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

By

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Abstract

The liquid layers at the inter-crystalline boundary and on the outer surface of test piece were confirmed with various metals to be present, by means of the X-ray diffraction method, at least, at the temperatures lower by less than $10^{\circ}\sim 20^{\circ}\text{C}$ below the melting point; and the grooving of the inter-crystalline boundary at such a high temperature was ascribed to the sucking up of the inter-crystalline liquid layer to the outer surface of the test piece by the action of the surface tension of the liquid. The presence of the inter-crystalline liquid layer was detected also with bismuth differently. When a test piece of bismuth is cooled from such a high temperature, the expansion due to the crystallization of the inter-crystalline liquid layer is revealed by an uneven bulging of both sides of the inter-crystalline groove as well as by the eruption as small spheres of the interior part of the liquid layer remaining still uncrystallized. According to rough measurements, the thickness of the inter-crystalline liquid layer decreases from several tenth mm. at extreme vicinity of the melting point to almost nil at the temperature $10^{\circ}\sim 20^{\circ}\text{C}$ below.

By recrystallization of metals at high temperature a smoothing of the surface of the test piece was observed, and it was ascribed to the sweeping of small surface irregularities by the passage of the intersection of the inter-crystalline liquid layer with the liquid layer on the outer surface of the test piece.

§ I. *Introduction.* The presence of an amorphous layer on well polished metal surface was pointed out first by Beilby,¹ as is known as Beilby's amorphous hypothesis. Rosenhain² and others extended Beilby's hypothesis of amorphous layer to inter-crystalline boundaries of metals, and by assuming the presence of cementing amorphous layer in inter-crystalline boundaries, they explained the fact that the inter-crystalline boundaries are mechanically stronger at room temperature than interior of the crystals with which a metal block is composed.

1. G. Beilby: *Aggregation and Flow of Solids*, (1921).

2. W. Rosenhain and D. Ewen: *J. Inst. Metals*, 8, 149, (1912).

About ten years before Prof. U. Yoshida and Mr. K. Koyanagi¹ made a research on the formation of grooves at inter-crystalline boundaries of a metal by heating it to a temperature just below the melting point, and ascribed it to the fluidification of the inter-crystalline amorphous layers by softening. They found the grooves at inter-crystalline boundaries with commercial aluminium plate as well as the purest one obtainable at that time. Their experiments were made with such recrystallized aluminium plate that is consisted of only a few large crystals. From these facts they considered that the fluidification of the inter-crystalline boundaries is due to the intrinsic property of the metal crystals, but not the result of the lowering of the melting point caused by the accumulation of some impurities.

Next, starting from this consideration they proposed a theory of recrystallization of metals: When a metal is heated to the recrystallization temperature the inter-crystalline amorphous layer softens and becomes fluid, and some crystal nuclei become to be formed there. These crystal nuclei grow gradually by consuming the old strained crystallites by the aid of an intervening action of the fluid. Further Prof. U. Yoshida² enunciated very clearly from various sides the possibility of formation of inter-crystalline layer (liquid or amorphous solid) and its persistency.

Whether the amorphous layer does or does not exist at the inter-crystalline boundaries is an essentially important question for the theory of metals, especially for the theory of plastic and elastic deformations and of recrystallization; and the writer has undertaken an experimental research to ascertain the presence of the inter-crystalline liquid layer by the softening of the amorphous layer at the temperatures at least just below the melting point, and to know, if it really liquidify, the thickness of the liquid layer at various temperatures. Moreover it was also one of the objects of the research to make clear why the inter-crystalline boundaries become grooved on the test piece by being heated to the temperature immediately below the melting point.

