

# Structure of the Crystal Boundaries of Metals and the Phenomenon of Recrystallization

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## Abstract

The presence of the cybotactic amorphous layer at the boundaries of the metal crystals formed by crystallization in the melt and at the intercrystalline boundaries developed by the process of slipping at the slip plane by the plastic deformation is inferred. Assuming the permanency of the intercrystalline amorphous layer, the theory of recrystallization of metals, proposed by the writer and K. Koyanagi some years ago, was reviewed.

## Introduction

In other papers<sup>1)</sup> recently published, the writer proposed a cybotactic theory concerning the manner of molecular grouping in liquid and in amorphous solid; and it has been found that this theory, though a rough one, is very fruitful in understanding qualitatively various physical properties of liquids and amorphous solids. In connection with it, the mechanism of crystallization and of melting of a substance was also considered; and the possibility was inferred of formation of the Beilby's amorphous layer on a metal surface by polishing and at an intercrystalline boundary developed between the atomic planes of a metal crystal by the process of slipping by a plastic deformation. Ordinarily, in an amorphous solid, individual molecules are supposed to be distributed entirely at random. But according to the writer's cybotactic idea, some of the molecules are in an aggregated state as cybotactic crystals; every one of these consists of a certain number of the molecules arranged in the same crystal lattice as in the adult crystal of the same substance, and is comparable in size with that of the unit cell of the crystal. These cybotactic crystals have no permanent stability. They are formed and decomposed suddenly by chance among the free molecules in a random distribution. Thus the proportion of the number of molecules in the state of the cybotactic crystals as compared with that of the free molecules is conceivable only in a statistical sense, and it increases continuously with decrease

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1. U. Yoshida; These Memoirs A, **23** 207, 225 (1941).

of the temperature, without any discontinuity such as is seen at the melting point of adult crystals. When the temperature is lowered without forming crystal nuclei of any considerable size below the melting point of the substance, which is peculiar to the adult crystal of the substance, it has become super-cooled; and by a further continued cooling it comes at last to a glassy state or a state of amorphous solid consisting partly of free molecules but very largely of cybotactic crystals, both being arranged and distributed entirely at random.

### **Structure of the Crystal Boundary of Metals**

It is well known that the crystal boundary of a metal is harder at low temperatures and is softer at high temperatures than the interior of the crystal. This fact is explained if we assume the presence of the amorphous layer at the crystal boundary as is described above. As the melting point of the metal is approached by raising the temperature, the amorphous layer exhibits the property of the liquid by virtue of the increased proportion of the free molecules as compared with the cybotactic crystals. On the contrary, at low temperatures, the amorphous layer comes to the state of amorphous solid due to an enormously increased proportion of the cybotactic crystals oriented entirely at random. The average life of the cybotactic crystals is now very much increased and the motion of the free molecules constrained in narrow interstices between neighbouring cybotactic crystals is so much restricted that they cannot behave freely any more as they did in the liquid state. In such a state the amorphous layer has no slip plane and slip direction, which is the direction of the minimum resistance in the crystal against an external stress applied; and it is endowed with uniform strength for all directions which is higher than the minimum resistance in the slip direction.

Plastic deformation of a metal is considered to be caused mainly by the slip along a slip direction in a slip plane. But the process of the ideal slip alone, seems to be insufficient to account for the plastic deformation. We know from X-ray examination, that the metal crystals become finer and scattered in their orientation by cold working even in the simplest case of a single crystal stretched or compressed plastically in one direction. This seems to imply that some other process such as separation and consequent mutual rotation of neighbouring portions of the crystal at a certain atomic plane at some localities takes place simultaneously with the ideal slip in plastic

deformation. The reason for the forcible process such as separation and mutual rotation can be sought for in the imperfection of the crystal lattice and in the coercionary stress called forth near the rather irregular crystal boundary by the slip interference at the crystal boundary where two crystals of different crystallographic orientation are bound together firmly. By such forcible process accompanying the crystal slip some part of the crystals will be smashed into extreme fineness comparable with the cybotactic crystals and will suffer considerable lattice distortion. By virtue of the enormous lowering of the melting point caused by these two facts the local heating caused by the process of the crystal slip will be sufficient to melt at least some of the fine and distorted crystals. If this occurs during the process of the slip, mutual cohesion between two parts of the crystal which are separated by such a thin molten layer will be very much weakened, and this will call forth an irregular and forcible stress distribution in their vicinity even in the simplest case of a single crystal stretched or compressed plastically in one direction. This again will cause at some localities smashing and distortion and consequently melting of the crystallites in the interior of the crystal; and at the same time separation and mutual rotation of the two parts separated by the molten layer may take place as long as the slipping process is continued. When the slipping process is stopped by removing the external stress, the melted portions will be cooled so suddenly that they come to the supercooled solid state or the cybotactic state as is stated before. Thus after the slip, the crystal is divided into finer crystallites of scattered orientation, and the boundaries of the crystallites become cemented to a considerable degree by the amorphous layer. This way of explaining the formation of the Beilby's amorphous layer by the crystal slip was proposed in the former paper.<sup>1)</sup>

