquid layer by heating and the contraction (expansion with Bi) due to the crystallization of the liquid layer by cooling. With regard to this point various experiments were made. First, among the single crystal test piece of Sn, Pb and Al in the form of rectangular plate, such specimens were selected that the boundary between two neighbouring crystals runs in transversal direction of the test piece. These specimens were heated to the required temperature and then cooled in the furnace, by laying horizontally on a flat stand or rollers so that they can expand or contract freely, or by hanging vertically in the furnace. But, no difference in the breadth and the depth of the grooves could be detected in these three cases. Next, with the specimens of the same kind as above, the distances between two points marked, once very closely and then remotely, on both sides of the inter-crystalline boundary were measured very accurately with a microscope before and after the heating to form the inter-crystalline boundary, and examined whether some expansion or contraction of the test piece had arisen in the direction perpendicular to the inter-crystalline boundary. If the groove be formed by the cause as is considering now, the excess mass forced out by the formation of the groove of considerable size should be spent in expanding the test piece in a detectable degree. But, the measurement did not show any trace of such expansion or contraction, and does not agree with the expansion and contraction theory. Further, the writer carried out a similar measurement with test pieces consisted of comparatively large number of small crystals, but any trace of the expansion or compression by the formation of the groove at the inter-crystalline boundaries could not be detected. If the expansion and contraction theory would be correct, we are to expect that the outer boundary of a crystal which is entirely surrounded by neighbouring crystal, would be grooved. But, the fact contradicts this expectation, and the grooves are always formed at inter-crystalline boundaries of all kinds. Of course, the writer admits, as will be stated later, the presence of some effects of the expansion and contraction on the formation and the shape of the inter-crystalline boundary; but he believes that the expansion and contraction which happens by the formation of the groove is not an essential cause for its formation. When, by the heating up of a test piece in a furnace, its surface is looked with a magnifying glass through a glass window set on the wall of the furnace, we can detect that at the same time as the inter-crystalline groove is formed suddenly at a certain temperature, the part of the outer surface of the test piece in the neighbourhood of groove pulsates. As already mentioned, the fluidification of the outer surface and of the inter-crystalline boundary begins at the same lowest temperature. Considering from this and the pulsation of the outer surface of the test piece as stated above, it may be legitimately imagined that the inter-crystalline groove is formed by the drawing out of the inter-crystalline liquid layer into the outer surface (probably beneath the oxide film) of the test piece by the action of the surface tension. When the surface of a test piece on which the inter-crystalline grooves are formed is inspected closely, we can detect that the sharp vertices and edges of the crystals is rounded and the surface looks like to be covered by a rather solidified layer of the melt. Fig. 1, Plate II is the photograph of an aluminium test piece which was heated to a comparatively high temperature and has wide grooves on its surface, and we can see clearly wavy wrinkles on its surface. This seems to suggest that the inter-crystalline liquid layer is sucked beneath the oxide film covering the outer surface of the test piece and is in accord with the bulging of the lower end of the test piece, as stated before, when it is suspended and heated sufficiently in a furnace.

The writer made his experiments on the formation of inter-crystalline grooves with bismuth too. Differing from other metals, bismuth expands by crystallization, and an effect which is different from the case of other metals is expected to be present in the formation of the inter-crystalline grooves.

(a) The case of sudden cooling: A test piece of bismuth (BI), which was defined in § II, was suspended and heated at 265°C for 5 minutes in a vertical furnace, and then it was cooled suddenly by dropping it into the water under the furnace. The appearance of the inter-crystalline boundary of the specimen thus cooled is shown in Fig. 2, Plate II. The inter-crystalline boundary in this case protruded instead of becoming a groove, and at the summit of such protuberance some small spheres were formed due probably to the eruption of the inter-crystalline liquid layer.

(b) The case of slow cooling: A test piece of bismuth (BI) is heated in the same way as above. After having been kept at 265°C for 5 minutes, the test piece was cooled slowly in the furnace by cutting the electric current through the furnace. As is shown in Fig. 3, Plate II, the inter-crystalline boundary became grooved in this case as in the case of other metals; and a few small spheres, much less in number than in the former case, were formed in the groove. In the case of slow cooling, both exterior and interior parts cool rather uniformly, and the expansion due to the crystallization of the inter-crystalline liquid layer will be distributed rather evenly over the whole parts of the test piece and will not much strain locally the inter-crystalline boundary.

