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On the "Precursory Recrystallization" in Copper and Brass Foils prepared by the Mechanical Rolling

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Abstract

A peculiar phenomenon as may be called a "Precursory Recrystallization," which had been found in our foregoing investigation with iron and nickel pulverized [1] or rolled [2] mechanically, was inferred to occur not only in the transition elements as stated above, but also in most metals undergone by some severe inner strain. To make clear whether such an inference were correct or not, the progress of the structural change by rising the temperature of the copper and brass foils of uniform thickness prepared mechanically by rolling them in various degrees (reduction percentages in thickness amount to 62.70%~99.89% in copper, while 95.00%~99.20% and 93.70% in α and β brass respectively), was examined with X-rays in the present experiment, similarly as in the previous ones.

As the consequence of this X-ray examination, it was confirmed that the usual recrystallization phenomenon in all the copper foils examined, takes place at 100°C~250°C, a temperature somewhat lower than that generally accepted as the recrystallization temperature of copper, almost irrespectively of the duration of annealing (2 min.~5 hr.): i. e., at the temperature above stated, the growth of the micro-crystals forming these foils, which tended to arrange themselves in a fibrous way, each having initially one of its ⟨111⟩ axis parallel to the direction of rolling, was observed to take place in comparatively short time, together with the conversion of the fibrous axis from the aforesaid ⟨111⟩ axis to ⟨100⟩ axis.

Among these copper foils, those corresponding to the reduction percentage 97.31%~99.68% were especially noticed to give rise to the "Precursory Recrystallization" as had previously been found with iron and nickel undergone by a severe mechanical work. By this "Precursory Recrystallization," two fibrous arrangements of the micro-crystals of considerable size were seen to be newly formed. One of these fibrous arrangements consisted of the micro-crystals, each having its ⟨111⟩ axis parallel to the direction of rolling; while in the other, the micro-crystals were so arranged that their common axis of the same indices

1. H. Hirata, H. Fujihira and E. Fujii, Rev. Phys. Chem. Japan, Commemoration Vol., 86, (1946).

2. H. Hirata and M. Yanagisawa, Rep. Inst. Chem. Research, Kyoto Univ., **18**, 94, (1949).

coincided with the normal to the aforesaid direction, in the plane of the surface of the foils. Here, it must be remarked that such a structural change due to the "Precursory Recrystallization" in the foils belonging to this category, was also given rise to by aging these foils at the room temperature for a few days.

The reason why the "Precursory Recrystallization" could hardly be detected in copper foils belonging to the other categories, were found to be explainable by the same consideration, which assumes the existence of two different kinds of the potential barriers of atoms in the metals undergone by a severe mechanical work, as previously reported in connection with iron and nickel. Especially, with regard to these which had been worked more severely than those displaying the "Precursory Recrystallization," it was confirmed that the "Precursory Recrystallization" had already taken place in the midst of the mechanical rolling, by an information deducible from the inner structure of the copper foils inflicted the heating and the rolling procedures alternately, as well from the change of their corrosibility, observed in the present experiment.

Moreover, it must be postscribed that the recrystallization phenomenon could also be detected to take place with α and β brass foils, by which the common axis of the micro-crystals forming a fibrous structure parallel to the direction of rolling, was seen to convert from ⟨110⟩ axis to ⟨100⟩ axis of the face-centred and body-centred cubic lattices respectively, in company with the augmentation of each micro-crystal, at a temperature a little higher than that of the copper foils. Nevertheless, within the scope of our examination, the "Precursory Recrystallization" could not be observed to occur with these brass foils.

Introduction

From the results of our foregoing X-ray examination on the structural change due to the annealing of iron and nickel, which had previously been undergone by a severe mechanical work as pulverization or rolling, it was confirmed that the recrystallization in these metals takes place in two distinct steps by heating; i. e., the growth of crystal grains takes place not only at the recrystallization temperature (about 600° C in iron and 700° C in nickel), but at a certain temperature (about 420° C and 470° C in iron and nickel respectively) far lower than the recrystallization temperature.

Such a peculiar phenomenon as may be called a "Precursory Recrystallization" (for the sake of abbreviation, let us denote it by "P. R." hereafter), that occurs at a temperature far lower than the recrystallization temperature, was inferred not to be presented as a characteristic of the transition elements above stated, but by a general property of the most metals containing some potential barriers of atoms considerably lowered due to the mechanical work. To make clear whether the aforesaid inference were correct or not, the writers were induced to repeat essentially the same X-ray examination as before, with copper and brass by the Laue method, utilizing the heterogeneous X-rays emitted from Cu anticathode. In this X-ray examination, the photographic plates were

always placed perpendicularly to the incident beam at a distance of 3 cm. behind the specimen, unless otherwise stated. The results thus obtained will be briefly described below.

Specimens

The specimens used in the present experiment were prepared by rolling electrolytic copper (99.977 % in purity), which had previously been annealed in vacuum at 600° C for 1 hour, in various degrees. Supplementary to these copper foils, some foils of α brass (25.62 % Zn—Cu) and β brass (50.22 % Zn—Cu) prepared by essentially the same procedure were also examined. The detailed conditions under which they were prepared are given in the following Tables 1 and 2 :—

TABLE 1.