§ II. *Test Pieces.* As the effect of presence of impurities is oft-

1. U. Yoshida and K. Koyanagi: *Memoirs Coll. Science, Kyoto Imp. Univ.*, A, 18, 9, (1935).

U. Yoshida: *ditto* 23, 325, (1941).

2. U. Yoshida: *Memoirs Coll. Science, Kyoto Imp. Univ.*, A, 24, 99, (1944).

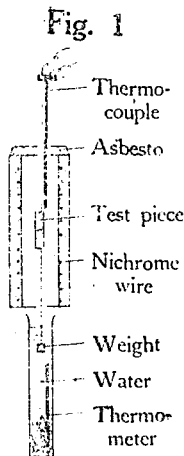
en emphasized in the discussion on the structure of inter-crystalline boundaries of metals, the experiments were carried out with purest specimens obtainable at hand: Aluminium plates having the purity of 99.996%, tin plates of the purity of 99.98%, and commercial bismuth and lead in the form of plates which are called to be purest. The melting points measured by a thermocouple for these metals are tabulated in Table I.

(a) *Aluminium*: Aluminium plates having the size of $1 \times 13 \times 70$ [mm³] were first annealed for 4 hr. at 350°C, then elongated plastically by 3%, and lastly recrystallized by heating for 10 hr. at 630°C. Aluminium test pieces prepared in this way by recrystallization will be called as (AR). Aluminium plates having the same size as above were placed on asbestos plate and melted in horizontal position by heating at 700°C in an electric furnace. Aluminium test pieces obtained by gradually cooling such molten pieces will be called as (AI).

Metals	Melting Point in °C
Al	660.0
Sn	225.0
Bi	271.5
Pb	327.0

(b) *Tin*: Tin plates having the size of $1 \times 10 \times 30$ [mm³] were plastically rolled by about 10% after the annealing of 4 hr. at 150°C, and then they were recrystallized at 210°C for 50 hr. These test pieces of recrystallized tin will be called as (SR). Tin plates having the size of $0.5 \times 5 \times 60$ [mm³] and are provided with shoulders were also prepared as casting by pouring the melt into aluminium mould. These plates will be called as (SI).

(c) *Bismuth and Lead*: With these metals only the casting test pieces prepared in the same way as tin were used. Bismuth and lead test pieces will be called as (BI) and (LI) respectively.



§ III. X-ray Examination of the Outer Surface of Test Piece and the Sectional Surface of Inter-crystalline Boundaries Disclosed by Tearing.

(a) *Apparatus*: The heating of the specimen was done in the furnace as shown in Fig. 1. The test piece was hung in a vertical porcelain tube which is open at its lower end and is to be heated electrically from outside by means of nichrome wire wound around it. A proper weight

was so suspended with a wire at the lower end of the test piece that the weight situated outside the porcelain tube. To the lower open end of the tube is connected a glass tube filled with water at its bottom. The purpose of this device is to cool suddenly the part of the test piece which has fallen out of the electric furnace being torn at a crystal boundary by the suspended load at high temperature. The rapidity of heating the test piece in the furnace was 5°C per minute from the room temperature to about 20°C below the melting point, and was about 0.5°C per minute above. For taking the diffraction photograph, X-ray tube provided with tungsten target was operated with 80 kV, and a cylindrical camera was employed.

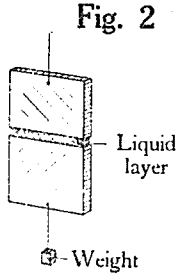
(b) *Experiments*: As the purpose of the X-ray diffraction experiment is to examine the thin layer of the outer flat surface of the test piece and of the sectional surface of inter-crystalline boundary which is developed by tearing, it was carried out with the test pieces (SR), (BI), and (LI) whose density is high. When a test piece consisting of large crystals, whose boundary runs across the entire section of the test piece, is hung in the furnace, in the manner as is stated before and is heated up to a certain high temperature, the test piece get asunder into two pieces at the crystal boundary by being pulled with the load applied to the lower end of the test piece. The piece which has dropped into the water under it cools very rapidly so far as about 15°C , and the other piece remaining in the furnace is made to cool very gradually in it by cutting the electric current flowing through the furnace. By this experiment the temperature at which the tearing of the test piece happens, can be controlled at least to some extent by changing the load applied to the test piece. However below a certain temperature, which is proper to the kind of the metal, the separation of the test piece at the crystal boundary does never take place even with very heavy load.

