Formation Mechanisms of G.P. Zones and θ' -Phase in Al-Cu Crystals

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In the previous report, it was shown by high resolution electron microscopy that four types of G.P. Zones are formed in Al-1.6 at%Cu crystals by aging, and that only one of them changes to θ' -phase. In the present report, local contents of Cu-atoms in these G.P. Zones have been estimated from the results obtained by an *in-situ* experiment of electron irradiation induced diffusion.

Based on these results, mechanisms on the diffusion of Cu-atoms, the formation of Cu-atom clusters, the formation of various types of G.P. Zones, and the transition from G.P. zones to θ' -phase are discussed in terms of Al-Cu atom-pairs.

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I. Introduction

Recently, it has been shown in Al-Cu alloys⁽¹⁾⁻⁽⁶⁾ that both content and distribution of Cu-atoms in G.P. zones⁽⁷⁾⁽⁸⁾ should be investigated again. For such purpose, more information is necessary to obtain on the detailed behavior of Cu-atoms during aging.

In the previous report, it was clarified that various types of G.P. zones are formed in Al-1.6 at%Cu crystals by aging at low temperatures as follows: (a) Pre-G.P. zones are formed at the beginning of aging at both 373 and 437 K, respectively. (b) In 373 K aging, pre-G.P. zones change to G.P.-1 zones and/or G.P.-2(3) zones whose Cu-rich planes are separated with three Al-rich {100} planes. These G.P.-2(3) zones change to multi-layered G.P.-2(3) zones. Both G.P.-1 and G.P.-2(3) zones disappear at room temperature by electron irradiation at 300 kV⁽⁹⁾. (c) G.P.-2(2) zones whose Cu-rich planes are separated with two Al-rich {100} planes are formed through pre-G.P. zones in 423 K aging, and followed by formation of multi-layered G.P.-2(2) zones. The latter changes to θ' -phase by both aging at 523 K and electron irradiation induced diffusion at room temperature.

On the other hand, one of the authors already reported⁽¹⁰⁾ that new three peaks appear by aging in aluminum L_{2,3} VV spectrum of Auger valence electron spectroscopy in Al-2.2 at%Cu crystals, and that this fact is considered to result from the formation of Al-Cu atom-pairs.

In the present work, local content of Cu-atoms in various types of G.P. zones has been estimated from the

results obtained by the irradiation effects. Based on both positions of Cu-rich planes and the local content of Cu-atoms in G.P. zones, formation mechanisms of various types of G.P. zones and θ' -phase are discussed in terms of Al-Cu atom-pairs.

II. Specimens and Experimental Procedure

The specimens used were plate-like single crystals of an Al-1.6 at%Cu alloy which are oriented for the {100} surface. The specimens were aged at specific temperatures, and then electropolished for electron microscope observation. An electron microscope used was of a Hitachi H-9000 type high resolution electron microscope operating at 300 kV, and an *in-situ* experiment of electron irradiation induced diffusion at room temperature was carried out at 300 kV. Here, the spherical and chromatic aberration constants of the microscope are 0.9 and 1.5 mm respectively at 300 kV, and the resolving power becomes 0.19 and 0.1 for the point to point resolution and the many-waves lattice fringes respectively. Furthermore, electron microscope observation has been done under the following conditions: (1) The incident electron beam was always kept parallel to the $\langle 100 \rangle$ direction of specimens. (2) An objective aperture used was 50 μm in diameter which covers all of {220} and {200} diffraction spots. (3) Micrographs were taken under the Scherzer focus condition whose amount of defocus was -55 nm . (4) The observed areas of specimens were always about 10 nm in thickness, so that both G.P. zones and θ' -phase which are on edge exist across the specimens from the top to the bottom surface. Many-waves lattice fringes were taken under such reflecting, defocus and specimen conditions. Under the Scherzer focus condition, Cu-rich {100} planes always show bright contrasts compared with the

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Al-matrix $\{100\}$ planes because of higher scattering power of Cu-atoms⁽³⁾ when the lattice distortion is not so large.

