

# On the Possibility of Formation and Persistence of the Amorphous Layer on Polished Metal Surface and in Intercrystalline Boundaries

by

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## Abstract

The possibility of formation of the amorphous layer on polished metal surfaces and in intercrystalline boundaries by plastic deformation of metals is inferred. The liquid layer at high temperatures or the amorphous layer at low temperatures, when once formed in intercrystalline boundaries, is reasoned to be persistent irrespectively of the temperature change, by keeping the thickness of the layer in equilibrium with the temperature. Lastly it is stated that Mr. Hasinguti's objection to the writer's theory of recrystallization can not be accepted.

## Introduction

Beilby's hypothesis assuming the formation of an amorphous layer on the surface of metals by polishing and in the intercrystalline boundaries of metals by plastic deformation is a subject variously discussed for a long time. This is a very important problem, and whether such an amorphous layer really exists or not is a key point to determine the direction of the general tendency of the theory of metals. In the previous papers<sup>1</sup> concerning the recrystallization and plastic deformation of metals, the explanation was made by assuming the presence of amorphous layer; and now the possibility of its formation and persistence will be considered in detail.

## Formation of Amorphous Layer

F. P. Bowden and K. E. W. Ridler<sup>2</sup> measured thermo-electrically the temperature at the contact surface of two different metals by mutual sliding, and found that the temperature at the contact

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1. U. Yoshida and K. Koyanagi: These Memoirs, 18, 9, (1935); U. Yoshida, S. Nogata and Ch. Mitsuki: These Memoirs, 19, 169, (1936); U. Yoshida: These Memoirs, 23, 207, (1941); 23, 351, (1941); 彙線, 2, 152. (昭 16).

2. Proc. R. S., A, 154, 640, (1936).

points could be raised up to the lower melting point of the two metals by sufficient magnitudes of the speed of sliding and of the compressive force. From this experiment F. P. Bowden and T. P. Hughes<sup>1</sup> reasoned the possibility of formation of the amorphous layer on the surface of metals by polishing and in the intercrystalline boundaries by plastic deformation. They considered that some microscopic localities on the polished surface of a metal or in the glide plane of the metal crystals are melted instantaneously by being heated locally by polishing or by plastic deformation. As the temperature of the bulk of the metal is not raised during this local melting, the molten localities solidify almost at the same instant as they are melted. Thus having no time to crystallize they solidify as amorphous solid by keeping unaltered the manner of molecular aggregation as in the liquid. Next F. P. Bowden and L. Leben<sup>2</sup> investigated the sliding motion of two metals minutely. They pressed by a spring a small polished metal ball against a polished flat surface of another metal, by constraining the metal ball in its lateral motion by bifilar springs. The flat metal was made to move very slowly by hydraulic pressure in the horizontal direction with a uniform velocity irrespectively of the frictional force against the ball; and the accompanying lateral motion of the ball was measured in a very magnified scale by means of reflection of a light beam from a mirror attached to the ball. The motion of the metal ball thus examined was found to be fluctuating very violently, and that it proceeds by the repetition of very small "stick and slip" process; the ball sticks to the plate at an instant and moves with it with the same velocity for a short time, then the ball slips against the plate suddenly and sticks again to the plate. In some cases using the combination of two metals of different kinds the temperature variation at the contact point was observed thermoelectrically by means of a string galvanometer, and it was found that the temperature rises violently only in the slipping period, but not at all in the sticking period. Bowden and Leben made their experiments with various combinations of different metals and alloys having different hardness and melting points, and they examined microscopically the tracks of slide impressed on the surface of the flat plate during the sliding process. As to the ultimate mechanism of the stick and slip process, they could confirm by a careful measurement and

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1. Proc. R. S., A., **160**, 575, (1937).

2. Proc. R. S., A, **169**, 371, (1939).

a microscopic examination that there was no direct correlation between the discontinuities of the sliding motion and the surface scratches, and came to the conclusion that the stick was caused by the creation of local metallic junctions formed by a sudden solidification of the molten localities on the contact surface, which were due to the local heating during the slipping process just previous to the sticking period.

All the experiments of Bowden and others indicate that by the frictional sliding of two solid surfaces, there takes place so unexpectedly a violent local heating that the local melting of the solids happens without much difficulty. As the local melting is entirely in microscopically narrow region, and the solids in bulk are not particularly heated in this case, the molten localities solidify suddenly as amorphous solids almost at the same time as they were melted. As regard to the formation of the amorphous solid by a rapid cooling of the melt, Luyet's experiment<sup>1</sup> seems to be worthy of mentioning. He pressed very suddenly a stream of running water at room temperature by two copper disks which had been cooled by liquid air. On examining very quickly the solidified piece of water through the crossed nicols, he found that the solidified water was amorphous, and the crystallization to ice was observed to occur only at much higher temperatures. In the case of common metals we are unable, of course, to detect the presence of their amorphous solid state conclusively. However, considering from Luyet's experiment, it seems not unreasonable to presume the formation of the amorphous solid by sufficiently rapid cooling in this case.