Consequently the inter-crystalline groove formed at high temperature is supposed to be retained after cooling. Differently from this, the exterior part of the test piece crystallizes firstly in the case of rapid cooling, by leaving the interior of the inter-crystalline liquid layer unsolidified, and the expansion due to the crystallization of the exterior part, gives rise to the protrusion of that part as is shown in Fig. 2, Plate II. When such a crystallization of the exterior part proceeds inwards, the expansion accompanying it gives forth the eruption, as small spheres, of the melt remaining still unsolidified in the interior through some weak localities in the solidified exterior part. In the case of slow cooling, the inward advance of the solidification also happens, though more slowly and the eruptions of the unsolidified part of the interior as small spheres is also expected to take place in much smaller number. Considering in such a way, the formation of such small metal spheres by eruption can be regarded as another strong evidence, in addition to the result of X-ray examination for the existence of the inter-crystalline liquid layer at the temperatures lower than the melting point of the metal.

Next with tin and bismuth, the depth and the shape of the inter-crystalline groove were investigated by means of an Ultropak microscope and the cross-sectional view thus obtained is shown in Figs. 7 and 8.

The test piece of tin, investigated in the case of Fig. 7, was in the form of plate. After having been heated at 223°C for 3 minutes in horizontal position in a furnace, it was cooled slowly in the furnace. In the case of bismuth shown in Fig. 8, the surface of a rod obtained by casting was etched so slightly that the inter-crystalline boundary was clearly visible without forming any

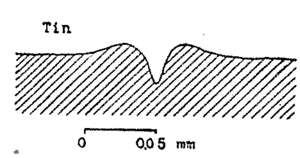

Fig. 7

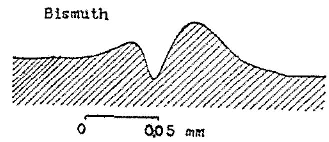

Fig. 8

groove. Then the rod was sealed in an evacuated glass tube, heated at 265°C for 5 hr in horizontal position in a furnace, and cooled very slowly by lowering the temperature of the furnace gradually. As is evident from the figures the both sides of the groove are swollen up in both case, only slightly in the case of tin and especially remarkably on one side in the case of bismuth. This peculiarity of bismuth is not limited to this case shown in Fig. 8, but was observed almost in all cases examined by the writer. According to the writer's view such swelling up of both sides of the groove in both cases is due partly to the sucking up of the melt at the inter-crystalline boundary to the outer surface of the test piece in the immediate neighbourhood of the groove. There is another factor in the case of bismuth that the expansion due to the crystallization of the inter-crystalline liquid layer by the cooling after heating affects a considerable pressure upon the neighbouring portion. This pressure forces out, on one hand, the still remaining melt in the interior as small spheres as stated before, and on the other hand, it deforms plastically the neighbouring crystals and causes them to bluge outwards. As stated before, the bluges formed on both sides of the groove is generally uneven. The crystal axes and accordingly the slip planes and the slip direction of two crystals on both sides of the groove are generally in different directions, and consequently the easiness to suffer plastic deformation due to the crystallization of the inter-crystalline liquid layer is different, so that uneven bluges are formed on both sides of the groove.

§ **VI** *Displacement of the Inter-crystalline Boundary by Recrystallization.* As mentioned before, Prof. U. Yoshida and Mr. K. Koyanagi considered the recrystallization phenomenon of metals as to take place by the growth of the crystal nuclei formed in the inter-crystalline liquid layer by consuming the old strained crystallites by means of an intermediary action of the inter-crystalline liquid layer. If their consideration is correct, then when the recrystallization is made to occur rapidly at such high temperature as to bring forth the inter-crystalline groove, an interesting question arises whether the displacement of the inter-crystalline groove can be detected. The writer's experiments on this point are very insufficient at present. But a trace of such displacement of the inter-crystalline groove at high temperature could be detected.