Next let us consider as before the growth of the crystals of a substance in its melt. The growth in this case takes place only at the boundary surface of the crystals with the melt. Let  $N_l$  be the surface density of the liquid molecules at the crystal boundary, and  $N_c$  be that of the molecules situated at the crystal lattice on the boundary surface of the crystal. Then at a certain temperature a certain proportion  $\beta$  which may be called the melting factor, of the molecules

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1. loc. cit.

2. loc. cit.

$N_c$  situated at the crystal lattice will be released and enter the liquid phase; and at the same time a certain proportion  $\alpha$ , which may be called the crystallizing factor, of the liquid molecules  $N_l$  will be bound to the crystal lattice. Thus so far as  $\alpha N_l > \beta N_c$  the growth of the crystals will continue until the stage is reached where neighbouring crystals come almost into contact with each other. In this last state the melt confined in very narrow interstices between neighbouring crystals will be deprived of communication from outside, and with most metals, the average value of  $N_l$  will become smaller so far as the crystal growth continues, due to the contraction accompanying the crystallization from the melt. As to the manner of the internal structure of the thin liquid layer in such state of reduced value of  $N_l$  and consequently of the reduced pressure, we are entirely ignorant, and we cannot make any definite statement. But let us assume for the present that the number of liquid molecules which fall into the lattice point of the crystal at its surface in unit time is still proportional to  $N_l$  and is equal to  $\alpha N_l$ , keeping the values of  $\alpha$ ,  $\beta$  and  $N_c$  unaltered; and see what follows from this: It follows from the above assumption that the decrease of the average value of  $N_l$  at the narrow interstices acts to prevent the further growth of the crystals toward the liquid layer in the narrow interstices; and this crystal growth will be entirely stopped when, with the decreased value of  $N_l$ , the value of  $\alpha N_l$  becomes equal to  $\beta N_c$  even at a temperature lower than the melting point. This signifies the persistence of a thin liquid layer in the narrow interstices between neighbouring crystals. In addition to the reason given above, the disturbance to the regular crystallizing force at the surface of the crystal by the nearest approach of the other crystal differently oriented will assist at least to some extent the persistence of the thin liquid layer. When the temperature is very much lowered from the melting point, the value of  $\alpha$  will increase and that of  $\beta$  will decrease; and by this cause alone the crystal growth will be accelerated. But at the same time the number  $N_l$  of free liquid molecules which are to be entrapped into the lattice point of the adult crystals will be remarkably reduced by virtue of the crystal growth and of the enormous increase in number of the cybotactic crystals. As this fact counteracts the crystal growth due to the former cause, the thin liquid layer can still persist in the super-cooled solid state or in a glassy state at very low temperature, even down to absolute zero.

The above argument may be correct only in a statistical sense. When considered microscopically the widths of the narrow interstices between neighbouring crystals will be different from place to place and from time to time; and direct contact between neighbouring crystals will occur at some localities in the narrow interstices, by leaving the major part of the narrow interstices as the liquid or amorphous layer in the manner described above.

In a few cases, as of bismuth and others, where the substance expands on crystallization, the circumstances are different. In this case the decrease of  $N_i$  at the narrow irregular interstices between neighbouring crystals by the crystal growth cannot be possible. On the contrary various parts of the thin liquid layer will be subjected to enormous and irregular pressure, and this enormous and irregular pressure will act to melt the crystal at its surface partly by lowering the melting point of the crystal and partly by destroying the crystal into finest crystallites and by giving at the same time considerable distortion. Considering this, though the reason is different, the persistence of the amorphous layer is not inconceivable in this case also.

