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Behavior of Cu-atoms in formation of G.P. zones and θ' -Phase in Al-Cu Alloys

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Abstract. — Al-Cu crystals have been investigated by *in-situ* aging with a high resolution electron microscope. Results obtained are summarized as follows: a) Four types of G.P. zones are formed by aging at low temperatures. b) In these G.P. zones, pre-G.P. zones, G.P.-1 and G.P.2(3) whose Cu-rich {100} planes are separated with three Al-rich {100} planes disappear at room temperature by electron irradiation at 300 kV. c) G.P.-2(2) zones whose Cu-rich {100} planes are separated with two Al-rich {100} planes easily transform to θ' -phase at room temperature by the same electron irradiation. d) The local content of Cu-atoms in these G.P. zones have been estimated from the results obtained by *in-situ* experiment of electron irradiation induced diffusion. Based on these results, mechanisms on the diffusion of Cu-atoms, 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.

1. Introduction.

It is well known that so-called G.P. zones [1, 2], which are a sort of atom clusters, are formed at the beginning of aging in Al-base alloys. The formation of G.P. zones is important not only as the pre-nucleation process of stable phases but also as a useful strengthening mechanism of light metals, and thus many experimental and theoretical work have been carried out. However, detailed processes of both the formation of G.P. zones and their transition to θ' -phase in Al-Cu alloys have not been made clear yet. Recently, the high resolution electron microscopy [3-5] and the atom-probe FIM [6] have been applied to this subject to obtain the detailed atomic information. Those results show that both content and distribution of Cu-atoms in G.P. zones, which have been considered to be concluded by Gerold [7] and others, should be investigated again. Furthermore, it has been suggested from a new nucleation theory [8, 9] that the denuded zones are difficult to be formed around an isolated Cu-atom plane because of remarkable increase in the interfacial energy of G.P. zones. These mean that more information is necessary to obtain on the detailed behavior of Cu-atoms during aging.

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The author already reported that the same behavior of lattice defects as in bulk specimens can be dynamically observed by *in-situ* experiments with electron microscopes when the specimen thickness is larger than the mean free path of the lattice defects [10]. Since the specimen is generally about 10 nm in thickness for the high resolution electron microscopy in order to suppress the inelastic scattering of electrons, applications of the *in-situ* experiment are very limited by the above necessary condition. The mean free paths of both point defects induced by electron irradiation and constituent atoms of Al-Cu alloys are in the atomic scale at low temperatures. Furthermore, the threshold voltage for electron irradiation damage in Al-Cu alloys is about 150 kV [11], and the vacancy diffusion occurs even at room temperature in these alloys. And thus, it is expected in Al-Cu alloys that the same behavior of Cu-atoms as that in aging of bulk specimens can be investigated directly with high resolution electron microscopes operating at 200 kV or more by using the electron irradiation induced diffusion at low temperatures.

From this point of view, in the present experiment an *in-situ* experiment has been carried out at room temperature with a 300 kV high resolution electron microscope on the behavior of Cu-atoms during aging in Al-Cu alloys.

Based on the results, formation processes of various types of G.P. zones and the transition from G.P. zones to θ' -phase are discussed.

2. Specimens and experimental procedure.

Mother crystals used were plate-like single crystals of an Al-1.6at% alloy which are oriented for the {100} surface. Disks of 3 mm in diameter and 130 μm in thickness were cut out from the mother crystals, and water quenched after solution treatment at 800 K for 36 ks. These {100} disk specimens were aged at specific temperatures, and then electropolished for electron microscope observation. An electron microscope used was of Hitachi H-9000 type high resolution electron microscope operated at 300 kV, and an *in-situ* experiment of 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 nm for the point to point resolution and the many-waves lattice fringes. Therefore, the information about the atomistic structures of G.P. zones can be expected to markedly increase with the 300 kV electron microscope. Furthermore, an 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 the specimens. 2) An objective aperture used was 50 μm in diameter which covers all of the {220} and {200} diffraction spots. 3) The observed areas of the 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. 4) Micrographs were taken under the Scherzer focus condition whose defocus amount was -55 nm. 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 Al-matrix {100} planes because of higher scattering power of Cu-atoms [5] when the lattice distortion is not so large.