Procedures of preparing the Copper Foils

No. of the Specimens	Thickness of the Specimens (in μ.) Before Rolling (d_0)	After Rolling (d)	Reduction % (R) $R=\frac{d_0-d}{d_0}\times 100$	Remark
A	574	204	62.70	
B	1865	50	97.31	On the way of the procedure of rolling the foil was placed between two copper plates for the furtherance of reducing its thickness.
C	ditto	20	98.93	
D	ditto	6~9	99.68~99.52	
E	ditto	2~3	99.89~99.84	
F	ditto	5	99.73	On the way of the procedure of rolling the foil was folded, for the furtherance of reducing its thickness.
G	ditto	2	99.89	

TABLE 2.

Procedures of preparing the Brass Foils

No. of the Specimens	Composition of the Specimens	Thickness of the Specimens (in μ) Before Rolling (d_0)	After Rolling (d)	Reduction % (R) $R=\frac{d_0-d}{d_0}\times 100$	Remark
H	Cu 74.38 %	1000	50	95.00	α Brass
I	Zn 25.62 %	ditto	8~10	99.20~99.00	
J	Cu 49.78 % Zn 50.22 %	800	50	93.70	β Brass

By the way, it must be noted in connection with the thickness of the foils d_0 given in the second columns of Tables 1 and 2, that the values indirectly determined from the weight and the area of the foils, were

always seen to coincide fairly well with those measured directly by means of a varnier caliber (when $d > 50\,\mu$) or Shimazu's minimeter (when $d < 50\,\mu$). This shows us without doubt that all the foils under consideration were of the uniform thickness. Moreover, it should be postscribed that among these specimens here tabulated, Specimens C~G were obtained from Specimen B by the furtherance of the rolling procedure.

Except for Specimen A which was found too thick to give rise to any reliable diffraction pattern of X-rays, each one of the specimens above tabulated was annealed again in vacuum at various temperature (50° C~800° C) for various durations of annealing (2 min.~5 hr.), just before it was illuminated by X-rays, unless otherwise stated. However, to render Specimen A suitable for X-ray examination, the writers were obliged to remove its outer portion by pickling this specimen in dilute nitric acid, after the aforesaid heat-treatment. In addition to the aforesaid specimen, metallic copper deposited by putting a small piece of zinc into a solution of copper sulphate of the concentration 10 %~13 % in weight, was also used as the standard specimen by the way of comparing the effects of the mechanical work.

Experimental Results

Some of the Laue photographs obtained in the present experiment are reproduced in Figs. 1~20, Plate 1 and Figs. 22~26, Plate 2. In each one of these Laue photographs, the corresponding annealing temperatures and durations of annealing of the specimen, are respectively denoted by the abbreviations T and D. To take the Laue photographs here reproduced except for Fig. 20, Plate 1, each specimen was so placed that its foliate surface was perpendicular to the incident X-ray beam, by setting the direction of rolling vertically, while, Fig. 20, Plate 1 was obtained on the photographic plate placed at a distance of 2 cm. behind the specimen, when the direction of rolling was tilted by an angle of 45° from its vertical position towards the incident beam.

Supplementary to Plates 1 and 2, the outlines of the diffraction patterns in some Laue photographs, most of which were not reproduced, were described in Tables 3 and 4 classifying with one another. Here, it must be postscribed that the patterns inserted in Tables 3 and 4, as well as those reproduced in Plates 1 and 2 were only those given rise to by the specimens annealed for 1 hour after the mechanical rolling, unless especially remarked in the brackets. Nevertheless as can be seen from Figs. 7~9 and 11, 12, Plate 1, when the specimens rolled by an equal amount, were annealed at an equal temperature, their structural changes were found to

remain almost unaltered with one another, irrespectively of the duration of annealing. This shows us that the structural changes above stated

TABLE 3. Constituents of Each Diffraction Pattern taken with the Copper Foils.

No. of the Specimens \ Annealing Temp. (in °C)	Room Temp.	50	70	100	120	150	160	200
A	cR cCB				cR cCB	AL cR cCB	dR	dR
B	cR ↑ cSB ⟨111⟩			cR ↑ cSB ⟨111⟩	cB ↑ cCB ⟨111⟩ dCB		dR dCB	
C	ditto		cR ↑ cSB ⟨111⟩	↑ dSB ⟨111⟩ cR ↑ cSB ⟨111⟩		↑ cSB ⟨100⟩ ↑ dSB ⟨111⟩ dR		
D	ditto	↑ cSB ⟨111⟩ cR ↑ dSB ⟨111⟩		↑ cSB ⟨100⟩ ↑ dSB ⟨111⟩ ↑ cSB ⟨111⟩ cR		↑ cSB ⟨100⟩ ↑ dSB ⟨111⟩ dR		↑ cSB ⟨100⟩ ↑ dSB ⟨111⟩ dR
E	ditto		cR cSB ⟨111⟩			cR ↑ cSB ⟨111⟩		
F	ditto			↑ cSB ⟨111⟩ cR	cR ↑ cSB ⟨111⟩ cB		↑ cSB ⟨111⟩ dR cR	
G	ditto			(a little) ↑ cSB ⟨111⟩ cR	cR ↑ cSB ⟨111⟩		↑ cSB ⟨111⟩ cR	↑ cSB ⟨111⟩ cR

TABLE 3. (continued)