It was stated<sup>2</sup> in one of the previous papers that by the plastic deformation of metals a severe process, such as the destruction of the metal crystals into very fine crystallites having scattered orientation, occurred at the same time as the ideal crystal slip along the slip direction in the slip plane. If we consider the frictional sliding between neighbouring crystallites in the same way as in the case of the surface friction between metals, the formation of the amorphous solid layer between neighbouring crystallites will be readily accepted by imagining the occurrence of the local heating, melting and subsequent sudden solidification.

Bowden and others regard the local heating which takes place by the frictional sliding as the cause for the formation of the amorphous

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1. B. J. Luyet: *Phys. R.* **56**, 1244, (1939).

2. U. Yoshida: *These Memoirs*, **23**, 351, (1941); *應用物理*, **11**, 1, (昭 17).

layer on the polished surface or in intercrystalline boundaries of metals. In addition to this cause, the writer reasonably assumes that the crystallites, which are smashed into very minute particles and severely distorted in their crystal lattices and endowed with internal stresses of considerable amount during the process of plastic deformation or of polishing, are much easier to melt and consequently their melting points fall noticeably. According to the writer's opinion<sup>1</sup> the phenomenon of recrystallization of cold worked metals proceeds by the growth of the crystal nuclei formed spontaneously in the melt at the crystal boundaries by consuming the old small and distorted crystallites. If the writer's opinion is to be admitted the above assumption that the smaller and more distorted crystals are easier to melt than larger and less distorted ones is necessary in explaining the mechanism of recrystallization. As the crystal lattice is most stable when there is no internal stress or lattice distortion, the potential energy of the constituent molecules of the crystal lattice is higher when it is internally stressed or distorted, and consequently the latent heat of fusion becomes smaller in this case. If we plot in graph the relation between the molecular latent heats of fusion of monoatomic elements and their melting points expressed in the absolute scale we can see clearly the general tendency that the melting point is lower when the molecular latent heat of fusion is smaller. Moreover, with the elements belonging to the face-centred cubic lattice and the close packed hexagonal lattice, where the manner of molecular arrangement is almost the same in both lattice types, the melting points are approximately proportional to the molecular latent heats of fusion. Considering from this view point it will not be unreasonable to imagine that the melting point of an element becomes lower than the normal value when its crystal lattice is distorted or stressed internally. Next, if we consider the case of extremely small crystallites similarly as in the case of very small liquid droplets, their vapour pressure ought to be much higher than the normal value; and consequently the latent heat of sublimation and the latent heat of fusion should be much reduced in this case. The lowering of the melting point in this case which just corresponds to the lowering of the boiling point of very small liquid droplets can be imagined by such decrease of the latent heat of fusion. Considering in the above way, the lowering of the

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1. U. Yoshida: *These Memoirs*, **23**, 325, (1941).

melting point of the crystallites, when they are extremely minute and distorted in their lattice and internally stressed, can be clearly understood. According to the experiments made by Farren and Taylor,<sup>1</sup> when a metal or alloy is cold-worked the most part of the work done during this process is generated as heat, but the remaining part amounting to 5—15% is imparted in increasing the potential energy of the constituent molecules. This increase of the molecular potential energy corresponds at least mostly to the decrease of the latent heat of fusion of the crystallites, which are smashed into very minute ones and distorted in their lattice by the process of cold-working.

Very recently Jaeger and Zuitoff<sup>2</sup> measured at temperatures higher than about 500°C the specific heats of two specimens of cobalt, one composed of comparatively large crystals and the other 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 made by Sato,<sup>3</sup> Quinney and Taylor.<sup>4</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 reemitted on heating the metals and alloys at high temperatures. These facts are in accordance with the writer's view that the latent heat of fusion is smaller with smaller and distorted crystal, and consequently that the smaller and the distorted crystals are easier to melt than larger and the 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 the 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.

1. W. S. Farren and G. I. Taylor: *Proc. R. S., A*, **107**, 422, (1925).
2. F. M. Jaeger and A. J. Zuitoff: *Proc. Amsterdam*, **43**, 815, (1940)
3. S. Sato: *Sci. Rep. Tohoku Imp. Univ.* **20**, 140, (1931).
4. H. Quinney and G. I. Taylor: *Proc. R. S.* **163**, 157, (1937).

