Formation Process of α_2 Phase in Cu-Al Alloys

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The process of formation of α_2 Cu-Al phase was investigated in the slow-cooled specimens decomposed into $\alpha + \gamma_2$ phases as well as the quenched ones of β'_1 phase. The specimens aged at 350°C for various times were examined by means of X-ray diffraction and electron microscopy. The results obtained are as follows:

(1) In the decomposed specimens the domains of α_2 phase of the long period superlattice in x -, y - or z -orientation are randomly distributed in the matrix. They do not grow more than 1000Å in diameter after aging for about 60 days.

(2) In the quenched specimens the α_2 phase is formed coherently with the matrix. When aged for about 60 days, the quenched specimen contains the domains of α_2 phase with a particular orientation and a diameter of several microns.

(3) The antiphase boundaries in the β_1 phase are retained until the matrix finishes transforming to the α_2 phase through β'_1 and X phases.

(4) In the quenched specimens aged for a long time straight boundaries as well as curved ones between domains of different orientations are observed.

(5) In the quenched specimens of Cu-23.1 at% Al, the γ_2 phase never appears throughout the long aging at 350°C.

(Received August 30, 1976)

I. Introduction

Various investigators have been paying much attention to a phase which appears near 350°C in Cu-Al alloys containing about 23 at%Al. Haynes⁽¹⁾ first reported that a "pink phase" appears in the martensite aged isothermally at 350°C for several days, and suggested that the pink phase might be an Al-supersaturated α phase. West and Thomas⁽²⁾ also recognized the pink phase both in martensite and in decomposed $\alpha + \gamma_2$ specimens aged at 340°C. From their X-ray powder patterns they observed the existence of several additional lines and the broadening of fcc fundamental lines and designated the phase as X tentatively. Cope⁽³⁾ obtained a detailed time-temperature-transformation diagram for Cu-Al martensite. Jewett and Mack⁽⁴⁾ designated the new phase as the α_2 phase because of its similarity in

structure to the α phase of fcc , and determined its peritectoid temperature to be 363°C. The phase diagram proposed by them is indicated in Fig. 1, in which the metastable diagram is also shown. Sugino *et al.*⁽⁸⁾ suggested that there might exist a superlattice of an fcc structure which has a composition of Cu_3Al , pointing out that the anomalies in specific heat and electrical resistivity were observed on the martensite decomposing at a low temperature.

The investigations mentioned above confirmed the new phase or α_2 phase to be an equilibrium one, though its detailed structure was not made clear. Gaudig and Warlimont⁽⁹⁾ investigated the α_2 phase, which precipitated coherently in a supersaturated α phase, by means of electron microscopy and determined its structure as illustrated in Fig. 2(b). Since then, several studies have been made by performing electron microscopy of the α_2 phase. Lefever and Delaey⁽¹⁰⁾, for instance, reported that the β'_1 martensite transforms into the α_2 phase via "X phase" which has the same 18R stacking mode as β'_1 but has a long period superlattice (LPS). The structure of the X phase proposed by them⁽¹⁰⁾ is illustrated in Fig. 2(a). Similar results were also obtained by Duval

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Fig. 1 The phase diagram for Cu-Al alloy.

—: after Jewett and Mack⁽⁴⁾
 ---: after Kurdjumov⁽⁵⁾
 - · - ·: after Swann and Warlimont⁽⁶⁾
 ·····: after Duval and Haymann⁽⁷⁾

Fig. 2 Schematic drawings of the structure of Cu-Al alloy. (a) X phase⁽¹⁰⁾, (b) α_2 phase⁽⁹⁾. The X phase is represented as a monoclinic cell.

and Haymann⁽¹¹⁾. As seen in Fig. 2(a) and (b), the atomic arrangement on the basal plane of the X phase is the same as the one on the close-packed plane of the α_2 phase. Then, if the stacking sequence of the X phase, ABCBCACAB, is modulated again adequately to ABCABCABC, the structure turns out to be the α_2 phase. Thus, it is quite interesting to

investigate how such a mutual similarity in the structure influences the process of the transformation.

In the present work the formation process of the α_2 phase in the decomposed $\alpha + \gamma_2$ specimen and in the β'_1 martensite specimen aged at 350°C for various times was investigated by means of X-ray powder diffraction and electron microscopy. Especially, we were interested in the difference in the texture between the α_2 phases formed in the decomposed and the quenched specimens.