No. of the Specimens \ Annealing Temp. (in °C)	250	300	350	450	500	600	700	800
A								AL
B		dR dCB	dR dCB		dCB dR	dCB AL	dCB AL	dCB AL
C	←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩ dR		←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩ dR	←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩ dR		(5 hr.) ↑ cSB ⟨100⟩ ←↑dSB ⟨111⟩	←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩ AL	←↑dSB ⟨111⟩
D	↑ cSB ⟨100⟩ ←↑dSB ⟨111⟩ dR	↑ cSB ⟨100⟩ ←↑dSB ⟨111⟩		←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩		←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩	←↑dSB ⟨111⟩ dR ↑ cSB ⟨100⟩	(5 hr.) ←↑dSB ⟨111⟩ ↑ cSB ⟨100⟩
E	↑ cSB ⟨100⟩ dR			↑ cSB ⟨100⟩ dR		↑ cSB ⟨100⟩ dR		↑ cSB ⟨100⟩ dR
F	dR ↑ cSB ⟨100⟩							dR
G		dR ↑ cSB ⟨111⟩					dR ↑ cSB ⟨100⟩	

usually comes to the end in a comparatively short time. Consequently, the description in Tables 3 and 4 may be deemed to hold usually good to

all the diffraction patterns taken in the present experiment with copper and brass foils annealed for various durations.

TABLE 4.

Constituents of Each Diffraction Pattern taken with the Brass Foils.

No. of the Specimens \ Annealing Temp. (in °C)	Room Temp.	100	150	200	250	300	400	500
H (α Brass)	↑ cSB ⟨110⟩ cR	↑ cSB ⟨110⟩ cR	cR cSB ?	cR cSB ?	cR	cR	cR	dR
I (α Brass)	cR cWB	cR cWB	cR cWB	cR cWB	cR ↑ cSB ⟨100⟩	↑ cSB ⟨100⟩ dR	↑ cSB ⟨100⟩ dR	↑ cSB ⟨100⟩ dR
J (β Brass)	↑ cSB ⟨110⟩ cR	↑ cSB ⟨110⟩ cR	cCB cR	cCB cR	dR	dR		

P.S. In each block of Tables 3 and 4, the constituents of the diffraction pattern in each Laue photograph are represented in the order of their predominance by the following abbreviations, here the constituents observed before the heat-treatment being underlined. Among these constituents, discontinuous ones consisting of a number of intense spots are designated by the prefix d against c corresponding to the continuous ones.

CB: complex distribution of radiating bands given rise to by an irregular assemblage of several fibrous-like structures; ↑SB ⟨hkl⟩: a set of radiating bands given rise to by a single fibrous structure corresponding to the rotation of micro-crystals around ⟨hkl⟩ axis parallel to the direction of rolling; ↙↑SB ⟨hkl⟩: two sets of radiating bands given rise to by two fibrous structures corresponding to the rotations of micro-crystals around the axes parallel and normal to the direction of rolling respectively; WB: intense bands on Debye rings showing the presence of the fibrous nature of weak degree; R: Debye rings; AL: assemblage of a number of small Laue spots.

Discussion of the Experimental Results

1. Copper Foils

Among the experimental results above stated, those represented in Plate 1 and Table 3 lead us to the following considerations with respect to the copper specimens :—

First of all, the rolled copper foils prior to the annealing procedure were found to give rise to the diffraction patterns in the Laue photographs, reproduced in Figs. 1, 3, 6 and 17, Plate 1, as well those inserted in the second column of Table 3. As can be seen in these patterns, those which were produced by the foils of the comparatively small reduction percentage as Specimen A (its reduction percentage R amounts to about 62.70 %), consisted of a set of continuous Debye rings due to the (111) and (200) reflections of the characteristic radiations Cu K_α and Cu K_β from the face-centred cubic lattices of copper crystals ; on these Debye rings, the intense segments attributable to the superposition of the complex congregation of radiating bands also came to appear, showing the presence of an irregular assemblage of several fibrous-like structures. While, in the foils of the larger reduction percentage as Specimens B~G ($R \geqq 97.31$ %), the aforesaid complex congregation of radiating bands was found to fuse together into a set of radiating bands given rise to by a fibrous arrangement of the micro-crystals, each having its $\langle 111 \rangle$ axis parallel to the direction of rolling. Accordingly, the specimens of the copper foils used in the present experiment, to begin with, may be deemed to be composed of the micro-crystals of the diameter 10^{-3}cm.~10^{-4}cm. before they were annealed. It can also be inferred with regard to these specimens prior to the annealing, that the copper foils of the smaller reduction percentage of the order 62.70 %, are composed of an irregular aggregation of the micro-crystals, which arrange themselves quite confusedly, except only those forming several fibrous-like structures ; while, in the foils of the larger reduction percentages than 97.31 %, the micro-crystals are seen to arrange themselves in a definite fibrous way, with one of their $\langle 111 \rangle$ axis parallel to the direction of rolling.

Next, let us reflect upon the structural change of these specimens due to the annealing procedure. Among these specimens, with respect to those undergone by a comparatively slight mechanical work as Specimen A, it can be seen from Figs. 1 and 2, Plate 1 as well as from the second row of Table 3, that the congregation of the radiating bands already mentioned, grew less conspicuous and an irregular assemblage of small spots became newly appreciable, at a temperature of about 150° C.