III. G.P.-2(2) Zone $\rightarrow$ θ' -Phase Transition by Electron Irradiation Induced Diffusion

As already reported⁽⁸⁾, both G.P.-1 and G.P.-2(3) zones disappear at room temperature by electron irradiation at 300 kV, but G.P.-2(2) zones easily transform to θ' -phase. Figure 1 shows the formation process of θ' -phase at room temperature within a multi-layered G.P.-2(2) zone by electron irradiation induced diffusion at 300

kV. Figure 1(a) shows a multi-layered G.P.-2(2) zone in the specimen aged at 423 K for 14.4 ks, and each arrow indicates a Cu-rich plane. When the same area of the specimen was irradiated at room temperature with a dose rate of about 1×10^{22} e/m²·s at 300 kV, the atomistic structure gradually changes within the multi-layered G.P.-2(2) zone as follows: (1) One of the two Al-rich $\{100\}$ planes bounded with two Cu-rich $\{100\}$ planes becomes darker, but the other increases its brightness, as seen in Fig. 1(b). (2) At the same time, both the position and the spacing of bright spots on the Cu-rich planes also change gradually, while the position of the original Cu-rich planes of the multi-layered G.P.-2(2) zone does not

Fig. 1 Multi-layered G.P.-2(2) zone to θ' -phase transition induced by electron irradiation at 300 kV. Electron irradiation was carried out at room temperature with a dose rate of about 1×10^{22} e/m²·s. Each arrow in the micrographs shows a Cu-rich $\{100\}$ plane.

Fig. 2 Formation of θ' -phase in inner regions of a multi-layered G.P.-2(2) zone by aging at 523 K. Micrograph (d) shows a well-developed θ' -phase.

change so much. (3) After that, a new type of lattice fringes, which is similar to that of θ' -phase, appear in regions where the structure change preferentially occurred, as seen in a region indicated by arrows in Fig. 1(c) and (d). (4) These structure changes always occur in inner regions of the multi-layered G.P.-2(2) zone, but scarcely occurs in peripheral regions.

Figure 2(a)–(d) were picked up from the lattice fringes taken in the bulk specimens aged at 523 K for 10.8 ks. In Fig. 2, micrograph (d) shows a well developed θ' -phase, and each arrow also shows a Cu-rich {100} plane. It is to be noted in Fig. 2(c) that the formation of θ' -phase also occurs in the inner regions of a multi-layered G.P.-2(2) zone in the same manner as in the case of electron irradiation induced diffusion in Fig. 1. Namely, it is concluded that the behavior of Cu-atoms is the same in both aging at 523 K and electron irradiation induced diffusion at room temperature.

IV. Formation Mechanisms of Various Types of G.P. Zones and θ' -Phase

Local content of Cu-atoms in the G.P. zones can be estimated from the experimental results obtained by the *in-situ* experiment of electron irradiation induced diffusion. Based on both high resolution electron micrographs of G.P. zones, which were reported in the previous report, and the determination of local content of Cu-atoms in these G.P. zones, the formation mechanisms of various types of G.P. zones and θ' -phase are discussed.

1. Estimation of local content of Cu-atoms by electron irradiation effects

It was shown in Fig. 1 that a multi-layered G.P.-2(2) zone, whose Cu-rich planes are separated with two Al-rich {100} planes, changes to θ' -phase by electron irradiation induced diffusion at room temperature, and that the formation of θ' -phase preferentially occurs in inner regions of the multi-layered G.P.-2(2) zone. These facts mean that the average content of Cu-atoms in the multi-layered G.P.-2(2) zone is the same as that of θ' -phase, Al_2Cu . Namely, aging temperature 423 K for G.P.-2(2) zones is not sufficient to form θ' -phase, but the average content of Cu-atoms already reaches the same amount as that of θ' -phase.

Furthermore, it is noted in Fig. 1 that the intensity of bright spots corresponding to Cu-atom-chains in θ' -phase is always stronger than those of the Cu-rich planes in the multi-layered G.P.-2(2) zones. This means that the maximum content of Cu-atoms in local regions increases in the transition from multi-layered G.P.-2(2) zone to θ' -phase. On the other hand, in order to reduce the interfacial energy of each Cu-rich plane, local content of Cu-atoms should be gradually changed in G.P. zones⁽⁴⁾⁽⁵⁾, as expected from the formation of buffer layer in the vicinity of θ' -phase⁽¹¹⁾.

By considering the above experimental results and condition, the local content of Cu-atoms in the multi-layered G.P.-2(2) zones can be estimated. Namely, each Cu-

richmost {100} plane of the G.P.-2(2) zones is separated with two Al-rich {100} planes, and the average content of Cu-atoms should be $1/3 \times 100$ at%Cu which is equal to that of θ' -phase, Al_2Cu . Therefore, the content of Cu-atoms on each Cu-richmost plane becomes 50 at% when the Cu-richmost plane is sandwiched with Al-rich {100} planes whose Cu-atom content is assumed to be a half of 50 at%. As mentioned later, these estimated values of Cu-atom content in G.P.-2(2) zones show a good coincidence with those obtained by the Al-Cu atom-pair model.