II. Experimental Procedure

The specimens of binary Cu-Al alloys were made by melting 99.99% pure copper and aluminum in vacuum in a high frequency induction furnace, followed by homogenizing at a high temperature for 24 hr. A specimen for X-ray experiments, which had been homogenized in the β phase region and then quenched into ice brine, was filed into powder under 200 mesh and sealed in an evacuated silica capsule. The powder specimen was annealed in order to relieve stresses and quenched into ice brine to produce a martensite (quenched specimen), or slow-cooled to room temperature to decompose into $\alpha + \gamma_2$ phases (decomposed specimen). A specimen for electron microscopic observations, which had been hot-rolled to a thickness of 0.3 mm, was annealed at 800°C for 12 hr and then quenched into ice brine (quenched specimen). Another one was held at 550°C for 24 hr and slow-cooled (decomposed specimen). Both specimens for X-ray and electron microscopic experiments were aged at 350°C for various times and quenched before measurements.

The X-ray measurements were made by a diffractometer method using a filtered Cu K_α radiation. The thin foils for electron microscopy were prepared by polishing them mechanically to a thickness of 0.1 mm and then by electropolishing at -30°C in an electrolyte containing two parts CH_3OH and one part conc HNO_3 . All the electron microscopic images and diffraction patterns were observed using a JEM-200 electron microscope operated at 200 kV.

Chemical analysis showed the X-ray specimen was of 23.1 at%Al, and the quenched and the decomposed specimens for electron microscopy were of 22.1 and 20.0 at%Al, respectively. Although it is desirable to use the specimens of the same composition, those of the above compositions were used because of the difficulty of electropolishing. However, the structural difference between 22 and 23 at%Al alloys should be little because both of them have a β'_1 martensite structure when quenched, and they are in the region of α_2 phase at 350°C in the equilibrium phase diagram. The alloy of 20 at%Al is in the region of $\alpha + \alpha_2$ mixture. But the α_2 phase which appears in a decomposed specimen is to form peritectoidly at a pearlite of $\alpha + \gamma_2$, the mean concentration of which is 24 at%Al. The circumstances of Al concentration at a pearlite seem almost the same for the 20 at%Al alloy and the 22 or 23 at%Al alloy. The α_2 phase observed in the decomposed specimens in the present experiment should be the one which was formed peritectoidly from α and γ_2 phases, because the specimens were aged at 350°C and then immediately quenched so that the α_2 phase could not precipitate in a supersaturated proeutectoid α phase.

III. Results and Discussions

1. X-ray powder diffraction

Figure 3 shows the X-ray diffractometer tracings of the decomposed specimen of 23.1 at%Al aged at 350°C for various times. The diffraction pattern for the as-furnace-cooled specimen consists of the lines from α and γ_2 phases. When the specimen is aged for 2 days, the superlattice lines of α_2 phase appear and increase in intensity with the aging time. The line profile of the fundamental *fcc* lines, for example, 222[†] becomes broader gradually with aging time so that the doublet of K_{α_1}

Fig. 3 X-ray diffractometer tracings of the decomposed ($\alpha + \gamma_2$) specimen of Cu-23.1 at% Al aged at 350°C for various times. The lines of α or α_2 phase are indexed. (a) as furnace-cooled, (b) aged for 2 days, (c) 4 days, (d) 10 days, (e) 20 days, (f) 30 days.

and K_{α_2} is not resolvable clearly, although the profile of γ_2 lines indicates little change on aging. This shows that the α_2 phase whose lattice parameter is a little different from that of the saturated α phase develops during the aging.

Figure 4 shows the X-ray diffractometer tracings of the quenched specimen of 23.1 at%Al aged for various times. All the lines of the as-quenched specimen is interpreted as the ones of β'_1 martensite. After aging for 2 days, an *fcc* fundamental line 200 appears at $2\theta = 49.5^\circ$, where θ is the Bragg angle. One can see slight changes in the lines of the martensite; for example, the shape of the lines becomes sharper accompanying little change in integrated intensity, and a pair of lines near $2\theta = 27^\circ$ shifts to a higher angle side. These changes may be due to the annihilation of dislocations, microtwins or stacking faults which existed statistically in a martensite. The weak line at $2\theta = 35^\circ$ which becomes visible after aging for 2 days is not from the α_2 phase but from the β'_1 martensite, because the intensity of the line is much stronger than the one expected for the superlattice line of α_2 phase

[†] In this paper, the indices with a subscript *fcc*, as well as the ones with no subscript, are for α or α_2 phase, and they refer to a fundamental *fcc* lattice. On the other hand, those with a subscript 18R, for instance, hkl_{18R} , refer to an orthorhombic structure with the 18R stacking mode.

