Melting of Metal-Crystals at their Boundaries, and a Theory of Recrystallization of Metals

By

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Abstract

It is found that when the temperature of a metal is raised to a value just below its melting point, the metal melts at its crystal-boundaries. Next, by assuming that the metal melts at its crystal-boundaries in its recrystallization-temperature, a theory of the recrystallization of metals is proposed.

Melting of Metal-Crystals at their Boundaries

When the writers were endeavouring to get large single crystal plates of aluminium by the stress-annealing method, it happened rather accidentally that the recrystallizing temperature in the furnace was just below the melting point of aluminium (657°C). When the aluminium plates were taken out from the furnace, after a prolonged exposure to such temperature, the writers noticed that the surfaces of the plates were engraved with a zigzag network of shallow and thin grooves. This indicates that the aluminium was melted at these grooves. Next, the surfaces of the plates were etched by some reagent, and it was confirmed that the grooves were nothing but the boundaries of the single crystals of aluminium. This shows that the aluminium crystals are easier to melt at their boundaries.

The furnace used in the present experiment was a resistance type, consisting of a porcelain tube about one metre in length and five cms. in diameter and a nichrome wire wound uniformly around the former. The furnace was set vertically, and some long test pieces of metal plates of suitable size were hung in the middle part of the porcelain tube of the furnace. Though the temperature would be nearly uniform in the middle part of the tube, it would not be exactly so. The

temperature in the furnace is of course governed by the electric current passing through the nichrome wire. And though it is very difficult at a definite point in the furnace to keep the temperature just at or just below the melting point of the metal by the regulation of the electric current, this difficulty is not met with at the place in the furnace occupied by the specimens, as the present furnace has some non-uniform temperature-distribution. Assisted by such circumstances the writers could succeed in raising the temperature of the specimens just below the melting point of aluminium or that of some other metal, at least at some parts of them.

Some of the photographs of the surfaces of the metal plates exposed to such temperature for a long time are reproduced in Plate I. In the case of Figs. 1_a and 1_b in Plate I, a commercial aluminium plate having the size $39 \times 3 \times 0.1$ cm^3 was first annealed at the temperature of about 390°C for 80 hours, next it was elongated by 1.25% of its original length, and then it was subjected to the temperature just below the melting point of aluminium for about 70 hours. A zigzag network of thin and shallow grooves engraved on the surface of the plate in this case will be seen clearly in Fig. 1_a, Plate I. The width and the depth of the grooves are estimated to be of the order of 0.1–0.3 mm. in this case. Next the same part of the aluminium plate is etched by hydrochloric acid, and its photograph is shown in Fig. 1_b. By comparing these two photographs it will be clear now that the thin and shallow grooves engraved on the surface of the aluminium plate are nothing but the boundaries of single crystals of aluminium. This point was confirmed to be so with nearly all the specimens prepared similarly, which amounted to more than one hundred in all. However it occured rarely that the crystal boundary did not coincide exactly with the groove. This seems, in all probability, to be due to the growth of a crystal across the groove in the cooling state after the formation of the groove at the crystal boundary.

Thus the coarseness of the network of the grooves depends generally upon the size of the crystals. As is well known, the metal crystals produced by recrystallization in a piece of a metal which has not been subjected to any slight preliminary elongation, do not grow much. Consequently the network of the grooves engraved on the surface of such metal ought to be fine. A commercial aluminium plate, without any preliminary annealing and elongation, was directly exposed to the temperature just below its melting point for about two days.

The appearance of the surface of the plate thus prepared is shown by Fig. 2, Plate I, and it reveals clearly a fine network of the grooves as is expected.