If we consider in the above way, by the formation of the amorphous layer on a metal surface by polishing and in intercrystalline boundaries of a metal by plastic deformation, the temperature reached by the local heating does not need to be so high as the normal melting point of the metal, but is sufficient if it becomes the same with, or higher than, the decreased melting point of very small and distorted crystallites. The amorphous layer formed in intercrystalline boundaries softens in its softening temperature range, and becomes liquid when the temperature is raised still higher. In this state the crystal growth can be imagined to take place toward the liquid layer, and the question whether the liquid layer will be exhausted or not by such crystal growth becomes very important. However, for the writer's theory of recrystallization to be consistent, which assumes that the crystal growth by recrystallization takes place by means of an intermediary action of the liquid layer between neighbouring crystals, the liquid or amorphous layer should be permanent and persistent, and this point will be considered in the following.

#### Persistence of the Liquid or Amorphous Layer between Neighbouring Crystals

Let us suppose that two crystals of a substance are separated by a thin liquid layer of the same substance and that the crystals grow toward the intermediate liquid layer. As with most substances the volume contracts by crystallization, when thus crystals grow toward the intermediate liquid layer, the latter becomes subjected to a negative pressure. This negative pressure is enormous when the liquid layer is extremely thin. Let us consider, for example, that a thin layer of liquid water is sustained by its surface tension between two parallel plates. If we take the surface tension of water approximately as 70 dynes/cm, then the magnitude of the negative pressure becomes about one atmosphere with the width of  $1/1000$  mm of the layer of water. With several metals their surface tensions at temperatures above the melting points were measured and have been found to take the values of 3—25 times the value of water. If we take these values roughly as 10 times that of water, then the magnitude of the negative pressure of the melt existing between two neighbouring metal crystals will be 10 atmospheres with the thickness of  $1/1000$  mm of the layer of the melt. Moreover as the surface tension of a liquid increases with decreasing temperature, its value of the melt below the

melting point, which is the point in question in the present case, will be enormously greater than that above the melting point. If we take this roughly as 10 times that above the melting point, then the negative pressure of the melt of metals below the melting points will amount to about 100 atmospheres with  $1/1000$  mm thickness of the melt. Further, as the negative pressure increases in inverse proportion with the thickness of the melt, its amount will increase infinitely even to more than 1000 atmospheres when the layer of the melt becomes thinner than about  $1/1000$  mm and the temperature is still farther decreased.

When a liquid is subjected to a negative pressure, its vapour pressure decreases from its normal value. This just corresponds to the case of a solution, where the vapour pressure and consequently the freezing point of the solvent decreases by virtue of the presence of the osmotic pressure; and the lowering of the freezing point of the melt subjected to a negative pressure in very narrow interstices between two neighbouring crystals can thus be understood from the lowering of its vapour pressure. When the temperature decreases more and the layer of the melt between the two neighbouring crystals becomes much thinner by the growth of the crystals the increase of the negative pressure and consequently the lowering of the freezing point will proceed endlessly until the last stage is reached, where the extremely thin liquid layer solidifies as an amorphous solid and the crystal growth is entirely suspended. The liquid layers having enormous negative pressures as was considered above will not always be present over all the crystal boundaries and magnitude of the negative pressures will not necessarily be uniform for all parts of the liquid layers, so that they can act as a uniform hydrostatic tension on all the surfaces of the crystals, but the negative pressures will differ from place to place and further there will remain some portions in the crystal boundaries where they are not wetted by the liquid layer in the case of crystallization in the melt and of the recrystallization of cold worked metals, so that the negative pressures exercise heterogeneous stresses to the crystals. This also assists in lowering the melting point of the metals by giving lattice distortions and internal stresses to the crystals.

As to the freezing of water and some other liquids kept in very narrow cavities and interstices of silica-gels, clays composed of very fine particles and similar substances, researches by the dilato-

metric<sup>1</sup> and calorimetric<sup>2</sup> methods have been made by many authors. According to these investigations the water and other liquids confined in very narrow cavities and interstices freeze only at the temperatures much lower than their normal freezing points. For example Bouyoucos and his co-workers have found that there still remains some liquid water without freezing in very narrow interstices of clay particles at as low a temperature as  $-78^{\circ}\text{C}$ . The circumstances in this case are somewhat different from our case, where the liquid layer is the same substance as the crystals confining the liquid; but the essential cause for such remarkable lowering of the melting point seems to be the presence of an enormous negative pressure in the liquid layer, and consequently the above experiments may be looked upon as a confirmation of the writer's view.