### Recrystallization of Cold Worked Metals

Cold worked metal crystals recrystallize at a temperature much lower than the melting point of the metal. As to the ultimate mechanism of this phenomenon the writer and K. Koyanagi<sup>1)</sup> proposed a theory several years ago. In that theory the following three assumptions were made: 1) The metal crystals melt at their boundaries in the recrystallization temperature range, and the recrystallization takes place through the growth of the crystal nuclei formed in the melt. 2) The metal crystal is easier to melt at its contact surface with the melt than in its interior. 3) Distorted metal crystals are easier to melt than those without distortion. The third assumption was modified in the previous report<sup>2)</sup> as follows:— Distorted crystals and extremely small crystals are much easier to melt than undistorted larger ones. For the first two assumptions some explanation will be given here. It has already been stated that the amorphous layer in the cybotactic state may exist at the boundaries of the crystal grains formed by solidification from the melt. It is also considered

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1. U. Yoshida and K. Koyanagi; *These Memoirs*, A, 18, 9 (1935).

2. *loc. cit.*

that the boundaries of the crystallites formed by the process of slipping are cemented to a considerable degree by the amorphous solid layer of the cybotactic state. In the latter case there may still be some part of the boundaries not transformed into the cybotactic state. However the crystallites in these parts would have been smashed into considerable fineness and their lattices would have been distorted to a considerable degree; and these parts, together with the already existing amorphously solidified layer, will be reduced to the liquid state by raising the temperature to a recrystallization range. Thus at this temperature the larger part of the boundaries of the crystallites is changed to the liquid state; and this is nothing but the first part of assumption 1). When this state is reached, the liquid state or the cybotactic state can exist as such for all temperatures in very narrow interstices between neighbouring crystallites or crystals, as is considered before in the case of the crystallization in the melt. This property of the persistency of the liquid or amorphous layer at the crystal boundary seems to play an important rôle in the process of recrystallization of plastically deformed metals.

When a metal is deformed plastically above a certain degree, the majority of the crystallites are to be supposed to have a lattice distortion of various degrees after deformation. Now let us suppose

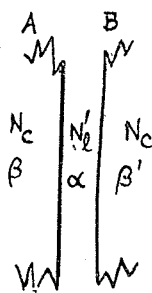


Fig. 1

that a crystal nucleus, which has no lattice distortion, is formed spontaneously in the liquid layer between the neighbouring distorted crystallites and has grown to a considerable size without suffering any distortion by the process of recrystallization. Then the molecular exchange between the undistorted and the distorted crystals will be made easily by means of the thin liquid layer between them which, when once formed, can persist for ever. In Fig. 1, suppose A and B to be the undistorted and distorted crystals respectively, which are separated by a thin liquid layer, and let  $N_c$  and  $N'_l$  be the surface density of the molecules of the crystals and the liquid at the boundary surfaces. Moreover let  $\alpha$  be the crystallizing factor and  $\beta$  and  $\beta'$  be the melting factors of the undistorted and distorted crystals respectively. Then, as the distorted crystal is supposed to melt easier than the undistorted one, the value of  $\beta'$  should be greater than  $\beta$ . As to the value of  $N'_l$ , it is considered to be much lessened from its normal value at a narrow interstice between

neighbouring crystals and at a recrystallization temperature which is of course much lower than the melting point of the crystal. Now consider that the growth of the undistorted crystal has reached such a state that the lessened value of  $\alpha N'_i$  has just become equal to the value of  $\beta N_c$ . Then as the value of  $\beta' N_c$  is greater than that of  $\beta N_c$ , that is than that of  $\alpha N'_i$ , some part of the outer surface of the distorted crystal will be transformed to the liquid phase. This increases the value of  $N'_i$ , and a further growth of the undistorted crystal will continue again. In this way the growth of the undistorted crystal will proceed further and further by means of the intermediary action of the liquid layer by consuming the distorted crystals, as long as distorted crystals remain. Ordinarily, with a cold worked metal, it is usual to have many undistorted crystal nuclei; and in this case the end of the crystal growth by recrystallization is reached when the undistorted, newly grown crystals have come into contact with each other with only a thin amorphous layers between them. In this way the presence of a persistent thin liquid layer between two neighbouring crystals enables the less distorted crystal to grow by consuming the more distorted one, as long as there is a contrast in the degree of lattice distortion, even of very small degree. It is already stated that very small crystals are much easier to melt than larger ones. Thus the contrast in size between neighbouring crystals acts for crystal growth, in exactly the same way as the contrast in the degree of lattice distortion, and the growth of the larger crystal by consuming the smaller one is more favourable than the growth in the reverse direction. A sharp end of a protuberance of a crystal which is surrounded by another crystal, like a very small crystal, will have the same tendency to melt more easily. This property of the effect of the shape and the size of the crystal may be stated simply as follows: the greater the convexity of a crystal the more easily it melts. The presence of a persistent thin liquid layer between neighbouring crystals seems to be very important in understanding the mechanism of the crystal growth in the process of recrystallization. By virtue of the existence of such a thin liquid layer the growth of the stronger crystal can proceed as long as there is some contrast, even in very small degree, in the melting tendency between two neighbouring crystals, such as is due to the degree of lattice distortion or to the degree of convexity. Thus the final state reached by sufficiently high and prolonged heating in recrystallization,

