Electron Microscopy Study of the Precipitation Processes in Cu-2wt%Be Alloy*

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In order to make clear the precipitation processes in Cu-Be alloy, the structural changes upon ageing of the 2wt% Be alloy were examined in detail through an electron microscopy in particular by the use of the selected-area electron diffraction technique. The change in electron diffraction patterns with increasing ageing time or temperature was as follows. In the earliest stage, long streaks appeared in the $\langle 001 \rangle$ directions due to the formation of G.P. zones. Upon prolonged ageing, the streaks become shorter and intensity maxima appeared at about $2/3$ of $\{002\}$ reciprocal lattice vectors. This stage is distinct from the G.P. zone formation and may correspond to the formation of the γ'' phase. The structure of γ'' is considered to be a body-centered tetragonal, with Cu atoms at the corner and Be atoms at the body-center, and is different from that proposed by Geisler et al. Ageing at higher temperatures caused another superlattice reflection (CuAu(II) type, γ') to appear and $2/3$ reflections mentioned above to split. This splitting corresponded to the formation of the γ phase. From these observations, it has been concluded that the ageing sequence is $\alpha \rightarrow \text{G.P. zone} \rightarrow \gamma'' \rightarrow \gamma' \rightarrow \gamma$.

The structure of the final precipitate γ was identified to be the same as that of the equilibrium phase with the lattice constant $2.71\text{\AA}$. Then a new orientation relationship between the γ and α has been proposed, such that

$$\{103\}_{\gamma} // \{113\}_{\alpha}, \langle 010 \rangle_{\gamma} // \langle 1\bar{1}0 \rangle_{\alpha}.$$

Among several orientation relationships reported so far, only this one was consistent with our experimental results. In spite of the identity in structure, the final precipitates γ were associated with strain contrast around themselves, in contrast to the equilibrium phase. This fact suggests that the transformation γ' to γ might be martensitic in the nucleation stage. The mechanism of γ' to γ transformation is discussed along this line and from the viewpoint of coherency.

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I. Introduction

The precipitation processes upon ageing of Cu-Be alloys have been the subject of many investigations because of the unusual hardening and diffraction effects. Almost all of the investigations have arrived at a conclusion that the precipitation processes were initiated with a segregation of Be atoms on $\{001\}$ planes of the matrix, that is, with the formation of the so-called plate-like G.P. zones⁽¹⁾⁽²⁾. This conclusion seems to leave no doubt as to the formation of G.P. zones since it was reported recently that the G.P. zones were observed directly by transmission electron microscopy⁽³⁾⁽⁴⁾.

However, there have been dissenting views on the successive processes after the G.P. zone formation. Guinier and Jacquet⁽¹⁾ concluded from a single crystal X-ray diffraction study that no intermediate phase was formed before the equilibrium γ phase precipitated. On the other hand, Geisler et al.⁽⁵⁾ drew a different conclusion in spite of the use of the same experimental technique as that by Guinier and Jacquet; that is, they didn't recognize the existence of G.P. zones and concluded that the equilibrium γ phase precipitated through two intermediate phases in such a way that the precipitation sequence was $\alpha \rightarrow \gamma'' \rightarrow \gamma' \rightarrow \gamma$. Subsequently many other

workers have supported not the existence of the γ'' phase but the alternative precipitation sequence of $\alpha \rightarrow \text{G.P. zone} \rightarrow \gamma' \rightarrow \gamma$. However, two different kinds of the crystal structure of the γ' phase have been reported: One⁽⁴⁾⁽⁶⁾ was a *bct* lattice advocated by Geisler et al. and the other was a *bct* lattice of $c/a = \sqrt{2}$ which was equivalent to the CuAu(I) type ordered *fcc* lattice^{(7)~(9)}. It has also been reported that the final γ phase is not formed in grains but at grain boundaries. In this way, there remain many unsolved problems concerning the precipitation processes after the G.P. zone formation.

The present experiment was made in order to clarify the problems through an electron microscopy in particular with the use of the selected-area electron diffraction technique.

II. Experimental Procedure

The materials used were an electrolytic copper (99.99%) and a Cu-4% Be alloy (manufactured by Japan Gaisi Co.; the chemical composition of 4Be, 0.09 Si, 0.08 Fe and 0.03 Al in weight pct). These materials were prepared in a high purity aluminum crucible to

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have the composition of 2 wt% Be, melted by a high frequency vacuum furnace and then cast into an iron mould in vacuum.