Since, when a worked test piece of a metal is recrystallized at once by heating it suddenly to high temperature, the displacement of the inter-crystalline boundaries will be too much complicated, the writer performed the recrystallization in two steps: Firstly, the recrystallization was carried out at a comparatively low temperature so that the boundaries between new large crystals obtained by recrystallization are not grooved and that the recrystallization is almost but not perfectly completed. Next, the test piece, after having been recrystallized firstly, was heated suddenly for a short time at such high temperature as the inter-crystalline grooves are to be obtained; and by comparing the photographs taken before and after this heating the displacement of the inter-crystalline grooves was inspected.

The recrystallization at high temperature proceeds very rapidly, and consequently the displacement of the inter-crystalline grooves too. In the present experiment, the furnace provided with a narrow slit at its upper end, as is shown in Fig. 9, was used. The slit was kept open always and was so narrow that only the test piece can pass freely through it longitudinally, and that the temperature in the furnace does not fluctuate in any detectable degree by putting in and taking out the test piece. By keeping the temperature in the furnace at a desired high degree, the test piece was put into the furnace, and heated for a few minutes, and then it was taken out and cooled in the air.

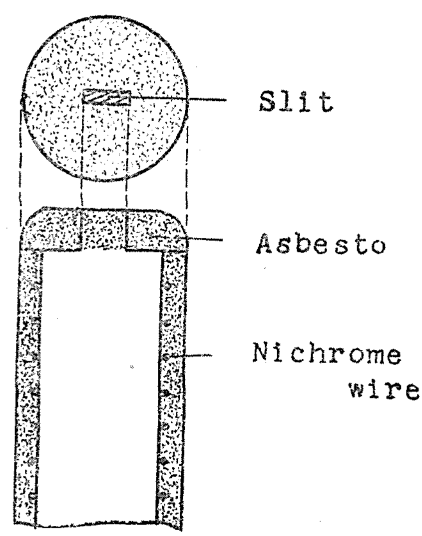

Fig. 9

The experiments were made with tin and aluminium. In the case of tin, an uncrystallized test piece having the same size as (SR), which has been defined in the previous report, was etched with concentrated hydrochloric acid, subjected to a rolling of 10 %, and was then recrystallized for the first time by heating for 5 minutes at 210°C. With such heating the recrystallization was almost but not entirely completed.

After taking the photograph of the inter-crystalline boundaries of the test piece thus recrystallized firstly, the temperature of furnace was raised to and kept at 224°C; and the test piece was heated for 3 minutes at this temperature and was then cooled in the air. The inter-crystalline grooves, formed on the surface of the test piece recrystallized thus for the second time, are shown in Figs. 5 (a) and 5 (b) in Plate II. In Fig. 5 (a), the groove running down vertically is formed by the second heating at the crystal boundary developed by the first heating, and the neighbouring part appearing white in a shape of wide band in the photograph is the trace traversed by the inter-crystalline boundary by the second heating and in the dark portion at the left end of the white band there situates the new inter-crystalline groove formed by the second heating at the final position of the displaced inter-crystalline boundary, though it is invisible in the photograph by unsuitable illumination. Fig. 5 (b) is the photograph taken to make this invisible groove visible by different illumination, and the one running down from the intersection of three grooves meeting at the upper part of the photograph, is this groove. Moreover, the other two grooves meeting at the upper part become clearer in this figure in place of the disapearance of the first groove which had appeared clearly in Fig. 5 (a). If the displacement of the inter-crystalline boundary takes place after its becoming a groove, then the part of the surface of the test piece which was traversed by the boundary would be roughened, and this was the writer's expectation. But, against this expectation, this part of the surface of the test piece becomes rather smoothed when compared with the other part, as will be seen in the photograph. This point, together with the fact that the grooves are formed only at the initial and final position of the inter-crystalline boundary, seems to be acceptable by considering in the following way: The formation of the groove at high temperature requires some duration of time. At the end of the recrystallization the inter-crystalline boundary does not move no more and it has sufficient time at its fixed position to be grooved, and at the beginning the start of the displacement of the inter-crystalline boundary commences after a lapse of the time and during which the grooving of the inter-crystalline boundary arises. The displacement of inter-crystalline boundary which is obtained with the recrystallization, at such a high temperature as is very near to the melting point, as in the present experiments, takes place very rapidly. Therefore, the inter-crystalline boundary moves very swiftly, without having sufficient time to be grooved, beneath the surface liquid layer which was formed at such a high temperature; and small surface irregularities of the test piece which have existed initially, become rather smoothed by the displacement of the intersection of the inter-crystalline and the surface liquid layers. The writer carried out similar experiments with aluminium, and the results were entirely the same as with tin.