(c) *Results*: The tearing of the test pieces of (SR), (BI) and (LI) at the crystal boundary was done at various temperatures in the manner stated former section. The sectional surfaces of the crystal boundaries of the test pieces which were developed by tearing and their outer flat surface, with both rapidly and slowly cooled ones, were examined by the X-ray reflection method; and entirely similar photographs were obtained with every metal. The

photographs obtained with lead are shown, as examples, in Plate I. As is seen in Fig. 3 and 4 in the plate, slowly cooled specimens gave only ordinary Laue-spots consisting of a small number of intense spots due to a single piece of crystal, with both the outer flat surface and the sectional surface developed by tearing at the crystal boundary. Differing from this, a lot of weak spots appeared, in addition to a small number of intense spots, with both kinds of the surfaces of rapidly cooled specimens, as is shown by the photographs a, b, c, d in Fig. 1 and 2 in the plate.

As to the origin of these weak Laue-spots it is reasonably considered that the surfaces of both kinds of the specimens become covered with a thin layer of the melt at the temperature of tearing and that this molten thin layer solidifies in polycrystalline structure by rapid cooling, having not enough time to be occupied by the base crystal by its growth. It may be differently imagined that the weak Laue-spots in question originate in the small crystals formed by the destruction of the original large crystal by being cooled rapidly. However, as will be seen from the photographs in Plate I, the appearance of the weak Laue-spots is limited to the melting point, and when the heating temperature is lower, we get only a small number of the intense Laue-spots arisen from the original large crystal. This indicates the inadequacy of the latter view. The weak Laue-spots weaken as the heating temperature lowers below the melting point, and become almost undetected at the temperature of about 10°C below the melting point, being more or less different according to the kind of metals. This arises from the thinning of the liquid layer in the inter-crystalline boundaries and on the outer flat surface of the specimen with lowering of the heating temperature; and this point will be more clearly shown later in §IV, where the results of measurements of the thickness of the liquid layer are given.

The liquidification of the outer flat surface of the specimen at high temperature can also be detected in different way. When a plate consisting of only a few number of crystals is suspended vertically in the furnace and is heated up to the temperature of 2° or 3°C below the melting point, there appears a vestige of the flow of the melt on the surface of the specimen, and a bulge at the lower end of the plate which is evidently due to the accumulation of the flowed melt. The photograph, taken in end-on direc-



tion, of the bulge formed in such a way at lower end of an aluminium plate is shown in Fig. 4, Plate II. As the plate preserved its general form in this case, the fluidification should be considered to be limited to the outer surface of the plate and the inter-crystalline boundaries, leaving the interior unliquidified. As to the question why the outer surface of the metal is easier to melt than the interior, the writer's opinion is as follow:

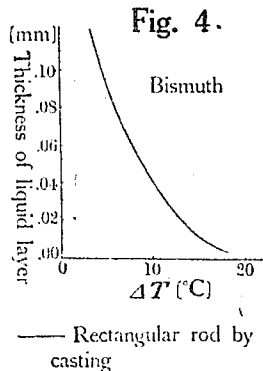
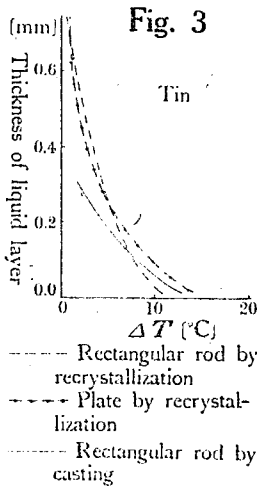
If we consider that the metal surface is covered with oxide film, then the boundary between this film and the crystal beneath it will be essentially the same nature as the inter-crystalline boundary; and consequently the melting is as easier at the former boundary as at the latter.

§ IV. The Thickness of the Liquid Layer Existing at the Inter-crystalline Boundary.

As it has become almost evident from the experiments described above, that with metals the liquid layer exists at the inter-crystalline boundary at the temperatures which are at least a little below the melting point, the writer tried to measure its thickness at various temperatures.