Furthermore, at about 160° C, the rearrangement of these spots so as to form a set of discontinuous Debye rings was observed, together with the complete extinction of the former radiating bands. But, such a regular distribution of the intense spots sitting in rings was violated again, when the foils were heated at 800° C. Here, it must be remarked parenthetically that a piece of metallic copper deposited from the solution of copper sulphate by the procedure as already mentioned, were seen to give rise to a series of the Laue photographs (not reproduced), which showed that the growth of the newly germinated crystal nuclei begins by heating at about 300° C in such a specimen inferred free from any severe inner strain due to the mechanical works. This shows us that even in Specimen A undergone by a comparatively slight rolling, the temperature at which the growth of the crystal nuclei began to take place, was somewhat lowered by the mechanical work. Thus, Specimen A may be deemed to lose its fibrous-like nature at 150° C~160° C by the growth of the micro-crystals newly generated, then to display the augmentation of these micro-crystals at about 800° C, up to those of the diameter 10^{-2}cm.

When the reduction percentage of the copper foils was promoted to 97.31 %~99.68 % as was the case of Specimens B, C and D, a set of radiating bands each consisting of innumerable feathery spots became newly observable accompanied by the old ones, in the diffraction patterns, at an annealing temperature 50° C~120° C, as can be seen in Fig. 7, Plate 1 and in the third, fourth and fifth rows of Table 3. It goes without saying that the appearance of such coarse radiating bands indicates the segregation of the micro-crystals of a considerable size (10^{-2}cm.~10^{-3}cm. in diameter), arranged themselves in a fibrous way. The temperature at which these coarse bands begin to appear, was noticed to be far lower than the recrystallization temperature of copper generally accepted (about 200° C), not to mention about that of the deposited copper due to the difference of the solutional pressures as already stated. It was also observed that this temperature was the more lowered the more increased the reduction percentage of the specimen. Especially, from Specimen D of the largest reduction percentage among the specimens belonging to this category, the aforesaid coarse radiating bands were noticed to be produced, when it was kept even at the room temperature for a few days. Thus, the appearance of such radiating bands may be conceived to be due to the "P. R." in copper, similar to those previously detected with iron and nickel.

If we inspect the diffraction patterns in which the coarse radiating bands above stated are visible as in Figs. 4, 5, 7, 13, 16, Plate 1, and as some

of those inserted in the third, fourth and fifth rows of Table 3, it can be remarked that the angular distribution of these bands coming to appear from Specimen B undergone by a comparatively slight mechanical work, is rather confused; while, the bands taken with Specimens C and D rolled more severely than the above, are found to be distributed symmetrically to the direction of rolling. This fact shows us that when the copper foils are heated at a low temperature, the micro-crystals separate out without any remarkable influence of their orientation effect, in the specimen of the comparatively small reduction percentage of the order 97.31 % ; but in the specimens of the somewhat larger reduction percentages of the order 98.93 %～99.68 %, they tend to arrange themselves in a fibrous way. Further, the fibrous nature beared by the specimens of the somewhat larger reduction percentage above stated as Specimens C and D, was conceived from the diffraction patterns containing the coarse radiating bands of a regular distribution as shown in Fig. 7, Plate 1, to consist of two fibrous arrangements of the micro-crystals newly formed. One of these fibrous arrangements was made of the micro-crystals with their ⟨111⟩ axis parallel to the direction of rolling, while in the other, the micro-crystals being so arranged that their common axis ⟨111⟩ coincided with the normal to the aforesaid direction in the plane of the surface of foils. It can also be seen in Figs. 10, 12 and 15, Plate 1, together with the fourth and fifth rows of Table 3, that four radiating bands distributed symmetrically to the direction of rolling come to appear from Specimens C and D at a temperature about 100° C ～150° C, besides those given rise to by the " P. R." already mentioned. Such radiating bands were detected too, even with Specimen B, by the annealing at a temperature 160° C, though they are faint and rather confused (cf. Fig. 4, Plate 1). By rising the annealing temperature, these radiating bands were seen generally to grow the more conspicuous at the outset, then to tend fainter and fainter, until they became sometimes indetectable at 800° C especially in such a specimen as Specimen C (cf. the fourth row, Table 3). The annealing temperature at which the aforesaid bands came to appear most markedly, was confirmed also to vary according to the degree of the mechanical work: i. e., this temperature was observed to rise with the increase of the reduction percentage of the specimen, as to attain 700° C in Specimen C (cf. Fig. 11, Plate 1 and the fourth row of Table 3), when the mechanical work inflicted upon the specimen was comparatively small, but it lowered by the further increase of the reduction percentage. In addition to those above stated, these continuous bands were inferred from Figs. 10, 12 and 15, Plate 1,

to be given rise to by a fibrous arrangement of micro-crystals of the diameter 10^{-3}cm.$\sim 10^{-4}$cm., each having its $\langle 100 \rangle$ axis parallel to the direction of rolling.

To make clear the cause of such a structural change above stated, let us refer to the Laue photographs taken in the present experiment with the specimens belonging to the same category as Specimens C and D, which were reannealed immediately after the procedure of the annealing, at a certain temperature lower than that of the succeeded reannealing. According to this reference, the inner structures of the specimens indicated by these Laue photographs, were seen to remain nearly the same as those caused by the simple annealing at the reannealing temperature (say 600° C$\sim$800° C in the case of Specimen C) without preannealing, provided that the preannealing temperature was not so high (say 70° C$\sim$100° C in Specimen C) as to give rise to the aforesaid continuous band. On the contrary, if the preannealing temperature were high enough to produce these bands (say 350° C in Specimen C), the inner structures of the specimens were confirmed almost unaltered, as is clear by comparing Figs. 13 and 14, Plate 1, with those of the same specimens simply annealed only once at that preannealing temperature, irrespectively of the occurrence of the reannealing procedure. Thus, the aforesaid fibrous structure having $\langle 100 \rangle$ axis of the micro-crystals in common being tolerably stable, it may be deemed to arise from the usual recrystallization.