The alloy ingot of 3 cm diameter was homogenized in argon atmosphere for 100 hr at 820°C and then subjected to hot-forging, annealing (for 24 hr at 820°C in vacuum), hot-rolling, annealing (the same as before) and cold-rolling. Finally ribbons of 0.15 mm in thickness were obtained. They were cut into plates of 2×2 cm², and the plates were solution-treated for 1 hr at 820°C in vacuum followed by quenching. These quenched specimens were aged for various periods at 250° and 350°C in a salt bath which is a mixture of nitrate and nitrite.

Thin foils for transmission electron microscopy were prepared by chemical-polishing and electro-polishing. The chemical polishing solution was a mixture of phosphoric acid 5, nitric acid 3 and acetic acid 2, and the electro-polishing solution was a saturated solution of chromic acid in phosphoric acid and the window method was employed. The electron microscope used was a Hitachi HU-11 D equipped with a tilting device, the accelerating voltage being 100 kV.

III. Experimental Results

Photo. 1 is an example of selected area electron diffraction patterns taken from the specimen aged for 10 hr at 250°C, the beam direction being parallel to the $[1\bar{3}0]$ of the α matrix. Streaks are seen along the $[001]_{\alpha}^*$ direction passing through all the diffraction spots. The appearance of streaks indicates the formation of G.P. zones on (001) planes of the α matrix, as many workers have reported so far. G.P. zones should also be formed on other two equivalent cube planes, $(100)_{\alpha}$ and $(010)_{\alpha}$, and then reciprocal lattice points might also be elongated along two directions normal to the planes. Extra spots ($\uparrow$) in Photo. 1 can be considered to correspond to the intersections of such reciprocal rods with the Ewald sphere.

Photo. 2 is a series of diffraction patterns showing how the $[001]_{\alpha}^*$ streaks linked with (000) and $\{002\}_{\alpha}$ spots change as the ageing time and temperature are increased. In these photographs, the figures inserted at the right upper corner indicate ageing temperatures and times, and those at the right lower corner the beam

directions. The streaks in (a) become shorter and the intensity maxima ($\uparrow$) appear at about $2/3$ of $\{002\}_{\alpha}$ reciprocal lattice vectors. The appearance of $2/3$ spots means the formation of precipitates with a characteristic crystal structure (γ''). As will be described later in detail, the γ'' precipitates can be considered to be products evolved from G.P. zones and to correspond to G.P. (2) or θ'' in Al-Cu alloys. In (b), the $2/3$ spots from γ'' increase in the intensity and have a tendency of spreading-out into a fan-shape. Such a tendency increases with the ageing time, and finally the fan-shaped spots change to triangle-shaped ones as clearly seen in (d) of the specimen aged for 140 hr at 250°C. When the ageing temperature was increased,

Photo. 1 Selected-area electron diffraction pattern showing $[001]_{\alpha}^*$ streaks due to the formation of G.P. zones.

Photo. 2 A series of electron diffraction patterns showing the change in $[001]_{\alpha}^*$ streak between (000) and $\{002\}_{\alpha}$ reflections upon ageing.

the triangle-shaped spots start splitting into two spots of the upper and lower sides as seen in (e) and finally splitted perfectly after the ageing for 5 hr at 350°C as shown in (f). (g) is a diffraction pattern taken from the same specimen as that in (f) together with the Debye-Scherrer rings from TiCl which was evaporated on the specimen surface. Referring to the diameters of the Debye-Scherrer rings, the spacings of lattice planes corresponding to the splitted spots were determined to be $d = 2.71 \text{ \AA}$. This value coincides with the $\{100\}$ lattice spacing of an equilibrium γ phase. It can, therefore, be concluded that the final precipitate in the specimens aged for a long period at 350°C is the γ phase. Splitting of two $\{100\}_{\gamma}$ spots are due to the formation of two groups of precipitates with different orientations, as will be explained later. Thus, fan-shape or triangular-shape spots in (b), (c) and (d) are considered to occur as a result of the simultaneous appearances of a $2/3$ spot from γ'' and two $\{100\}$ spots from γ . At higher ageing temperatures, γ'' precipitates dissolve into the α matrix accompanying the disappearance of the $2/3$ spot and finally only the two $\{100\}$ spots might be observed as in (e) and (f). By the way, according to the orientation relationship between the γ and α phases which will be shown later, the two $\{100\}_{\gamma}$ spots cannot be observed in other zonal patterns than the $\langle 110 \rangle_{\alpha}$ zone pattern. Therefore, those in (c) and (d) are considered to appear due to local bucklings of specimens or streakings of reciprocal lattice points.