The fact that the grooves are formed at the crystal boundaries will still clearly be seen in Figs. 3_a and 3_b in Plate I. Fig. 3_a shows the etched surface of a single crystal plate of aluminium prepared by ordinary stress-annealing method. The recrystallization temperature in this case was lower by about fifty degrees than the melting point of aluminium, and any trace of the grooves could not be detected at the crystal boundaries by the naked eye. Next the same specimen was subjected to the temperature just below the melting point of aluminium for about twenty hours, and then comparatively deep and wide grooves were formed at the crystal boundaries. The etched surface of the specimen thus prepared is shown in Fig. 3_b in the plate. By comparing Figs. 3_a and 3_b it will clearly be seen that the crystals did not grow further and the grooving occurred exactly at the crystal boundaries by the second recrystallizing treatment. Here it must be noted that one portion in Fig. 3_b, which looks like a single crystal formed by the unification of two neighbouring single crystals in Fig. 3_a, is not really single but is composed of the same two crystals seen in Fig. 3_a. The cause of this ambiguity is nothing but an improper illumination of the specimen in taking its photograph. With the actual specimen no doubt is left on this point.

It is already stated that the grooves at the crystal boundaries are formed by the melting of the metal there. This consideration will be strengthened by the following instances. Once it occurred to the writers, with comparatively long aluminium plate and with sufficiently high temperature of the furnace which was able to form deep grooves, that the lower part of the plate fell down to the bottom of the furnace, by being separated from the upper part of the plate at their crystal boundary; and moreover that the fallen lower part was nearly broken at the crystal boundaries into several pieces. Still it occurred to the writers, with sufficiently high temperature which was able to form deep grooves, that a whole single crystal formed in an aluminium plate slipped a little from one side of the plate to the other. These instances show clearly that the metal became soft at the crystal boundaries in consequence of the melting of the metal there.

It is already stated that the temperature in the furnace used in the present experiment is not exactly uniform, but a little different

according to the position in the furnace.   In a long furnace such as
employed by the present experiment the temperature will become
gradually lower from the maximum in the middle towards each end.
As in the case of the specimen shown by Fig. 3ₚ in Plate I, the lower
end of the specimen reached nearly to the middle of the furnace, the
temperature was expected to become higher gradually from the upper
part of the specimen to its lower part.   The lower end of the specimen
was melted as a whole in this case, as seen in Fig. 3ₚ; therefore the
temperature of the specimen is supposed to become lower toward its
upper end from the melting point of aluminium at its lower end.
According to this temperature distribution the grooves formed at the
crystal boundaries became thinner gradually toward the upper end.
This fact that the grooves become thicker as we approach to the melt-
ing point of aluminium was confirmed by the writers with more than
30 specimens.

The question why the crystal boundaries become grooved by melt-
ing is not clear yet; but so far as the writers have experienced three
following causes seems to be conceivable.   1) Single crystal pieces are
displaced a little differently by gravity.   2) The melted part at the
crystal boundaries is evaporated more strongly than at other places.
3) The molten part at the crystal boundaries flows downward by
gravity.   Among these three causes the third one seems to be very
rare, and it happens only when the groove is pretty thick.   It is
seldom, too, that we can detect clearly that the grooving is due to
the first cause.   Consequently the second cause, i. e. the evaporation
of the metal, seems to be the most predominant factor in forming the
groove at the melted crystal boundaries

As to the lowering of the melting point at the crystal boundaries
two causes seems to be conceivable.   1) Accumulation of some im-
purities at the crystal boundaries.   2) It is a proper nature of the metal
itself that it is easier to melt at its crystal boundaries even when there
is no accumulation of the impurities.   If we assume that, in recry-
stallizing the metal, the impurities contained in the metal are displaced
to the crystal boundary, the accumulation of the impurities must be
located in a very thin sheet at this boundary.   Thus if we assume
that the melting of the metal at its crystal boundaries is due to the
first cause, the groove formed by the melting of the metal should be
correspondingly thin always.   However this does not accord with the
actual observation, as the width of the groove sometimes attains to

one or more than one millimetre, as seen in Fig. 3b or in Figs. 4a and 4b in Plate I. Next the writers repeated the same experiment as before with pure aluminium plate (99.8% Al + 0.08% Si + 0.12% Fe + x% O_2), and it was confirmed that the network of the grooves was also produced at the crystal boundaries similarly as with commercial aluminium plate. Such grooves obtained with pure aluminium plates are shown in Figs, 4a and 4b in Plate I. Here Fig. 4a represents the appearance of the unetched surface, and Fig. 4b that of the etched surface.