Previously, it has been inferred that the common axes of the fibrous structures produced by the "P. R." were two $\langle 111 \rangle$ axes intersecting perpendicularly with each other; while, that corresponding to the usual recrystallization was deemed to be $\langle 100 \rangle$ axis of the micro-crystals. To decide whether the above inference were correct or not, the writers tried to take a Laue photograph with Specimen C, which had been annealed at 800°C for 1 hour to give rise to the precursory as well as the usual recrystallizations, by tilting by an angle of 45° the direction of rolling from its vertical position towards the incident X-ray beam, as already stated. The Laue photograph thus obtained was reproduced in Fig. 20, Plate 1. In the annexed figure, Fig. 21, the theoretical positions of the radiating bands due to the "P. R." and the usual recrystallization calculated following to the

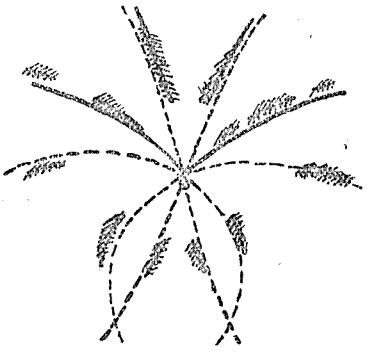

Fig. 21.

aforesaid inference by the aid of Nishikawa's formula,[3] are represented respectively by the dotted and full lines: while, the shaded part of the same figure is the copy of the diffraction pattern in the original plate[4] of Fig. 20, Plate 1. As may be seen from Fig. 21, the agreement between the calculated curves and the observed ones is satisfactory. Accordingly, it must be concluded that our foregoing inference is correct.

The facts which have hitherto been stated in connection with Specimens C and D, show us that in some district of the copper foils rolled at the reduction percentage 97.31 %～99.68 % the "P. R." takes place by heating these foils at a temperature (the room temperature～120° C) far lower than the usual recrystallization temperature. By this "P. R." the superposition of two fibrous structures are newly generated besides the former one due to the foregoing mechanical work, each one of these fibrous structures given rise to by the "P. R." being confirmed to be composed of the micro-crystals of the diamater 10^{-2}cm.～10^{-3}cm., so arranged that their common axes of the indices ⟨111⟩ are situated parallel and perpendicular respectively to the direction of rolling.

Moreover, in the other district of these foils which has not been inflicted the "P. R.", the usual recrystallization also occurs at a temperature somewhat lower than the recrystallization temperature generally accepted. By this recrystallization, the tendency of the growth of the micro-crystals as well as that of the conversion of the fibrous axis from the ⟨111⟩ axis to the ⟨100⟩ axis, can be detected.

Lastly, let us advance our considerations to the cases of Specimens E, F and G, which had been inflicted a mechanical work so severe as to correspond to the reduction percentage over 99.73 %. Among these specimens, Specimen E was prepared by the same procedure as those of preparing the others hitherto been mentioned; while Specimens F and G were rolled by a somewhat different way as denoted in the remark of Table 1. It was noticed, as may be seen from Figs. 7～19, Plate 1 as well as the diffraction patterns recorded in the rows that follow the sixth row of Table 3, that any one of these specimens did not give rise to the coarse radiating band even after the procedure of the annealing: furthermore, such an indication of the occurrence of the "P. R." could not be detected, even when these specimens were kept in the room temperature for several days. Merely, it was found that when Specimens E, F and G were annealed at a temperature 250° C, the diffraction patterns taken

3. S. Nishikawa and S. Ono: Proc. Tokyo Math. Phys. Soc., **11**, 131, (1913).

4. It is to be noticed that the diffraction patterns reproduced in Plates 1 and 2 are interchanged from right to left as compared with those of the original plates.

with them always indicated the occurrence of the recrystallization : i. e., these diffraction patterns were in some cases seen to contain a set of discontinuous Debye rings consisting of a number of small intense spots, as had previously been observed with Specimen B, while in the other cases, the patterns were made of by a set of radiating bands disclosing the presence of a fibrous structure in which the micro-crystals rotated around their common axis ⟨100⟩ parallel to the direction of rolling, as had been the cases of Specimens C and D. Thus, Specimens E, F and G must be looked upon not to present the "P. R." in spite of the far more severe mechanical work inflicted on them. Such a peculiar fact may be inferred probably to be due to the occurrence of the " P. R." early in the very midst of the procedure of rolling.

To make clear the above inference more decisively, the writers repeated X-ray examination essentially the same as before with a copper foil undergone by the heat and mechanical treatments alternately. Speaking the more precisely in connection with the procedure of the heat and the mechanical treatments above mentioned, a copper foils as Specimen C, which had preliminarily been rolled by an amount somewhat smaller than those in the cases of Specimens E, F and G, was annealed at a temperature high enough to give rise to the " P. R." (e. g., at 250° C in the case of Specimen C), then rolled again until the total amount of its reduction percentage from the beginning amounts to 99.73 %, before the progress of its structural change by heating was examined with X-rays. As the consequence of this X-ray examination, the aforesaid progress indicated by the Laue photograph, was seen essentially unaltered from those traced with Specimens E, F and G. This fact is in good accordance with our foregoing inference.