Photo. 2 gives no information about the intermediate γ' phase which has so far been accepted to exist by many workers. According to their studies, two kinds of the structure of γ' have been reported: One is a bct lattice equivalent with the CuAu (I) type ordered fcc lattice and the other is a bct lattice suggested by Geisler et al. Therefore, the formation of the γ' phase should bring $\{110\}_{\alpha}$ superlattice spots in diffraction patterns from the α matrix or $\{100\}_{\gamma'}$ spots at the proper positions on $\{110\}_{\alpha}$ reciprocal lattice vectors. In either case, the existence and the structure of the γ' phase can be known by examining some changes along $\{220\}_{\alpha}$ reciprocal lattice vectors in diffraction patterns during the ageing. Photo. 3 is a series of such diffraction patterns. All the patterns are of the $(00\bar{1})_{\alpha}$ zone and thus changes along $\{020\}$ reciprocal lattice vectors can be observed at the same time, the ageing temperatures and times being inserted at the right lower corner of each photograph. In (a), intense spots are found at just $1/2$ of $\{220\}_{\alpha}$ reciprocal lattice vectors. Since $2/3$ spots on $\{002\}_{\alpha}$ reciprocal lattice vectors begin to spread out into a fan-shape, $\langle 001 \rangle$ streaks due to G.P. zones or γ'' precipitates should become shorter. Therefore, the $1/2$ spots are not intersections of $\langle 001 \rangle$ rel. rods through $\{111\}_{\alpha}$ rel. points with the Ewald sphere but diffraction spots belonging to the $(00\bar{1})_{\alpha}$ zone. That is, they are considered to be due to either $\{110\}_{\alpha}$ superlattice reflections from the CuAu (I) type ordered domains in the α matrix or due to $\{100\}$ superlattice reflections from the intermediate γ' precipitates which are entirely equivalent to the CuAu (I) type ordered domains. These $\{110\}_{\alpha}$ or $\{100\}_{\gamma'}$ spots appear to distort when $2/3$ spots

between (000) and $\{020\}$ spots become a triangular shape with increasing ageing time, as seen in (b). As the ageing temperature is raised up to 350°C as in (c), the distorted $\{110\}_{\alpha}$ or $\{100\}_{\gamma'}$ superlattice spots split into two along $\{220\}_{\alpha}$ reciprocal lattice vectors accompanying the precipitation of the final γ phase. The precipitation of the γ phase can be known from the changes in the $\{020\}_{\alpha}$ reciprocal lattice vectors. The inside spots are due to $\{100\}_{\gamma}$ reflections and the outside ones marked with D are due to double reflections. This splitting means the completion of the γ' to γ transformation with a relation that $\{110\}_{\alpha}$ or $\{100\}_{\gamma'}$ planes are parallel to $\{100\}_{\gamma}$ planes. The distortion of superlattice spots in (b) may be due to the coexistence of the γ' and γ phases.

From the above experimental results, the precipitation processes may be concluded as follows: Firstly G.P. zones are formed on $\{001\}_{\alpha}$ planes and then γ'' precipitates are formed upon ageing. Subsequently, the CuAu (I) type ordered domains (γ') are formed along $\{110\}$ planes of the α matrix as will be shown later, and the

Photo. 3 A series of $[00\bar{1}]_{\alpha}$ zone diffraction patterns showing the splitting of a $\{100\}_{\gamma'}$ reflection into a $\{100\}_{\gamma}$ superlattice and double reflections upon ageing at a higher temperature.

final γ phase begins to precipitate via the γ'' phase. Upon further ageing the γ'' precipitates dissolve into the α matrix and only the γ phase precipitates in the α matrix via γ'' phase. Finally, the γ precipitates are included in the so-called grain boundary products. Photo. 4 is an electron micrograph showing a growing boundary of the grain boundary products. The γ precipitates are seen in the left α grain and it can easily be deduced that the γ precipitates would be included soon in the right grain boundary products.

Photo. 4 Electron micrograph showing two types of precipitation of γ phase. In the left γ was precipitated as platelets inside the matrix, whereas in the right γ was produced by the so-called boundary reaction.