On the other hand, G.P.-1 and G.P.-2(3) zones disappear at room temperature by electron irradiation at 300 kV⁽⁹⁾. This means that the Cu-atom contents of these G.P. zones are not sufficient to form θ' -phase at room temperature⁽⁷⁾⁽⁸⁾, so that Cu-atoms on the Cu-rich planes migrate into the matrix at room temperature by the electron irradiation effects.

As mentioned above, the content of Cu-atoms on the Cu-richmost planes can be estimated as about 50 at% at maximum even in G.P.-2(2) zones, and thus the average content of both G.P.-1 and G.P.-2(3) zones becomes only 25 at% or less even when the Cu-atom content on local planes such as the Cu-richmost plane, its first nearest planes and its second nearest planes are assumed to be 50 at%, 25 at% and $1/2 \times 25$ at%, respectively. Based on these results, the Cu-atom content on a Cu-rich plane in pre-G.P. zones is also estimated to be less than $1/4 \times 100$ at% when the total content of Cu-atoms is assumed to be the same as that of G.P.-2(3) zones.

2. Formation of atom clusters and Al-Cu atom-pairs

One of the authors already reported⁽¹⁰⁾ that new three peaks appear by aging in aluminum $\text{L}_{2,3}\text{VV}$ spectrum of Auger valence electron spectroscopy in Al-Cu alloys. These peaks clearly appear at the beginning of aging, and each energy level of them is exactly the same not only in both all kinds of G.P. zones and θ' -phase but also even in θ -phase whose atomistic structure is quite different from the others. Furthermore, the peak height of each spectrum increases with decreasing the average interatomic distance between Al-atoms and Cu-atoms in these G.P. zones and θ' -phase, all of which have a similar atomistic structure each other. In the previous report⁽¹⁰⁾, it was concluded that the results are closely related to the formation of Al-Cu atom-pairs. A typical example of the atom-pair is the electric dipole. In the case of Al-Cu alloys, a bonding strength of Al-Cu atom-pair is 51.8 ± 2.5 Kcal/mol which is larger than that of the Al-Al pair, i.e., 44.5 ± 2.2 Kcal/mol⁽¹²⁾. In addition, Cu-atoms are considerably smaller than Al-atoms so that an isolated Cu-atom is intended to bind with only one of the neighboring Al-atoms. As a result, a 3p electron of Al-atom is transferred to a 4s level of the adjacent Cu-atom because of the electronegativity difference between them. Therefore, a kind of electric dipole is considered to be formed in Al-Cu alloys, especially around a vacancy in the matrix where the coordination number decreases. In the electric dipole, the Al-atom is positively charged to

decrease its atomic diameter, and the Cu-atom reverses. Increase of Cu-atom diameter, however, is not so large, because the transferred electron occupies the same 4s electron level.

Since the Cu-atom of the electric dipole strongly binds with only one adjacent Al-atom, the dipole behaves as a pseudo-diatomic molecule in the Al-matrix because of remarkable decrease in bonding strength against the others of surrounding host Al-atoms. Here, the electric dipole strongly interacts with a vacancy (V^-) which is negatively charged, as seen in Fig. 3. Namely, the host Al-atom (α) of electric dipole in Fig. 3(b) is dragged with the vacancy, but the guest Cu-atom is pushed out by electrostatic force of the vacancy. And thus, the guest Cu-atom interacts with another surrounding host Al-atom (β) to form a new electric dipole when Al-atom (α) moves toward the vacancy, as seen in Fig. 3(c). This process is repeated even at considerably low temperatures so that rotation of the electric dipole is easily carried out when it is combined with a vacancy. The electric dipole, however, hardly possible to move when it does not combine with a vacancy. Such an immobile electric dipole interacts with the mobile electric dipole nearby through the lattice distortion around both of them, and the axes of both electric dipoles can rotate by the mutual interaction, as seen in Fig. 4. Therefore, the mobile electric dipole migrates toward the immobile one to couple with each

Fig. 3 Diffusion mechanism of a Cu-atom by rotation of a mobile electric dipole, Cu-Al, in Al-Cu alloys. Movement of the electric dipole occurs by the aid of a vacancy, during which the partner Al-atom of the dipole is switched from α - to β -atom.