Fig. 4 X-ray diffractometer tracings of the quenched specimen of Cu-23.1 at% Al aged at 350°C for various times. The lines of the α_2 phase are indexed. (a) as quenched (b) aged for 2 days, (c) 5 days, (d) 10 days, (e) 15 days, (f) 60 days.

estimated from that of 200 line. The increase in the intensity of the line may be due to the developing of order in the β'_1 martensite.

The intensities of the superlattice lines of α_2 phase as well as the fundamental ones increase rapidly when the specimen is aged for 5 to 10 days. One can see that about 90% of the martensite^{††} has transformed into the α_2 phase after aging for 60 days, as the intensity of the martensite-line decreases to 10% of the initial value. It is the α_2 phase only that appears during a long aging. No diffraction lines of another phase, e.g. the γ_2 phase, could be recognized at all. In this experiment, a powder specimen of the filed martensite was annealed in the region of β phase and quenched again in order to produce a martensite without any influence of the filing. We found that when a cold-worked martensite or a cold-worked α_2 phase is annealed at a low temperature, it decomposed rapidly to $\alpha + \gamma_2$ phases, and that after a long annealing the α_2 phase forms from the α and γ_2 phases peritectoidly. This phenomenon will be described in detail elsewhere.

†† In this paper the term 'martensite' is used for a phase which has a martensitic structure, for convenience. Thus, the X phase is considered a kind of martensite.

2. Electron microscopy

Photograph 1 shows the $[001]$ diffraction pattern^{†††} from the α_2 phase which forms in the decomposed specimen of Cu-20.0 at% Al. The pattern is almost identical with that observed by Gaudig and Warlimont⁽⁹⁾, and indicates that the three $\langle 001 \rangle$ directions of one dimensional LPS are superimposed. The spots marked by x are superlattice spots from an α_2 phase of x-direction of LPS or 'x-orientation'. In order to examine the distribution of the α_2 domains having a particular orientation, a certain number of dark field (DF) images were taken with the spots of α_2 phase. The $[111]$ diffraction pattern is suitable for this purpose, because it contains the strong superlattice spots 110 from α_2 domains with x-, y- and z-orientations. Photograph 2 shows the $[1\bar{1}1]$ diffraction pattern for the decomposed specimen aged at 350°C for 60 days. In this pattern, the spots from α_2 of the three orientations are observed. The BF (bright field) and DF images of the identical area are shown in Photo. 3. The DF images were taken with the spots of α_2 phase marked by x, y or z in Photo. 2. Bright spots in the DF images are α_2 domains whose dimensions are approximately 700–900 Å. One can see the α_2 domains of each orientation are randomly distributed in the matrix. The matrix is considered a disordered α phase, for the diffraction pattern contains

Photo. 1 Electron diffraction pattern of α_2 phase which forms in the $(\alpha + \gamma_2)$ decomposed specimen of Cu-20.0 at% Al; beam along $\langle 001 \rangle_{fcc}$.

††† Hereafter, a diffraction pattern with a beam along $\langle hkl \rangle$ is abbreviated to the $[hkl]$ diffraction pattern.

Photo. 2 Electron diffraction pattern of α_2 phase which forms in the decomposed ($\alpha + \gamma_2$) specimen of Cu-20.0 at% Al aged at 350°C for 30 days; beam along $\langle 1\bar{1}1 \rangle_{fcc}$.

Photo. 3 Electron micrographs taken with the spots of Photo. 2. (a) BF image, (b) DF image with x -spot, (c) with y -spot, (d) with z -spot.

only the spots of fcc lattice. If there were the γ_2 phase with a quite large lattice parameter, its spots should appear around the central spot. The mode of the distribution of α_2 domains shown in Photo. 3 resembles that of α_2 domains which grew in a supersaturated α phase observed by Gauding and Warlimont⁽⁹⁾. One can easily suppose that Al atoms in the γ_2 phase diffuse into a saturated α phase and that α_2 domains precipitate coherently in the α phase. Thus, the mechanism of formation of the α_2 phase in the decomposed specimen might be essentially identical with that in the

supersaturated α phase. Whether α_2 domains form in the matrix of the γ_2 phase or not could not be clarified, for the γ_2 region tended to be dissolved preferentially when electropolished. Nevertheless, a few diffraction patterns of γ_2 which could be taken by chance contained no spots of α_2 phase.