§ VII *Conclusion.* By the present investigation it becomes now clear that with various metals the inter-crystalline boundary and the outer surface of the test piece fluidify at the temperature lower than $10^\circ \sim 20^\circ$ C below the melting point. This phenomenon is seen to take place with metals of very high purity as well as commercial ones, irrespectively whether the test piece is prepared by recrystallizaton or casting. Thus, it is inconceivable to be due to the presence of some impurities, and is rather appropriate to ascribe it to the proper nature of the metal crystals. According to the writer's measurement the inter-crystalline liquid layer becomes pretty thin at the temperature of about $10^\circ \sim 20^\circ$ C below the melting point, differing somewhat with the kind of metals, and below that temperature its presence could not be detected by the method of the present investigation.

With respect to this point it is improbable that the inter-crystalline liquid layer disappears abruptly at a certain definite temperature by cooling. Contrary to this, it seems to be more appropriate to consider after Prof. U. Yoshida that the inter-crystalline layer persists, as in liquid state or as in amorphous solid state, through all temperatures, even when it only becomes thinner with the lowering of the temperature.

As was stated before, the inter-crystalline boundary gets grooved by being heated at high temperature, and it has now become probable from the present investigation that this is due to the sucking of the inter-crystalline liquid layer to the outer surface (probably the interstice between the oxide film and the crystal beneath it) of the test piece by the action of the surface tension. It was found with bismuth that the expansion arising from the crystallization of the inter-crystalline liquid layer by cooling gives rise to the bulging of the neighbouring part of the test piece on one hand and the eruption as small spheres of still uncrystallized part of the liquid layer on the other hand.

Further the writer recrystallized the test pieces of tin and aluminium at such high temperature as to be grooved at the inter-crystalline boundary, and the trace left on the surface of the test piece by the displacement of the inter-crystalline boundary was seen to be comprehensible, at least to some extent, by an explanation based on the presence of liquid layers at the inter-crystalline boundary and on the outer surface of the test piece at high temperature.

Lastly the writer's sincere thanks are due to Prof. U. Yoshida, under whose kind supervision the present investigation was carried out.

Further it must be noted that the expense of this research has been defrayed from the Scientific Research Fund of Department of Education.

(June 20, 1945)

Plate II

Fig. 1 Grooves formed at Al crystalline boundaries.

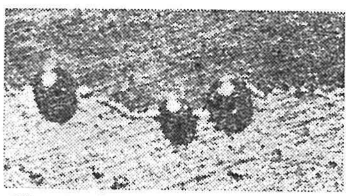

Fig. 2 Crystalline boundary of Bi (sudden cooling)

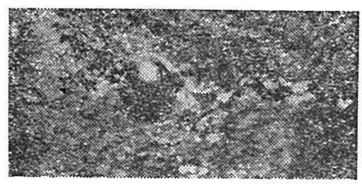

Fig. 3 Crystalline boundary of Bi (slow cooling)

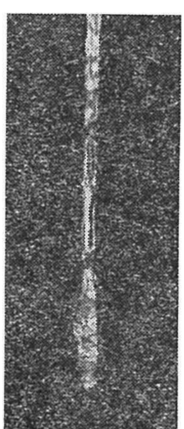

Fig. 4 Bulge formed at lower end of Al plate.

Fig. 5 (a)

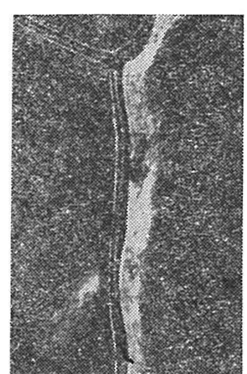

Fig. 5 (b)

Displacement of inter-crystalline boundaries.