By way of the further confirmation of the above inference, the writers examined the corrosibility of Specimens A, C and E kept at the room temperature for several days, by pickling them into a dilute nitric acid of the concentration 10 %. It is expected in this case, that if the " P. R." had not taken place either in the midst or in the afterwards of the procedure of mechanical rolling, the aforesaid corrosibility should have increased with the increase of the reduction percentage of the specimens.[5] But, contrary to the above expectation, this corrosibility was found to decrease in the order of Specimens A, C and E, with the increase of their reduction percentages. This shows us that not to mention about Specimen C but even in Specimen E, the activation energy of the atoms

5. E. g., D. Uno, H. Hirata and K. Niimi, J. Metallog. Soc. Japan, **6**, 372, (1942).

had been decreased by "P. R." Our foregoing inference being thus confirmed again, we may conclude without doubt that the "P. R." took place in Specimens E, F and G in the midst of the mechanical rolling.

II. Brass Foils

As has already been mentioned, the specimens of the brass foils used in the present experiment belonged to the categories of α and β brass, which are generally known to form the face-centred cubic and the body-centred cubic lattices respectively. The results of X-ray examination carried out with regard to the structural change of these specimens due to the procedure of the annealing, were represented in Plate 2 together with in Table 4.

According to these results, the diffraction patterns taken with the foils of α brass prior to the annealing procedure (cf. Fig. 22, Plate 2 and the second column of Table 4), were seen to consist of a set of the radiating bands due to the fibrous arrangement of micro-crystals of the diameter 10^{-3}cm.$\sim 10^{-4}$cm., having $\langle 110 \rangle$ axis of each face-centred cubic lattices parallel to the direction of rolling, when the reduction percentage of the specimen was of the order 95.00 % as in Specimen H; while, the specimen corresponding to the reduction percentage of the order 99.00 %$\sim$99.20 %, as Specimen I, did not display any fibrous nature all the more, but gave rise to a number of continuous Debye rings (not reproduced). The fibrous structure of Specimen H was observed to begin to be gradually violated at a temperature 100° C$\sim$150° C, henceforth the violation of this fibrous structure being continued, until it was replaced by an assemblage of the comparatively larger micro-crystals of the diameter 10^{-2}cm.$\sim 10^{-3}$cm. at 500° C, due to the recrystallization, which gave rise to numerous small intense spots on the Laue photograph. One part of these spots distributed themselves on the Debye rings showing an irregular assemblage of the micro-crystals; while, the others were seen to form a set of discontinuous radiating bands corresponding to the fibrous structure made of the micro-crystals, each having its $\langle 100 \rangle$ axis parallel to the direction of rolling. With regard to Specimen I, the Debye rings and the radiating bands made of numerous intense spots in the Laue photographs (cf. Figs. 23 and 24, Plate 2, together with the third row of Table 4), which represented the occurrence of the recrystallization, were found to appear at a temperature about 250° C, the rise of the annealing temperature merely causing the augmentation of each spot.

Next, in connection with the foils of β brass, our examination was

restricted only to Specimen J corresponding to the reduction percentage 93.70 %. The Laue photographs taken with this specimen prior to the annealing procedure, were found to consist of a set of the Debye rings together with the radiating bands (cf. Fig 25, Plate 2 and the fourth column of Table 4). Thus, Specimen J may be looked upon as to be made of by a fibrous structure having ⟨110⟩ axis of each body-centred cubic lattices parallel to the direction of rolling, which was buried into an irregular assemblage of the micro-crystals of the diameter 10^{-3}cm. $\sim 10^{-4}$cm. Still, the diffraction patterns in these Laue photographs altered by an annealing at 250° C, as can be seen in the fourth row of Table 4, to those consisting of a set of Debye rings formed by a number of intense spots. This shows us that the micro-crystals in the specimen grew up by the recrystallization due to an annealing at 250° C, to those of the diameter 10^{-2}cm.$\sim 10^{-3}$cm., rearranging themselves without any regularity.

Anyhow, it must be remarked that with the foils of α and β brass undergone a severe mechanical works, the recrystallization was observed to take place at a temperature a little higher than that of the copper foils prepared by a similar procedure. Neverthless, within the scope of our examination, the " P. R." could not be observed to occur with these brass foils.

Conclusion

The arguments which have hitherto been advanced with respect to the progress of the structural change of the rolled foils of copper and brass due to the procedure of the annealing, lead us to the following conclusions :—

First of all, the copper foils prior to the annealing were found to consist of the micro-crystals of the diameter 10^{-3}cm.$\sim 10^{-4}$cm., which aggregated without any regularity except for those forming the fibrous-like structure. These foils can be classified into three classes, by the difference of the progress of the structural change due to the annealing ; the reduction percentages of the foils belonging to each one of these three classes were estimated to be the orders 62.70 %, 97.31 %$\sim$99.68 % and 99.73 %$\sim$99.89 % respectively.