Photographs 4(a)–(c) show the $[831]_{18R}$ diffraction pattern for the quenched specimen aged at 350°C for 5 days, together with the BF and DF images. The diffraction pattern shown in Photo. 4(a), where the superlattice spots with an odd index of k_{18R} are splitting, indicates

Photo. 4 Electron diffraction pattern and micrographs of the quenched specimen of Cu-22.1 at% Al aged at 350 °C for 5 days. (a) $[831]_{18R}$ diffraction pattern, (b) BF image, (c) DF image with $10\bar{8}_{18R}$ spot.

that the area of the specimen has transformed to LPS or the X phase. Here k_{18R} is the second index of hkl_{18R} . As seen in Photo. 4(b), where striations have vanished and fringes which look like Moiré patterns have come out, stacking faults have been annealed out to some extent. This result corresponds to the observation that the shape of the X-ray diffraction lines of the martensite become sharper after aging for a few days. Many small ordered domains bounded by antiphase boundaries (APB) over

the matrix of the X phase are observed in the DF image shown in Photo. 4(c). The APB's do not end at the boundary between the variants of the martensite. Swann and Warlimont⁽⁶⁾ observed a similar image of APB's in the β'_1 martensite, and interpreted that they had formed in the β_1 phase of DO_3 structure which was formed previous to a martensitic transformation. APB's in the X phase seen in Photo. 4(c) are considered to have existed in the β'_1 martensite and hence in the β_1 phase.

Photograph 5 shows the diffraction pattern from the area where the α_2 phase developed to some extent. The pattern can be interpreted as consisting of the spots of the martensite attended with streaks and those of α_2 phase which can hardly be regarded as twinned martensite spots. By indexing these spots, the crystallographic relations between a martensite and an *fcc* structure, $\langle 100 \rangle_{18R} // \langle \bar{1}\bar{1}\bar{2} \rangle_{fcc}$, $\langle 010 \rangle_{18R} // \langle \bar{1}10 \rangle_{fcc}$ and $\langle 001 \rangle_{18R} // \langle 11\bar{1} \rangle_{fcc}$, were confirmed, where the structure of the martensite was regarded as an orthorhombic cell having the 18R structure⁽¹²⁾. These relations coincide with the ones which can be deduced by considering the correspondence between the martensite and the *fcc* structure through the close-packed planes. Photograph 6(a) is the BF image, (b) the DF image taken with the fundamental spot of martensite 208_{18R} , and (c) the DF image with the superlattice spot of α_2 phase 001_{fcc} in the identical area using the diffraction pattern shown in Photo. 6. As seen in the BF where striations have almost disappeared, stacking faults which had existed statistically or randomly in the martensite were found annihilated to a large extent. The region of the bright contrast in Photo. 6(b) is a remaining martensite and the one of a dark contrast is considered the α_2 phase. It is found that the martensite has a plate-like form of which the habit plane is parallel to a basal plane of the martensite, because the traces of the plane are perpendicular to the streaks as seen in Photo. 5. This micrograph and the diffraction pattern (Photo. 5) support the assumption that a martensite transforms to α_2 phase, with its stacking sequence changing 18R to 3R coherently, by eliminating the stacking faults which modulate the stacking

Photo. 5 Electron diffraction pattern from the quenched specimen of Cu-22.1 at% Al aged at 350°C for 5 days.

Photo. 6 Electron micrographs taken with the spots of Photo. 5, (a) BF image, (b) DF image with 208_{18R} , (c) DF image with 001_{fcc} .

sequence periodically. The DF image shown in Photo. 6(c) reveals that small ordered domains are distributed over the matrix similarly as seen in Photo. 4(c). It should be noticed that the APB's are continuous across the plate of the remaining martensite. If the ordering of the α_2 phase took place after a disordered α phase is constructed or if the α_2 phase formed incoherently with a martensite, the APB's should not conjoin with the ones in the neighboring α_2 phase beyond the remaining martensite plate. Consequently, the APB's generated in the β_1 phase are conserved until the matrix transforms to the α_2 phase through the β'_1 and X phases.