Photo. 5 (a) is a $[1\bar{1}0]_\alpha$ zone pattern taken from the specimen aged at 350°C for 5 hr. In the pattern, two $\langle 010 \rangle$ zone patterns from the γ phase are also seen as explained in (b). Extra spots other than these zonal spots may be due to double reflections and/or reflections from γ formed with different orientations (γ precipitates in a α grain have twelve orientations as variants of the orientation relationship). Now, the orientation relationship between the γ and α can be deduced from Photo. 5 (a) as follows: Both the $\{001\}$ spots of two $\langle 010 \rangle_\gamma$ zone patterns are situated at positions deviating from $\{002\}_\alpha$ reciprocal lattice vectors to the upper and lower sides by about 6.5°. If the planar parallelism of $\{121\}_\alpha // \{120\}_\gamma$ or $\{111\}_\alpha // \{110\}_\gamma$ was kept between the α and γ' or γ as suggested by Geisler et al., the (001) spots from γ' or γ would appear at positions of 8.7° or 9.7° from $\{002\}_\alpha$ reciprocal lattice vectors. However, these spots are found at positions inclined by 6.5° and therefore the orientation relationship of Geisler et al. does not hold in this case. If the parallelism of $\{131\}_\alpha // \{130\}_\gamma$ is assumed, the angle between the $[001]_\gamma$ and $[001]_\alpha$ directions is 6.8° and is nearly equal to the observed angle of 6.5°. Thus, the orientation relationship between γ and α in Photo. 5 (a) should be represented as

$$\begin{aligned} (103)_\gamma // (1\bar{1}3)_\alpha, [010]_\gamma // [110]_\alpha. \\ (10\bar{3})_\gamma // (1\bar{1}\bar{3})_\alpha \end{aligned}$$

This relationship suggests that the γ phase may precipitate on $\{113\}$ planes of the α matrix and that, if these precipitates are very thin plates, reflections from them may be elongated along the directions of $\langle 113 \rangle$. In fact, γ spots in Photo. 5(a) are accompanied by streaks along the directions inclined from $\langle 002 \rangle_\alpha$ by 25°, that is, along $[1\bar{1}3]$ and $[11\bar{3}]$ directions. In the

above relationship, one directional parallelism has two planar parallelisms as represented. Since there are six independent directional parallelisms, the orientation relationship has twelve variants in total, suggesting the possibility that the γ phase precipitates with twelve orientations in a α grain.

Photo. 5 (a) Electron diffraction pattern showing the orientation relationship between matrix α and precipitate γ .
(b) Key diagram of (a).
(c) Electron micrograph corresponding to the diffraction pattern (a).

Photo. 5 (c) is an electron micrograph corresponding to the diffraction pattern of (a). The precipitates observed in several directions are not only very small but are associated with strain contrasts around themselves. In other similar electron micrographs, there were seen moiré fringes and dislocations at the boundary regions between γ and α phases. These facts suggest that the γ phase precipitates retaining coherency with the surrounding α matrix although the structure of γ is quite the same as that of the equilibrium phase. On the other hand, the γ phase in grain boundary products appears to precipitate incoherently since the size is larger and strain contrast are not observed around them, as seen in the right half of Photo. 4.

IV. Discussions

1. Structure of γ'' phase

In Photo. 2 (a), intensity maxima were observed at about $2/3$ of $\{002\}_\alpha$ reciprocal lattice vectors. Apart from the position, such diffused intensity maxima can be expected to appear when a phase and/or intensity modulation occurs due to the formation of regularly spaced G.P. zones⁽¹⁰⁾. In that case, however, intensity maxima would appear on both sides of fundamental spots symmetric to the present observation. Therefore, it is rather reasonable to consider that the $2/3$ spots correspond to reflections from a certain crystal which is named the γ'' phase here. This consideration is basically equivalent to that by Guinier⁽¹¹⁾, Gerold⁽¹²⁾ and Graf⁽¹³⁾ for the G.P. (2) or θ'' in Al-Cu alloys although the present γ'' crystal is different in structure from those proposed by them. In this experiment, the γ'' crystal was assumed to be formed in such a way that G.P. zones of one layer thick form every two layers of $(001)_\alpha$ planes as shown schematically in Fig. 1. If so, the structure

Fig. 1 Illustration of a model of a γ'' platelet formed on $(001)_\alpha$ planes. The open and solid circles represent Cu and Be atoms respectively, the projection plane being $(100)_\alpha$.