Table II

Metals	Surface tension in dyne/cm	Remark
Sn	612.4	at 226°C in CO
Al	520.0	at 750°C
Bi	465.0	at 265°C in CO



The crystal boundary is of course pretty irregular. However the writer selected such specimens from the test pieces in the forms of plate or rectangular rod consisting of large crystals that the crystal boundaries devoid of much irregularity ran almost perpendicularly to the longitudinal direction of the test piece.

If we approximately assume that the crystal boundary is a horizontal plane perpendicular to the longitudinal direction of the test piece and that the liquid layer at the inter-crystalline boundary is of a uniform thickness as is shown by Fig. 2; then the force due to the surface tension of the liquid layer, which is equal to the tearing weight at the moment of tearing, can be calculated very easily. If we represent by γ the surface tension of the liquid, by t the thickness of the liquid layer, by A the area of the horizontal liquid layer which is taken to be the same as the horizontal cross sectional area of the test piece, M the tearing weight including the mass of the piece of the test piece which has fallen by the tearing, and by g the gravity acceleration, then we get $2\gamma A/t = Mg = 980 M$.

Thus from the values of γ , A and M , the thickness of the liquid layer t can be obtained. The values of surface tension for Sn, Bi and Al at temperatures somewhat higher than the respective melting points, which are given in Landolt-Börnstein's *Physikalisch-Chemische Tabelle*, are tabulated in Table II. The present experiments were carried out in air and at temperatures somewhat lower than the respective melting points, and consequently the values of the surface tension would have been different from those given in the table. However the writer used the values given in the table, by regarding them to be the same order of magnitude, in both cases.

The tearing experiments were made with the test piece (SR), (SI), (AR), (AI) and (BI) by means of the furnace shown in § III, (a). As the tearing temperature is different according to the tearing load, the experiments were made by applying many different loads for a same kind of the test piece. Thus by knowing the tearing load (including the weight of the fallen part of the test piece), the thickness t of the liquid layer was obtained by measuring the cross-sectional area A of the test piece. The relation between the temperature and the thickness of the liquid layer for Sn and Bi is shown in Fig. 3 and 4. In these figures the temperature is represented as its difference from the melting point and is expressed as ΔT .

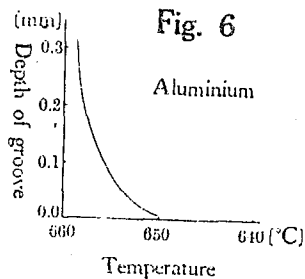
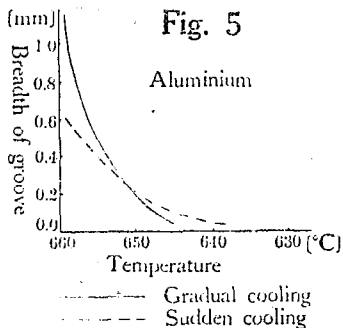
As is evident from the curves in the figures, the thickness of the liquid layer at the inter-crystalline boundary decreases as the temperature lower from the melting point, and becomes so thin at

the temperature of about $10^{\circ}\sim 20^{\circ}\text{C}$ below the melting point that it makes impossible to tear at the crystal boundary. Below this temperature we are unable to detect the presence of the liquid layer by the tearing method or by the X-ray method. However it is inconceivable that the liquid layer disappears abruptly below a certain temperature; and it seems more natural to suppose, as Prof. U. Yoshida has done, that the thin layer at the crystal boundary, be in the state of liquid or of amorphous solid, by far exists when it only becomes thinner as the temperature falls further and further.

It is now almost clarified that the crystal boundary of the melting point. When a test piece of a metal composed of large crystals is heated to such a temperature, the crystal boundary gets grooved as was stated before. Fig. 1, Plate II shows such grooves formed on the surface of an aluminium plate. As will be stated later, this seems to be caused by the fact that the liquid layer formed at the inter-crystalline boundary is sucked up beneath the oxide film on the outer surface of the test piece by virtue of the action of the surface tension.