The BF and 001_{fcc} DF images are shown in Photo. 7(a) and (b), respectively, for the quenched specimen aged for 5 days. Here the terms hkl DF image stand for the DF image taken with the hkl spot. The martensite has disappeared completely from the region, which is filled with the ordered domains of α_2 phase. In Photo. 7(a), the presence of the ordered domains are revealed in distinct contrast due to their strain. The difference in the contrast between the right- and left-hand sides of the photograph was attributed to the difference in the diffraction condition. Although the specimens shown in Photos. 4 ~ 7 were the quenched specimens aged at 350°C for 5 days, these are of different phases; the X phase (Photo. 4), the α_2 phase (Photo. 7), and the α_2 + X phases (Photos. 5 and 6). It is found that the martensite decomposed inhomogeneously. In this connection, Jewett *et al.*⁽⁴⁾, investigating by means

Photo. 7 Electron micrographs of the quenched specimen of Cu-22.1 at% Al aged at 350°C for 5 days. (a) BF image, (b) DF image with 001_{fcc} .

of optical microscopy, reported that a martensite begins decomposing at its grain boundary.

Photograph 8(a) and (b) show the BF and 001_{fcc} DF images for the quenched specimen for aged 15 days. Many APB's are observed in a dark or bright contrast in the DF image and in a faint contrast in the BF image. It can be noticed that a straight boundary between the α_2 phases of different orientations are observed in the micrographs. The trace of the boundary has a direction of nearly $\langle 311 \rangle$. In another region of the specimen, a curved boundary was also observed. The cause why such a straight boundary as well as a curved one appears is not clarified yet. Photograph 8(c) and (d) show the BF and 001_{fcc} DF images for the quenched specimen aged for 58 days. In the images the density of APB has decreased considerably and both straight and curved boundaries are visible. The α_2 domains have grown up to 2 or 3 μ . They are quite different in texture and size from the ones which grew in the decomposed specimen shown in Photo. 3.

Photograph 9(a) shows the $[001]$ diffraction pattern of α_2 phase in the quenched specimen aged at 350°C for 30 days. The pattern can be

Photo. 8 Electron micrographs of the quenched specimen of Cu-22.1 at% Al aged at 350°C. (a) and (b) are for 15 days, (c) and (d) for 58 day. BF images are in (a) and (c), and DF images taken with 001_{fcc} spot are in (b) and (d).

Photo. 9 Electron diffraction pattern of α_2 phase in the quenched specimen; beam nearly along $\langle 001 \rangle$. Photo. 9(b) was taken when the specimen was inclined slightly from the case of Photo. 9(a).

considered to indicate the dominant existence of one of the three $\langle 001 \rangle$ orientations, which is the same one as that observed by Lefever *et al.*⁽¹⁰⁾ However, when the specimen is inclined slightly, the spots of LPS with the other two orientations come out. (Photo. 9(b)) This fact presents that, by aging the martensite, domains of α_2 phase with the three orientations develop. How the domains of the three orientations form from the martensite is not made clear, although domains of a particular orientation develop within a variant of martensite.

In Photo. 9(a) and (b), one can notice that the spots are attended by fourfold diffuse streaks. These streaks are similar to the ones due to stacking faults, but they might not so, for very few stacking faults remained after aging for 30 days as seen in Photo. 8(a) and (b). Furthermore, some faint spots are visible between 000 and 020 spots, which cannot be explained only by the double reflection of the splitting spots of LPS. These spots might be due to the lattice modulation in α_2 phase because the pattern is quite similar to the one of Au_3Mn alloy⁽¹³⁾. An attempt to make the explanation of the diffuse streaks and a more detailed analysis of the additional spots are in progress.

IV. Conclusion

The process of the formation of α_2 phase of Cu-Al alloys in the previously decomposed ($\alpha + \gamma_2$) and the previously quenched (β'_1 martensite) specimens was investigated by

means of X-ray powder diffraction and electron microscopy. The conclusions obtained are as follows:

(1) In the decomposed specimen the α_2 phase appears in a disordered α phase after aging at 350°C for 2 days. The domains of α_2 phase with x -, y - or z -orientation of LPS are randomly distributed in a disordered matrix. But they grow up not more than 1000 Å in diameter after aging for about 60 days.

(2) In the quenched specimen, α_2 phase develops rapidly after aging at 350°C for 5 to 10 days. The α_2 phase forms coherently with the matrix of 18R martensite so that it has a particular orientation. When the quenched specimen is aged at 350°C for 60 days, about 90 percent of the martensite has transformed to α_2 phase and the domains of α_2 phase with a particular orientation have a diameter of several microns.

(3) The antiphase boundaries generated in β_1 phase are conserved until the matrix transforms to the α_2 phase via the β'_1 and X phases. They decrease in density on aging α_2 phase for a long time.

(4) Straight boundaries as well as curved ones between α_2 domains of different orientations were observed in the quenched specimen aged for a long time.

(5) In the quenched specimen of Cu-23.1 at%Al, γ_2 phase does not appear throughout the long aging at 350°C.

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