The freezing point of the liquid layer confined between two neighbouring crystals decreases with the decrease of the thickness of the liquid layer, and there exists an equilibrium between the temperature and the thickness of the liquid layer. Thus when temperature falls by a certain degree from that corresponding to an equilibrium condition the crystals grow and the liquid layer becomes thinner and attains the new equilibrium value corresponding to the decreased temperature. In this way, when temperature is decreased continuously the liquid layer gets thinner and thinner until the last stage is reached, where the extremely thin liquid layer solidifies in an amorphous solid state and the crystal growth stops. In other words the layer of liquid or of amorphous solid, when once formed in the boundary space between two neighbouring crystals of the same substance in the case of crystallization from the melt or of recrystallization of polycrystalline metals, can persist as such for ever at all temperatures by adaptation to the temperature change with the variation of its width. When the temperature is raised in a substance in which the intercrystalline boundaries are cemented by the amorphous solid layer at room temperature, and when it attains the softening temperature of the amorphous layer, this layer turns to a liquid. As the

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1. G. T. Bouyoucos and his co-workers: Mich. Agr. Coll. Expt. Sta. Tech. Bull., **24**, (1915); **27**, (1916); **31**, (1916); **36**, (1917); **37**, (1917); **42**, (1918); J. Agr. Res., **8**, (1917); **15**, (1918); **20**, (1920); **20**, (1921); Soils Sci., **11**, (1921).

H. W. Foote and Blair Saxton: J. Amer. Chem. Soc., **38**, 588, (1916); **39**, 627, 1103, (1917).

F. W. Parker: J. Amer. Chem. Soc., **43**, 1011, (1921).

Jones and Gortner: J. Phys. Chem., **36**, 387, (1932).

2. W. A. Patrick and W. A. Kemper: J. Phys. Chem., **42**, 369, (1938).



crystal nuclei can be formed in the liquid layer in this case, this softening temperature of the amorphous layer will be the lowest recrystallization temperature of the substance. When the temperature is further raised the thickness of the liquid layer increases correspondingly and it will attain a considerable amount at the temperatures just below the melting point, as is revealed by the occurrence of the grooves of noticeable width at the crystal boundaries on the surface of the specimen.

### On Mr. Hasiguti's Objection to the Writer's Theory of Recrystallization

Recently Hasiguti<sup>1</sup> considered the recrystallization process of cold-worked metals as a kind of "exchange of place" (Platzwechsel) of molecules as in the case of diffusion of metals, and applied the equation of velocity of chemical reaction of Boltzmann's type to the temperature variation of the velocity of recrystallization of copper and aluminium. For the activation energy thus calculated for the exchange of place of molecules he obtained the values of about ten times those of the heats of fusion of the respective elements, and concluded that the presence of such large values of the activation energy is a strong argument against the writer's theory of recrystallization which assumes the melting at the intercrystalline boundaries as an essential factor for the process. The literature cited by Hasiguti is only the first paper published on this subject by the writer and Koyanagi, and it seems that Hasiguti was then ignorant of the later papers and consequently the writer's opinion was not well understood by him. According to the writer's experience the crystal growth by recrystallization depends upon the relative contrast in the stability of the crystal lattice between the neighbouring crystals, and does not occur in one step, but goes on gradually in many steps by successively repeating the process of mutual eating between neighbouring crystals until the final state is reached, in which the growing powers of all the crystals are almost balanced. The crystal growth by recrystallization goes on in general very rapidly at first, but becomes slower gradually with the progress of the steps of recrystallization and finally it becomes almost stopped when an equilibrium of the growing power of crystals is nearly attained. Consequently the recrystallization velocity can not be taken

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1. Proc. Phys. Math. Soc. Japan, 24, 270, (1942); 日本金屬學會誌, 6, 282 (昭 17).

as constant throughout the whole process as Hasiguti did. Moreover the equation of velocity of chemical reaction can be applied to the case where the microscopic change of the ultimate particles takes place only in one direction. For example, consider the case of the vaporization of liquid molecules from the surface of a liquid. If all the evaporating vapour molecules could be perfectly pumped away and no vapour molecules would come back to the liquid, then the equation under consideration could be applied for the velocity of evaporation. However, when there are some vapour molecules which come back to the liquid, then the microscopic changes of molecules are in two opposite directions: i. e. evaporation and condensation; and the macroscopic velocity of evaporation becomes the difference of two velocities of these two microscopic changes in opposite directions. Thus in our case, which may be called a "semi-equilibrium change," the equation under consideration can not be applied. The fact that Richardson's formula for the thermionic emission from a hot body can only be applied to the case when all the emitted electrons are perfectly taken away to the anode, so that the current saturates, is a good example for the unidirectional microscopic change. According to the writer's theory of recrystallization the crystal growth of either one of the two neighbouring crystals A and B takes place by its consuming the other by means of the intermediary action of the liquid layer existing between them. The microscopic changes of molecules in this case consist of four different kinds: dissolution of the molecules belonging to the crystal A into the liquid phase, the condensations of the liquid molecules to the surfaces of the crystals A and B, and the dissolution of the molecules belonging to B into the liquid phase; and the macroscopic velocity of the crystal growth in this case becomes the algebraic sum of the velocities of these four different microscopic changes. In other words, the crystal growth in our case proceeds by a duplicated semi-equilibrium change and the equation of velocity of chemical reaction as was used by Hasiguti is not applicable here.

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