The writer measured with the test piece of aluminium the depth and the breadth of such grooves at the crystal boundary by means of Leitz's Ultrapak metal microscope, and investigated their relation with the highest temperature to which the test piece is heated up.

The procedure of experiment is as follows: When the temperature of the vertical electric furnace as is shown in § III, (a), reached 630°C , a test piece (AR) was hung into it, and when the temperature attained to the highest temperature required and



maintained at that temperature for two minutes, the test piece was either withdrawn up and was left to cool in the air, or cooled suddenly by dropping it into the water under the furnace.

The results of measurements obtained with various heating temperatures are represented by the curves in Fig. 5 and 6. The results of these measurements generally agree well with these obtained by the tearing method; and this shows that the thickness of the liquid layer measured by the tearing method is comparatively reliable. The breadth of the grooves which was measured microscopically by the present method is somewhat larger at high temperatures than the thickness of the liquid layer obtained by the tearing method. This is probably due to the fact that the edges formed by the liquid layer and the outer flat surface of the test piece become rounded and ill defined.

(to be continued)

Plate I

Lead

Fig. 1 The sudden cooling sectional surface of crystal boundary.

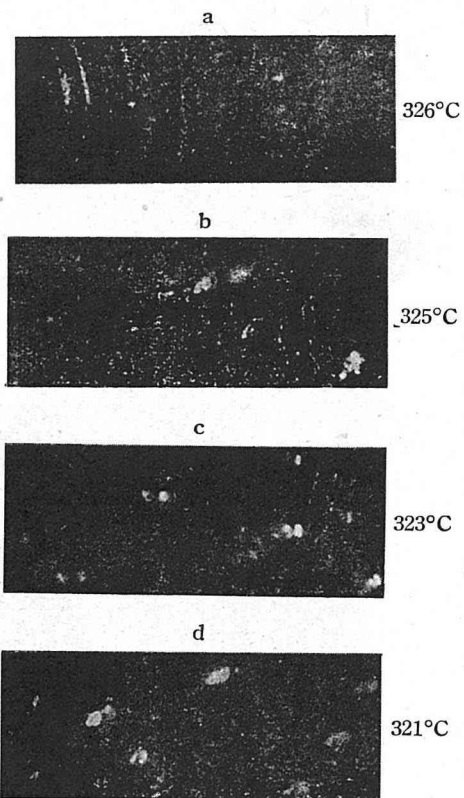


Fig. 2 The outer surface of sudden cooling specimen.

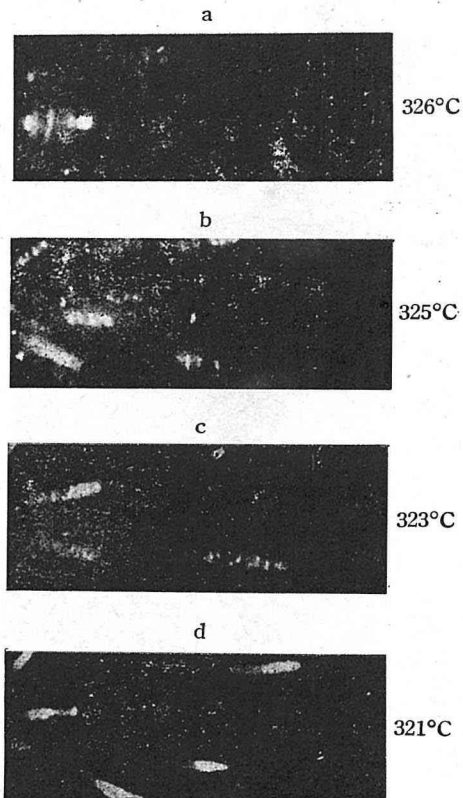


Fig. 3 The slow cooling sectional surface of crystal boundary.

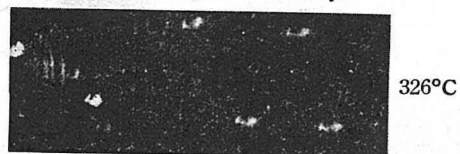


Fig. 4 The outer surface of slow cooling specimen.



Remark : The temperature shows the highest temperature,