will be such that there is little contrast in lattice distortion, in convexity and in crystal size between neighbouring crystals. This is in conformity with actual observation in comparative evenness of the size of new crystals formed by recrystallization, and in that their boundaries consist of rather continuous curves or lines without too much ruggedness. In respect to the latter fact T. Sutoki<sup>1)</sup> has made a very interesting observation. He observed that a crystal grows, in most cases, on its concave side by consuming the convex side of the neighbouring crystal in the final stage of recrystallization, where the lattice distortion contrast has seemed to have been almost removed. As to the evenness of the crystal size mentioned above, it is no more than a rough statement; and a considerable range of difference in crystal size is of course present. This signifies that the crystal growth cannot be determined by the crystal size contrast alone, but that there are still some other factors affecting this; and the writer's view simply regards the lattice distortion contrast as the most prominent among these factors. In the case of the growth of crystals to a considerable size in a specimen composed of very small crystallites, which have suffered different degrees of lattice distortion by the preceding process of cold working, it seems probable that it took place in many steps, and not in one step directly from all the nuclei to the final crystals by consuming the initial distorted crystals. At first a lot of nuclei will be formed rather evenly in the specimen, then by consuming all the old distorted crystallites situated in the region between them they will grow until they come into direct contact with each other. The release of the internal strain by this first step of crystal growth will of course, be considerable, but it will not be complete for all the new crystals on account of too many new crystals in an irregular manner and the different velocity of crystal growth and melting from crystal to crystal. Thus after this first stage of the crystal growth, there remains still the lattice distortion contrast and the crystal size contrast; and the crystal growth of the stronger and healthy ones will proceed further by consuming the weaker ones in succession, as long as there remains some lattice distortion and crystal size contrast between neighbouring crystals. This is like the players in a tennis tournament, and the final equilibrium is attained among the strongest crystals having almost the same strength. In this way, the displacement of all the initial

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1. T. Sutoki: *Sci. Rep. Tōhōku Imp. Univ.*, **17**, 857 (1928).



crystallites by new crystals in recrystallization seems to be explained clearly, with the aid of the idea of a persistent thin liquid layer between the neighbouring crystals.

During the growth of a crystal by recrystallization it may happen sometimes that its power of growth is reduced accidentally by some cause, such as by suffering some degree of distortion etc.; and consequently that the crystal, though it has started from a strong nucleus, is consumed by some other which has grown under more favourable circumstances. But statistically the crystals which can survive to the end will be those grown from the strongest nuclei. According to the writer's view, crystal nuclei are formed in the melt at the boundaries of the deformed crystallites. Consequently the strongest nuclei within a certain volume, will be formed at the localities in the metal where the crystallites have suffered severest disturbance by the process of cold working and have become easiest to melt. This consideration was stated similarly in a former paper,<sup>1)</sup> where a rough calculation was attempted of the number of crystals formed by recrystallization at different temperatures and with different degrees of cold working.

Next let us consider the effect of temperature on the thin and persistent liquid layer between neighbouring crystals having the same crystallizing power. Suppose that the thin liquid layer exists between two perfect crystals as shown in Fig. 2. In this case the surface density  $N_c$  of the molecules situated at the crystal lattice can be considered to be the same for different temperatures. But the other factors  $\alpha$ ,  $\beta$  and  $N'_l$  affecting the crystal growth must be considered to vary with the temperature. When the temperature  $T$  is raised  $\alpha$  will decrease and  $\beta$  will increase in the manner as is shown in Fig. 3. With most metals, which expand by melting, the proportion of the values of  $\alpha$  and  $\beta$  at its melting point will be such as is shown by the proportion of the lengths of the lines AC and BC;  $\alpha$  being somewhat greater than  $\beta$  corresponding to the value of  $N'_l$  which is smaller than  $N_c$ . When two neighbouring crystals are in equilibrium with the liquid layer between them at a temperature below the melting point, we have, corresponding to a reduced value of  $N'_l$ ,  $\alpha N'_l = \beta N_c$ , and consequently