The melting of the metal at its crystal boundaries just below its melting point is not confined to aluminium. The writers carried out similar experiments with commercial plates of tin and zinc, and the network of the grooves formed by the melting of the metal at its crystal boundaries was respectively observed with these two metals. The grooves formed on the surface of a tin plate are represented in Figs. 5a and 5b in Plate I: where Fig. 5a shows the unetched surface and Fig. 5b the etched surface. Considering thus it seems not to be unnatural to conclude that the melting of the metal at its crystal boundaries at a temperature below its melting point is a universal nature of the metals.

A Theory of the Recrystallization of Metals

It is already stated that when a metal is subjected for a long time to its recrystallization temperature which is very near to its melting point the grooves formed by the melting of the metal at its crystal boundaries become thinner as the recrystallization temperature decreases. Though, when the recrystallization temperature is still lowered, any trace of the grooves can not be detected at the crystal boundaries, still it seems not to be unnatural to suppose that the metal is melted by very thin layers at its crystal boundaries even in such a case; and standing on this assumption the writers attempted to establish a theory of recrystallization of metals.

It is already stated too that when the recrystallization temperature is just below the melting point of the metal, the width of the grooves formed by the melting of the metal at its crystal boundaries attains sometimes to one or more than one millimetre. This seems to indicate that the crystal is easier to melt not only at its crystal boundaries but also at the contact surface of the metal crystal with its melt than at the interior of the crystal. Moreover the writers assume that the

distorted metal crystal is easier to melt than that without any distortion. This assumption is somewhat different from that of Tarschisch[1], who proposed a theory of recrystallization of metals by assuming that the metal is easier to melt at the part where interatomic distances became larger by deformation, and that the crystal nuclei are formed in the part thus melted. However the second assumption made by Tarschisch that in the course of recrystallization the crystal nuclei are formed in the melted part of the metal seems to be supported at least to a certain degree by the investigation made by K. Tanaka[2] on the recrystallization of slightly deformed single crystals of aluminium. According to him, the orientation of the micro-crystals produced by a slight deformation of a single crystal of aluminium is not much different from that of the mother single crystal, and the orientation of the crystals formed by recrystallizing such slightly deformed single crystal is independent of the orientation of the micro-crystals in a slightly deformed single crystal of aluminium. Thus, as to the formation of the recrystallization nucleus, the writers assume with Tarschisch that the nucleus is formed in the melted part of the metal.

Now, relying upon the considerations stated above, let us consider the mechanism of the recrystallization of metals. When a metal is deformed by some mechanical treatment, the metal crystals are smashed into finer micro-crystals; and these micro-crystals are a little distorted, in other words they are strained, resulting to the lowering of their melting point. Next when such a metal is subjected to a recrystallization temperature, the metal will melt at the boundaries of the microcrystals by very thin layers, and then undistorted perfect crystals will be formed in the melts as the recrystallization nuclei, whose melting point is higher than that of the distorted micro-crystals. By such difference of the melting point between distorted and undistorted crystals, the recrystallization nuclei will grow gradually by the crystallization of the melts on their surfaces, and the distorted micro-crystals will melt correspondingly at their boundaries, resulting in the growth of the new undistorted crystals by the consumption of the distorted micro-crystals. Thus when all the distorted micro-crystals are consumed and the whole metal piece is occupied by new undistorted crystals the recrystallization process actually comes to an end; because the stability as a solid is the same for all the new undistorted crystals.

1. Tarschisch: Phys. Z. S., **35**, 469 (1934)
2. Tanaka: These Memoirs, **11**, 229 (1928)

It seems natural to consider that the degree of the lowering of the melting point of a distorted metal crystal depends directly upon the magnitude of the distortion or strain, and the melting point will decrease with increasing distortion. Thus when a metal is strongly deformed the locations in the metal where the micro-crystals suffer the strains of more than a certain value become numerous, i. e. the recrystallization nuclei become numerous, and the crystals formed by recrystallization become smaller in size. However when the deformation of the metal is small, for example one or two percent elongation as in the case of obtaining large single crystals by recrystallization method, the locations in the metal where the micro-crystals suffer the strains of more than a certain value become rare; i. e. the number of the recrystallization nuclei become rare, and thus the crystals obtained by the recrystallization process become larger.