of the γ'' crystal may be said to be a body-centered tetragonal lattice having a Be atom at the body center, the lattice constant being

$$a_{\gamma''} = a_\alpha / \sqrt{2} = 2.53 \text{ \AA}, c_{\gamma''} = 2.9 \text{ \AA}.$$

The value of $2.9 \text{ \AA}$ was determined from distances between the (000) and $2/3$ spots since the $2/3$ spots were considered to correspond to reflections from the (001) planes of the γ'' crystal. Then, the orientation relationship between the γ'' and matrix α may be represented as

$$(001)_{\gamma''} // (001)_\alpha, [100]_{\gamma''} // [1\bar{1}0]_\alpha.$$

In this case, diffraction spots from the γ'' crystal are expected to appear at positions marked with $\times$ in $[0\bar{1}0]_\alpha$ and $[\bar{1}30]_\alpha$ zone patterns as explained diagrammatically in Photos. 6 (b) and (d). Photos. 6 (a) and (c) are the zonal patterns obtained, in which the γ'' spots are seen at the expected positions as marked with arrows. The (101) spot marked with a double arrow in (a) is due to a

reflection from γ' , the c-axis of which is parallel to $[010]_\alpha$. The existence of the γ'' phase was also reported by Geisler et al., but the structure and the orientation relationship were different from those of the present results and could not explain the present diffraction patterns.

Photo. 6 (a) (c) Electron diffraction patterns of $[0\bar{1}0]_\alpha$ and $[\bar{1}30]_\alpha$ zones, respectively.

(b) (d) Key diagrams of (a) and (c), respectively.

The γ'' structure described above can be regarded as such a structure that the c-axis of the CuAu (I) type ordered lattice in the α matrix was contracted from 3.58 to $2.9 \text{ \AA}$. The contraction is about 20% and is too large to retain coherency with the α matrix. Therefore, the γ'' phase cannot exist stable and cannot become even an intermediate state for the precipitation of the final γ phase, thus dissolving into the α matrix. Here arises a question why the lattice constant of the γ'' phase is different from that of the γ' phase described below in spite of the similarity in their atomic arrangements and also why the γ'' phase dissolves into the α matrix forming newly the γ' phase. These may be due to the difference in their formation mechanism, that is, the former γ'' has evolved from G.P. zones on $\{001\}$ planes while the later γ' was precipitated along $\{110\}$ planes of the α matrix as will be described later.

2. Structure of γ' phase and its relation with α matrix

The crystal structure of γ' reported by Gruhl and Wassermann⁽⁷⁾ is the body-centered tetragonal lattice, the axial ratio being $c/a = \sqrt{2}$. This is perfectly equivalent to that of the CuAu (I) type ordered lattice in the α matrix (neglecting the tetragonality), as can easily be known from Fig. 4 (a). Therefore the reciprocal lattice of γ' can be represented by that of the CuAu (I) lattice as shown in Fig. 2. Although the typical

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(11) A. Guinier : Acta Cryst., 5 (1952), 121.

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(13) R. Graf : Théses Sci. Phys. Paris, A 2789, No. 3661 (1955).

$[100]_\alpha$ zone pattern was not obtained, other zonal patterns, Photos. 3, 6 (a), 7 (a) and (b), show the appropriateness of the representation in Fig. 2. Thus, it may be concluded that the structure of γ' and its relation with the α matrix accord well with the proposition of Gruhl and Wassermann. Geisler et al. and some other workers have reported a different structure and orientation relationship. In this experiment, however, no diffraction patterns were obtained in support of the reports of Geisler et al.

Fig. 2 Reciprocal lattice of γ' precipitate indexed in terms of the CuAu (I) type superlattice. The solid and open circles represent fundamental and superlattice reciprocal points, respectively.

Photo. 7 Electron diffraction patterns of $[102]_\alpha$ and $[112]_\alpha$ zones, respectively, which were taken from the specimen aged at 250°C for 140 hr.