Among these above classified, the foils belonging to the first class, which correspond to the reduction percentage of the order 62.70 %, are composed of the complex congregation of several fibrous-like structures buried into an irregular aggregation of the micro-crystals. These foils do not exhibit the " P. R." by heating. But, the growth of the micro-

crystals in these foils due to the recrystallization, begins at 150° C～160° C, a temperature somewhat lower than that generally accepted as the recrystallization temperature of copper. This shows us that the effects of the mechanical work upon the inner structure of the foils belonging to the first class, is not so severe as to produce the remarkable lowering of some potential barriers of the atoms forming these foils, as has already been stated in the previous reports.[1,2]

The foils belonging to the second class, which have been rolled mechanically so as their reduction percentage amounts to 99.31 %～99.68 %, are made of the micro-crystals arranged themselves in a fibrous way, having their ⟨111⟩ axis parallel to the direction of rolling, except for those irregularly aggregating, prior to the annealing procedure. These foils are distinguished for the "P. R." displayed by them, when they are annealed. The temperature at which the aforesaid "P. R." begins to take place, is varied from 120° C to the room temperature, according to the conditions. By this "P. R.", two fibrous arrangements of the micro-crystals of considerable size, each having the axis of the indices ⟨111⟩ in common. One of these fibrous arrangements has its common axis of the same indices coinciding with the normal to the aforesaid direction, in the plane of the surface of the foils. Anyhow, the occurrence of the "P. R." indicates that the mechanical work given to the copper foils belonging to the second class is severe enough to give rise to the remarkable of some potential barriers of atoms in these foils, as has previously been seen with iron and nickel inferred to bear a considerable amount of the inner strain due to the mechanical works of the pulverization or the rolling.

The usual recrystallization begins to take place in the foils belonging to the second class, by heating at a temperature of 100° C～150° C, which is seen generally to be lowered with the increase of the reduction percentage of these foils. By this recrystallization, the growth of the micro-crystals up to those of the diameter 10^{-2}cm.～10^{-3}cm., as well as the conversion of the fibrous axis from the axis of the indices ⟨111⟩ to that of ⟨100⟩, situated parallel to the direction of rolling, can be detected.

Lastly, the copper foils belonging to the third class, which have been rolled so severely as to correspond to the reduction percentage over 99.73 %, are seen prior to the procedure of the annealing to be essentially the same inner structure as those belonging to the second class. It is remarked that any indication of the occurrence of the "P. R." in these foils cannot be detected, notwithstanding the severe mechanical work inflicted on them. Merely the usual recrystallization is observed to take

place in these foils at a temperature about 250° C. Such a peculiarity of the foils belonging to the third class, can be attributed to the occurrence of the " P. R." early in the very midst of the procedure of rolling.

Next, the foils of α and β brass are confirmed also to be made of the micro-crystals of the diameter 10^{-3}cm.$\sim 10^{-4}$cm. prior to the procedure of the annealing. These micro-crystals aggregate without any regularity, except that some of them arranged themselves in a fibrous way, as those in the foils of α and β brass corresponding to the reduction percentages of the orders 95.00 % and 93.70 % respectively. This fibrous nature does not necessarily increase with the increase of the reduction percentage of the foils.

The axis of fibre is found to coincide with $\langle 110 \rangle$ axis of either face-centred or body-centred cubic lattices of α and β brass. In the former case, the recrystallization phenomenon takes place by the annealing at a temperature 500° C, which gives rise to a new fibrous structure with $\langle 100 \rangle$ axis situated parallel to the common direction as in the copper foils. But, the recrystallization temperature above stated is lowered with the increase of the reduction percentage, until it becomes to 250° C in the foils of α brass corresponding to the reduction percentage of 99.00 %$\sim$99.20 %. While, in the latter case, the foils of β brass recrystallize at a temperature of 250° C. Nevertheless it must be remarked that the " P. R." was seen to occur neither in α nor in β brass, within the scope of our examination.

In conclusion, the writers wish to express their best thanks to Dr. M. Sumitomo of the Sumitomo Metal Industrial Co., who supplied them with various samples of brass used in this experiment. Their thanks are also due to the Department of Education for the Scientific Research Expenditure defrayed in the present research.

PLATE 1. Laue Photographs of Copper Foils.

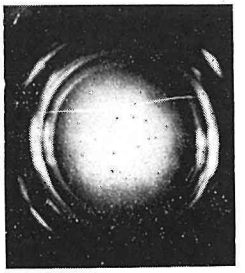

Fig. 1. Specimen A (before annealing)

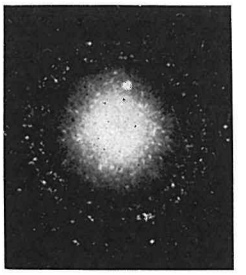

Fig. 2. Specimen A (T=160° C)

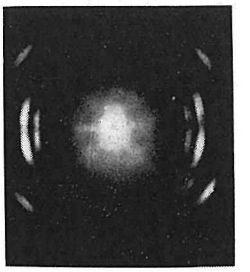

Fig. 3. Specimen B (before annealing)

Fig. 4. Specimen B (T=160° C)

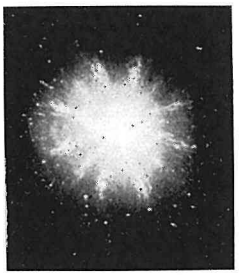

Fig. 5. Specimen B (T=800° C)