As is stated above, the writers assumed that the melting point of a metal crystal depends upon the strain it suffers. Though this consideration appears to be inconsistent with the fact that a metal has a definite melting point, actually it is not so. When the temperature of a deformed metal is increased gradually up to its melting point, all the distorted metal crystals will be replaced by new undistorted metal crystals by the recrystallization process before the temperature reaches to the melting point of the metal. Thus when the melting point of the metal is reached, the melting is not from initial distorted crystals but from new undistorted crystals to the liquid. Reversely in the solidifying state of a metal from its melt to its crystals, undistorted metal crystals formed by solidification are in contact with its melt. Considering in such a way, the actual melting point of a metal is nothing but the temperature at which the undistorted metal crystal is in contact with its melt, which is definite and proper to the undistorted crystals of the metal.

Till now the writers stated a theory of recrystallization of the metal, which stands on the consideration that the metal melts at its crystal boundaries at its recrystallization temperature. This consideration was confirmed to be so only at the temperature just below the melting point of the metal, and for a recrystallization temperature still lower than this it is no more than a hypothesis. However if this is an actual phenomenon, it will have an important bearing on various properties of the metals. For an example, such phenomenon as intermetallic diffusion may be caused by the melting of the metals at their crystal boundaries.
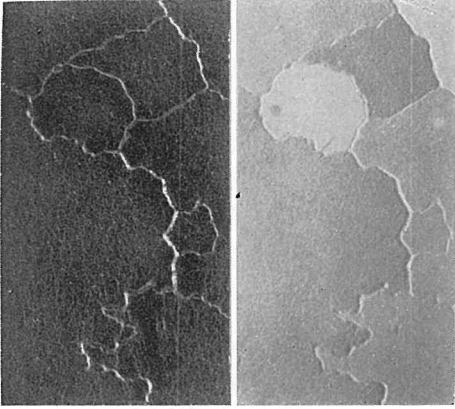
In conclusion the writers wish to express their hearty thanks to Professor D. Uno of the Metallographical Department for his kindness in furnishing the specimen of pure aluminium to the writers.

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Plate I
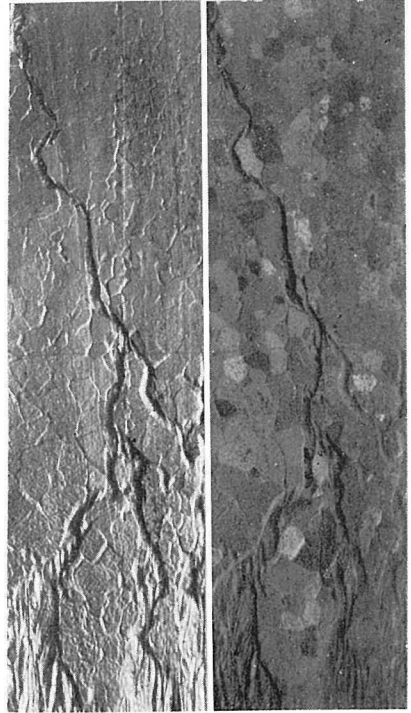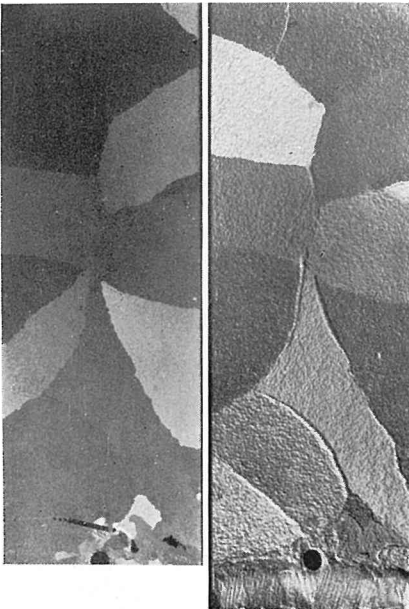
2 ×

Fig. 1a　　　Fig. 1b

1.3 ×

Fig. 4a　　　Fig. 4b

Fig. 2

Fig. 3a　　　Fig. 3b

2 ×

Fig. 5a　　　Fig. 5b