It is well known that striations parallel to $\{110\}_\alpha$ planes are found in the optical micrographs of aged Cu-Be alloys. Let us now discuss the relation between the striations and the γ' formation. Similar striations can also be found in the electron micrographs (Photo. 8 (b)). Recently Tanner⁽¹⁴⁾ found a more fine tweed pattern parallel to $\{110\}_\alpha$ planes in his electron micrographs, and explained⁽¹⁵⁾ them as strain contrasts accompanied by the formation of G.P. zones. Some workers have considered the striations in Photo. 8(b) to be of the same tweed pattern. If it was true, their striations would disappear when G.P. zones dissolve into the α matrix. In this experiment, however, the $\{110\}$ striations were seldom observed when long $\langle 001 \rangle_\alpha$ streaks appeared due to the formation of G.P. zones (Photo. 8(a)), whereas they were observed with intense contrasts when the γ

phase starts precipitating through the γ' intermediate phase after the dissolution of G.P. zones ((b)). Since the γ' formation is equivalent to an ordering of the α matrix in the CuAu (I) type, the $\{110\}_\alpha$ striations can be said to show intense contrast as the ordered domains grow. Thus, these striations are considered to be due to the formation of the CuAu(I) type ordered domains as observed in the ordering processes of CuAu and other alloys^{(16)~(18)}. On the other hand, the tweed patterns found by Tanner must be considered to disappear as G.P. zones dissolve into the matrix. Both the tweed pattern due to G.P. zone formation and the striation due to ordering into γ' are considered to originate in the elastic anisotropy of the α matrix.

Photo. 8 Electron micrographs corresponding to the diffraction patterns Photos. 1 and 7 (b), respectively.

3. Orientation relationship between γ and α and mechanism of γ' to γ transformation

From the analysis of Photo. 5 (a), the orientation relationship between the γ and α structures was proposed as

$$\{103\}_\gamma // \{113\}_\alpha, \langle 010 \rangle_\gamma // \langle 1\bar{1}0 \rangle_\alpha.$$

This relationship is different from that of Geisler et al. between γ' and α and between γ and α by only 2.2° and 3.2°, respectively. It is not so easy to distinguish the small differences by electron diffraction. However, it can more readily be made by using the direction of streaks which are considered to occur along the directions normal to the interface plane between the precipitates and the matrix. In many cases, the interface plane of precipitates is parallel to the plane involved in the orientation relationship between the precipitates and the matrix. If the precipitates are very thin, streaks should be observed along the direction normal to the interface planes of planar parallelism. According to Geisler et al., the matrix planes of planar parallelism were $\{112\}_\alpha$ and $\{111\}_\alpha$ for γ' and γ , respectively. If the γ' or γ precipitated on those planes, streaks would be observed along the direction normal to $\langle 112 \rangle_\alpha$ or $\langle 111 \rangle_\alpha$.

(16) M. Hirabayashi and S. Ogawa : J. Phys. Soc. Japan, 11(1956), 907.

(17) M. Hirabayashi and S. Weissmann : Acta Met., 10(1962), 25.

(18) J. B. Newkirk, R. Smoluchowski, A. H. Geisler and D. L. Martin : Acta Cryst., 4(1951), 507.

(14) L. E. Tanner : Phil. Mag., 14(1966), 111.

(15) Yu. D. Tyapkin : Sov. Phys. Cryst., 10(1966), 418.

that is, along the directions at 35° or 54.5° with the $\langle 010 \rangle_\alpha$ direction. However, the streaks in Photo. 5 (a) are observed along the directions at 25° with the $\langle 010 \rangle_\alpha$ directions. This angle is equal to that between the $\langle 113 \rangle_\alpha$ and $\langle 010 \rangle_\alpha$ directions, and so it can be considered that the $\{113\}_\alpha$ planes form the interface plane and the plane of planar parallelism as suggested above. A few papers have supported the orientation relationship of Geisler et al., but diffraction patterns presented in those papers are consistent with the present results in regard to both the direction of streaks and the position of $\{001\}_\gamma$ spots.

In Fig. 3, the atomic arrangement in the $(103)_\gamma$ plane is compared with that in the $(\bar{1}\bar{1}3)_\alpha$ plane. If the interatomic distances along the $[110]$ and $[\bar{3}32]$ directions of α are expanded by only 7.1% and 2.1%, respectively, they coincide with those along the $[010]$ and $[\bar{3}01]$ directions of γ , respectively. Moreover, the atomic arrangement of the upper and lower planes are also very similar. These coincidence and similarity justify the parallelism between the $(\bar{1}\bar{1}3)_\alpha$ and $(103)_\gamma$ planes and the possibility that these planes become an interface plane.

Fig. 3 Similarity in the atomic configuration in the $(\bar{1}\bar{1}3)_\alpha$ and $(103)_\gamma$ planes. Marks $\oplus$ and $\ominus$ represent the location of atoms in the upper and lower planes, respectively.