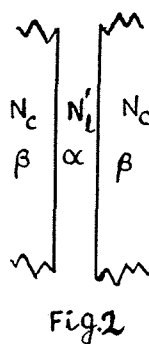


Fig. 2

1. U. Yoshida, S. Nagata and Ch. Mitsuki; These Memoire, A, 19, 169 (1936).

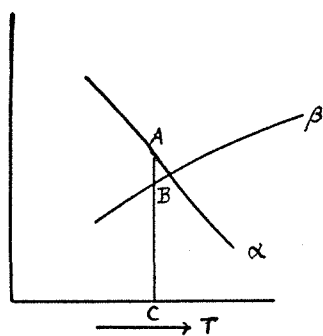


Fig. 3

$\beta/a = N'_l/N_e$ . As is seen from Fig. 3,  $\beta/a$  and consequently  $N'_l/N_e$  increase with increasing temperature: that is the surface density of the liquid molecules in the thin layer increases gradually with increasing temperature and approaches a normal value at the melting point. As the decrease of  $N'_l$  with decreasing temperature is assumed to be caused by the decreasing thickness of the thin liquid layer, the increase of  $N'_l$  with increasing temperature signifies the increase of the

thickness of the thin liquid layer as it approaches the melting point. When a metal such as aluminium is recrystallized by prolonged heating at a high temperature which is very near the melting point, the crystal boundaries become engraved as narrow grooves, the width of which increases with temperature and attains sometimes to about one mm. at a temperature just below the melting point. The formation of such grooves at the crystal boundaries was ascribed in the previous report<sup>1)</sup> to the melting at the crystal boundaries and consequently to the rapid evaporation occurring there. This is in harmony with the present theory.

In the light of these considerations, the mechanism of crystal growth by recrystallization is fully explained by assuming the presence of the persistent thin liquid layer at the crystal boundaries. By any theory which ascribes the crystal growth to sublimation and condensation, the rapid crystal growth at high recrystallization temperatures seems not to be accounted for. The consideration that the contrast in lattice distortion, in convexity and in crystal size between two neighbouring crystals is cancelled by the presence of the thin liquid layer at the crystal boundary in the process of recrystallization is nothing but the assumption 2) in the former paper,<sup>2)</sup> that the metal crystal melts more easily at its contact surface with the melt than in its interior. When a metal is cooled to the room temperature after recrystallization, part of the liquid layer existing between two neighbouring crystals will be solidified as the extension of one or both of them, but still a very

1. U. Yoshida and K. Koyanagi; loc. cit.
2. Ibid.

thin layer between them will be left as super-cooled amorphous solid in the cybotactic sense just as it is in the case of crystallization in a melt.

Very recently F. M. Jaeger and A. J. Zuithoff<sup>1)</sup> measured at temperatures higher than about 500°C the specific heat of two specimens of cobalt, one composed of comparatively large crystals and the other composed of very fine crystallites deposited by electrolysis. They found that the latter had a smaller specific heat, and moreover that the specific heat of the latter increased and became equal to that of the former when its crystals had grown to a considerable size by recrystallization. Similar observations on cold worked metals and alloys were also made by S. Sato,<sup>2)</sup> H. Quinney and G. I. Taylor.<sup>3)</sup> According to these authors some amount of energy is imparted as latent energy to the metals and alloys by the process of cold working, and this latent energy is re-emitted by heating the metals and alloys to high temperatures. These facts are in accordance with the writer's view that the latent heat of fusion is smaller with smaller and distorted crystals, and consequently that the smaller and the distorted crystals are easier to melt than the larger and undistorted ones. When the specific heat of the specimen composed of very fine and distorted crystallites is measured at high temperatures, the distortion will be released and small crystallites will melt and gradually recrystallize into larger ones; and by this process of annealing and recrystallization, heat evolution of some amount takes place by virtue of release of the distortion and of the preponderant latent heat of fusion of larger crystals as compared with that of smaller ones which melt and transform into larger ones by the recrystallization. Consequently the specific heat of the specimen will be reduced by this amount of heat evolved by the annealing and recrystallization.

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1. Jaeger and Zuithoff: Proc. Amsterdam, **43**, 815 (1940).
  2. S. Sato: Sci. Rep. Tôhoku Imp. Univ. **20**, 140 (1931).
  3. H. Quinney and G. I. Taylor: Proc. R. S., **163**, 157 (1937).