Fig. 4 Formation mechanism of a Cu-atom cluster by interaction between mobile (left) and immobile (right) electric dipoles.

other when the decrease of the free energy is larger than the increase of the strain energy due to the lattice distortion. Then the vacancy becomes free from the electrostatic force of the coupled electric dipoles. This is a formation process of Cu-atom clusters. When the electronegativity difference between host-atom and guest-atom reverses, the guest-atom is dragged with the vacancy to form guest-atom clusters in the same manner.

3. Estimation of atomistic structures of G.P. zones and θ' -phase

[A] Pre-G.P. zones: The rotation of electric dipole occurs on the $\{111\}$ planes, as shown in Fig. 4, and thus each electric dipole, such as B-E and C-D in Fig. 5, originally lies on one of the $\{111\}$ planes. When the content of Cu-atoms in the Cu-atom cluster is not so large that the spacing of $\{100\}$ planes does not change markedly, *e.g.*, considerably smaller than 25 at% on a Cu-rich plane, the electric dipoles couple face to face with each other in order to minimize the total electrostatic energy, as shown in Fig. 5(a). As a result, the unlike electric dipoles couple on one of the $\{100\}$ planes with each other, as recognized from Fig. 5(a). Under this condition, the coupled electric dipoles on different $\{100\}$ planes is also arranged face to face to minimize the total electrostatic energy, as shown in Fig. 5(b). This stage probably corresponds to the formation of pre-G.P. zones.

Fig. 5 A schematic illustration of formation process of a pre-G.P. zone. In these figures, open and close circles show Al-atom and Cu-atom positions respectively, and these atom positions on different $\{100\}$ planes are illustrated with different sizes of circles in (b).

[B] G.P.-1 and G.P.-2(3) zones: When the content of Cu-atoms increases more than about 25 at% on a Cu-rich plane, the spacing of $\{100\}$ planes considerably decreases. Therefore, guest Cu-atoms form electric dipoles, such as atom-pairs 20-21 or -22, 10'-19 or -18, etc. in Fig. 6(a), with host Al-atoms on the first nearest $\{100\}$ planes in order to reduce the lattice distortion. Namely, some Cu-atoms of the electric dipoles on the original $\{100\}$ planes move toward the adjacent $\{100\}$ planes along the $\langle 110 \rangle$ direction, as shown by arrows in Fig. 6(a), e.g., Cu-atoms 10 and 7 move to positions 10' and 7' respectively. As a result, these Cu-atoms form electric dipoles with Al-atoms on different $\{100\}$ planes at both sides of the Cu-richmost planes such as A_3 and A_1 planes in Fig. 6(a). And thus, these Cu-richmost planes are separated with three Al-rich planes, as shown in Fig. 6(a). Here it should be noted in Fig. 6(b) that a pair of such electric dipoles as 20-21 and 10'-18 becomes stable when their bonding axes are switched alternately from 20-21 to 20-22 and from 10'-18 to 10'-19 respectively, so that the torque moment ($\uparrow$) between dipoles 20-21 and 10'-18 is cancelled with that between 20-22 and 10'-19. Namely, in this process a Cu-atom (10' or 20) of the partner in coupled electric dipoles (20-21 and 10'-18 or 20-22 and 10'-19) is considered to promote the charge

Fig. 6 A schematic illustration of formation process of a G.P.-2(3) zone. An arrow in (a) shows a diffusion path of Cu-atom in aging. In (b), coupling of electric dipoles 20-21 or -22 and 10'-18 or -19 is stabilized by the resonance between bonding 20-21 and 20-22 and between 10'-18 and 10'-19 respectively.

transfer between adjacent Al-atoms (21 and 22 or 18 and 19) of its own Cu-atom so that the resonance between 20-21 and 20-22 and/or between 10'-18 and 10'-19 easily occurs just like the resonance between two Kekulé structures in a benzene-ring. The resonance between two electric dipoles may result in the formation of a pseudo-triatomic molecule of Al_2Cu . This is a stage of G.P.-2(3) zone formation. As a result, the content of Cu-atoms will approach to about 50 at% and 25 at% on the Cu-richmost $\{100\}$ plane and its first nearest planes respectively.

In the process mentioned above, when a pre-G.P. zone consists of five or less atomic planes, e.g., A_1 , B_1 , A_2 , B_2 and A_3 planes in Fig. 6(a), a G.P.-1 zone is formed around a single Cu-richmost plane, i.e., A_2 plane in Fig. 6(a). In this case, the content of Cu-atoms on the Cu-richmost $\{100\}$ plane is expected to be less than 50 at%, and that of the first nearest $\{100\}$ planes is about 25 at% or less, as expected from Fig. 6(a). Namely, Cu-atoms on Cu-rich planes in pre-G.P. zones migrate along the $\langle 110 \rangle$ directions symmetrically in the formation of both G.P.-1 and G.P.-2(3) zones, respectively, as shown in Fig. 7(b) and (c).