Finally, the mechanism of the γ' to γ transformation will be discussed. Figs. 4 (a) and (b) show the crystallographic relations of γ' and γ to the α matrix, respectively. In the precipitation phenomena, it is a conventional view that the γ phase with the orientation shown in (b) nucleates and grows within the γ' phase of the orientation in (a). The γ phase appears to be formed by contracting the c-axis of the CuAu (I) type γ' by 24%, by expanding uniformly the plane normal to the c-axis by 7%, and by rotating the crystal obtained by 6.5° around the $[010]_{\gamma'}$ ($[110]_\alpha$) axis. These lattice deformations and rotation can be regarded as the Bain distortion and the rigid-body rotation in the phenomenological crystallographic theory of fcc to bcc martensitic transformation. Therefore, the γ' to γ transformation can be speculated to be martensitic in the nucleation process at least though it is generally diffusion controlled. If the γ phase was produced by the pure diffusion control processes like the equilibrium γ phase in grain boundary products, no-strain contrast would be observed

in the surrounding α matrix. However, in Photo. 5 (c), strain contrasts were observed and hence the above consideration for the γ' to γ transformation is not a groundless argument. Of course, since the diffusion control takes part in the growth process, the strain around α matrix may be relieved as γ crystal grows, resulting in the disappearance of the contrast⁽¹⁹⁾.

Fig. 4 Illustration of the transformation from γ' to γ . (a) Unit cell of γ' , directly derived from matrix α by ordering. The plane indicated by broken lines is $(\bar{1}\bar{1}3)_\alpha$. (b) Unit cell of γ . The plane indicated by broken lines is $(103)_\gamma$. The cell is tilted by 6.5° so that the $(103)_\gamma$ plane becomes parallel to the $(\bar{1}\bar{1}3)_\alpha$ plane.

In the past, it was reported⁽²⁰⁾ that the α to γ transformation in Cu-Be alloys was martensitic. However, the study disregarded the existence of G.P. zones and intermediate phases, under the condition in which the γ precipitates 100 Å in thickness could not be detected. Therefore, the meaning of the word 'martensitic' is different from that in the present study which has considered the nucleation process of γ' to γ transformation to be martensitic. The crystallography of γ' to γ transformation is expected to be explained well by the phenomenological theory of martensitic transformation if a suitable lattice invariant shear system is assumed. The phenomenological treatments will be reported in a separate paper.

V. Conclusion

Electron diffraction patterns taken from aged 2 wt% Be alloy changed with increasing ageing time or temperature as follows. In the earliest stage, long streaks appeared in the $\langle 001 \rangle_\alpha$ directions due to the formation of G.P. zones. Upon prolonged ageing the streaks became shorter and intensity maxima appeared at about $2/3$ of $\{002\}_\alpha$ reciprocal lattice vectors. This stage was

(19) R. J. Price and A. Kelly : Acta Met., 11 (1963), 915.

(20) J. S. Bowles and W. J. M. Tegart : Acta Met., 3 (1955), 590.

distinct from G.P. zone and was designated as γ'' phase. The structure of γ'' was concluded to be a body-centered tetragonal lattice, Cu atoms being at the corner and Be atoms at the body-center, and was different from that proposed by Geisler et al. Ageing at higher temperature caused another superlattice reflections (CuAu (I) type, γ') to appear and 2/3 reflections mentioned above to split. This splitting corresponded to the formation of the γ phase. From these observations, it has been concluded that the ageing sequence in this alloy is $\alpha \rightarrow \text{G.P. Zone} \rightarrow \gamma'' \rightarrow \gamma' \rightarrow \gamma$. This sequence is very similar to that in Al-Cu alloys as far as the sequence is concerned.

The structure of the final precipitate γ was identified

to be the same as that of the equilibrium phase with the lattice constant 2.71 Å. Then the new orientation relationship between the γ and α has been proposed, such that

$$\{103\}_{\gamma} // \{113\}_{\alpha}, <010>_{\gamma} // <1\bar{1}0>_{\alpha}.$$

Among several orientation relationships reported so far, only this one was consistent with our experimental results. In spite of the identity in structure the final precipitates γ were associated with strain contrast around themselves, in contrast to the equilibrium phase. From this fact, it was suggested that the γ'' to γ transformation might be martensitic in the nucleation stage.