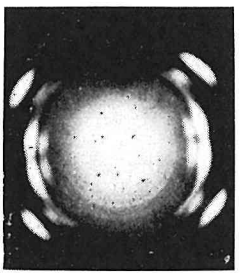

Fig. 6. Specimen C (before annealing)

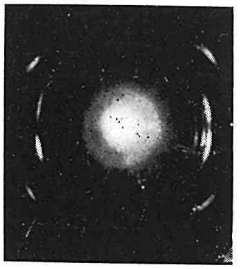

Fig. 7. Specimen C (T=100° C)

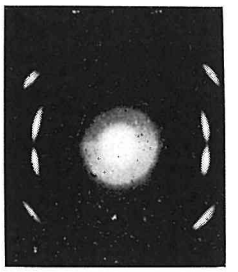

Fig. 8. Specimen C (T=100° C, D=5 min.)

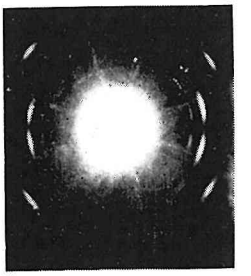

Fig. 9. Specimen C (T=100° C, D=30 min.)

Fig. 10. Specimen C (T=150° C)

Fig. 11. Specimen C (T=700° C)

Fig. 12. Specimen C (T=700 °C, D=5 hr.)

Fig. 13. Specimen C
(T=800° C)

Fig. 14. Specimen C
(T=350° C, D=1 hr. reannealed at T=800° C, D=1 hr.)

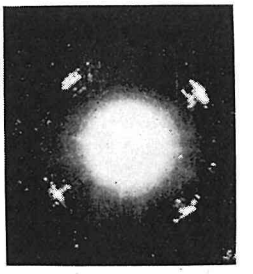

Fig. 15. Specimen D
(T=150° C)

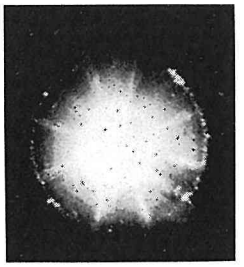

Fig. 16. Specimen D
(T=700° C)

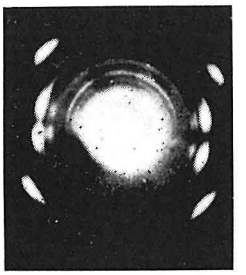

Fig. 17. Specimen E
(before annealing)

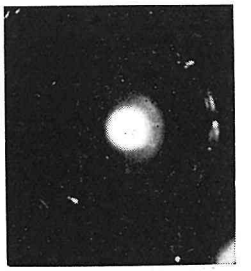

Fig. 18. Specimen E
(T=150° C)

Fig. 19. Specimen E
(T=800° C)

Fig. 20. Specimen C
(T=800° C obliquely illuminated)

PLATE 2. Laue Photographs of Brass Foils.

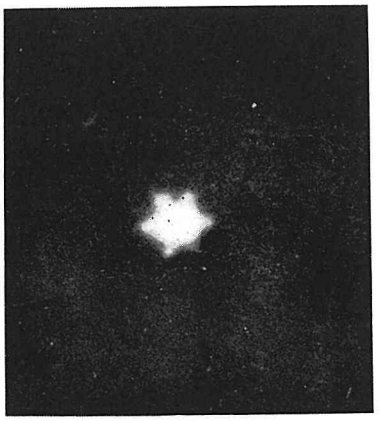

Fig. 22. Specimen H (before annealing)

Fig. 23. Specimen H (T=400° C)

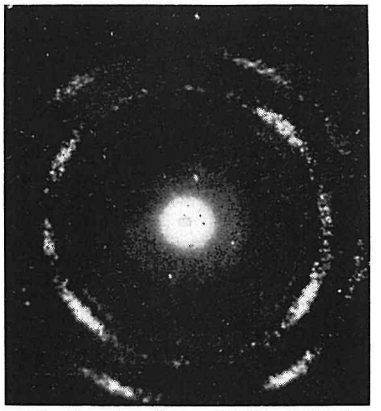

Fig. 24. Specimen H (T=500° C)

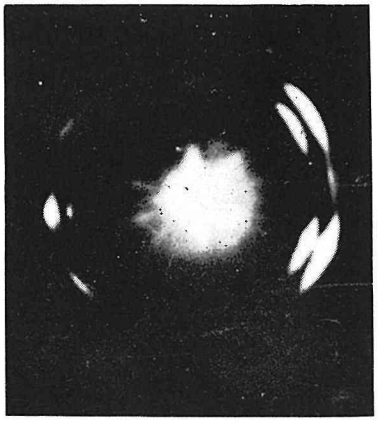

Fig. 25. Specimen J (before annealing)

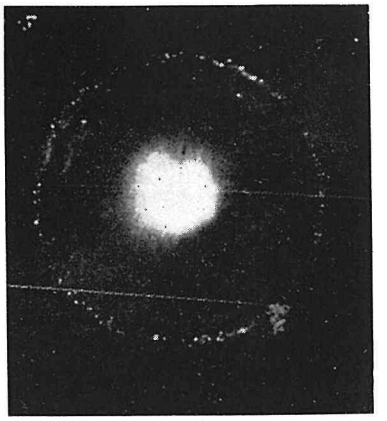

Fig. 26. Specimen J (T=250° C)