Fig. 7 Movement of Cu-atoms in transitions among different G.P. zones. (a) shows a distribution of Cu-atoms in pre-G.P. zones. (b), (c) and (d) show transition processes from pre-G.P. zones to G.P.-1, G.P.-2(3) and G.P.-2(2) zones, respectively. Broad and dotted lines in the figures show Cu- and Al-rich {100} planes respectively, and arrows diffusion paths of Cu-atoms along the $\langle 110 \rangle$ directions.

Fig. 8 A schematic illustration of an atomistic structure of a multi-layered G.P.-2(2) zone. A₂ and B₃ planes show Cu-richmost planes. In the multi-layered G.P.-2(2) zone to θ' -phase transition, parts of Cu-atoms are expected to be shifted along the $\langle 110 \rangle$ directions, as indicated by arrows.

Fig. 9 Projections of the atomistic structure of a multi-layered G.P.-2(2) zone onto the Z- (a) and X- (b) plane. (a) shows the atomistic structure of Cu-richmost plane A₂ shown in Fig. 8, and each Cu-atom-chain, such as 1-2--- and 4-3---, on this plane is illustrated with a large close circle in (b).

Fig. 10 Schematic illustration of change of atomistic structure in the transition from a multi-layered G.P.-2(2) to θ' -phase. θ' -phase is formed in the center region of each multi-layered G.P.-2(2) zone, and G.P. zone-like buffer layers are usually retained in the vicinity of the coherent interfaces of the θ' -phase. A pair of single and double arrows shows a diffusion path of the electric dipole. Atomic fraction of Cu-atoms on each plane is shown at the top.

[C] G.P.-2(2) zones: When the aging temperature increases so that the density of coupled electric dipoles, i.e., pseudo-triatomic molecules, approaches to that of θ' -phase, diffusion of Cu-atoms occurs asymmetrically in a pre-G.P. zone to form G.P.-2(2) zones, as shown in Fig. 7(d). Figure 8 shows an atomistic structure of these G.P.-2(2) zones. In this process, shift of the electric dipole is also considered to occur along one of the $\langle 110 \rangle$ directions. Projections of the atomistic structure of G.P.-2(2) zones to Z- and X-planes, which are perpendicular to Z- and X-axes respectively, are illustrated in Fig. 9(a) and (b). In Fig. 9(b), each Cu-atom on A_2 plane makes a coupling with a Cu-atom on either of adjacent planes B_1 and B_2 , e.g., Cu-atoms 1, 2, 3, 4, ... with Cu-atoms 1', 2', 3', 4' ... Here, there is two ways for making the coupling, e.g., Cu-atom 1 can also make a coupling with Cu-atom 1'' on plane B_1 with the same possibili-

ty as with Cu-atom 1'. As a result, the content of Cu-atoms on A_2 and B_3 planes becomes 50 at%, and those on B_1 , B_2 , A_3 and A_4 planes 25 at% respectively, as estimated from the experimental results obtained by using electron irradiation effects.

[D] θ' -phase: When parts of the electric dipoles in Fig. 8 are shifted along the $\langle 110 \rangle$ directions, as shown by arrows in Fig. 8 and with pairs of single and double arrows in Fig. 10(a), the atomistic structure of multi-layered G.P.-2(2) zones transforms to that of θ' -phase, as illustrated at the center region of Fig. 10(b) which consists of α , β and γ planes. By this movement of electric dipoles, all Al-atoms on the Cu-rich α planes move onto adjacent β planes, and a new Cu-plane γ is formed at the middle position between two Al-planes (β). As a result, 100 at% Cu-planes, whose atomic density is a half of that of an Al {100} plane, and 100 at% Al-planes are formed alternately. This is the formation process of θ' -phase of Al_2Cu .

V. Conclusions

In the present work, local content of Cu-atoms in various types of G.P. zones in Al-1.6 at% Cu crystals was estimated from the experimental results obtained by the electron irradiation effects. Based on not only these experimental results but also high resolution electron micrographs of these G.P. zones in the previous report, the formation mechanisms and atomistic structures of various G.P. zones, such as pre-G.P., G.P.-1, G.P.-2(3), and G.P.-2(2) zones, and θ' -phase were discussed in terms of Al-Cu atom-pairs.

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