3. Experimental results.

3.1 FORMATION OF VARIOUS G.P. ZONES — In the previous reports [12], formation processes of the G.P. zones and θ' -phase in Al-1.6at%Cu crystals have been investigated by the high resolution electron microscopy with the following results: a) Three dimensional Cu-atom clusters are formed

at the beginning of aging at both 373 and 423 K, respectively. b) In 373 K aging, these clusters change to G.P.-1 zones and/or G.P.-2(3) zones whose Cu-rich {100} planes are separated with three Al-rich {100} planes. Multi-layered G.P.-2(3) zones and sometimes G.P.-2(2) zones whose Cu-rich {100} planes are separated with two Al-rich {100} planes are formed by further aging at 373 K. c) In 423 K aging, the Cu-atom clusters change to G.P.-2(2) zones, and they are followed by the formation of multi-layered G.P.-2(2) zones. θ' -phase is formed within the multi-layered G.P.-2(2) zone by electron irradiation induced diffusion at room temperature in the same way as in aging at 523 K.

The results are summarized into figure 1 in which paths indicated with solid lines occur in general.

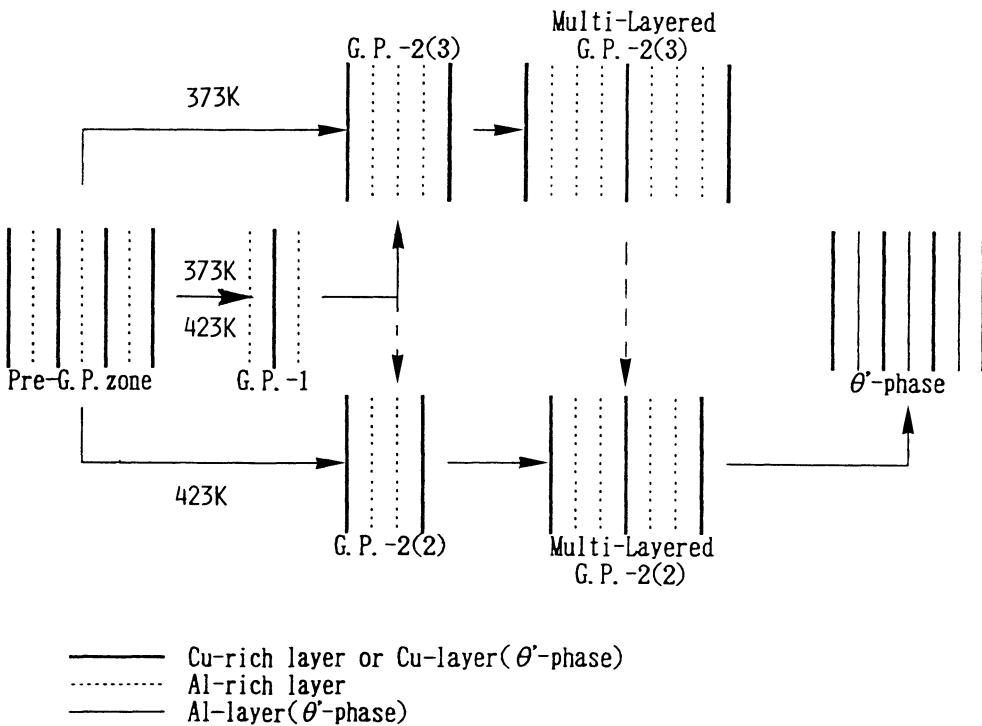


Fig. 1. — Formation processes of various types of G.P. zones and θ' -phase in Al-1.6at%Cu crystals. Transitions generally occur along solid lines, but sometimes along dotted lines. In the figure, broad solid and dotted lines in G.P. zones show Cu- and Al-rich {100} planes respectively.

3.2 STRUCTURE CHANGES OF VARIOUS G.P. ZONES BY ELECTRON IRRADIATION INDUCED DIFFUSION AT ROOM TEMPERATURE — Figure 2 shows atomistic structures of both G.P.-1(mark 1) and G.P.-2(3) zones (2-5) in a bulk specimen aged at 373 K for 14.4 ks. When the specimen is electron irradiated at 300 kV, the contrast of both types of G.P. zones gradually disappear, as seen in figures 2b and c [13].

On the other hand, G.P.-2(2) zones are formed in bulk specimens aged at 423 K, and they easily transform to θ' -phase by the same electron irradiation. Figure 3 shows the formation process of θ' -

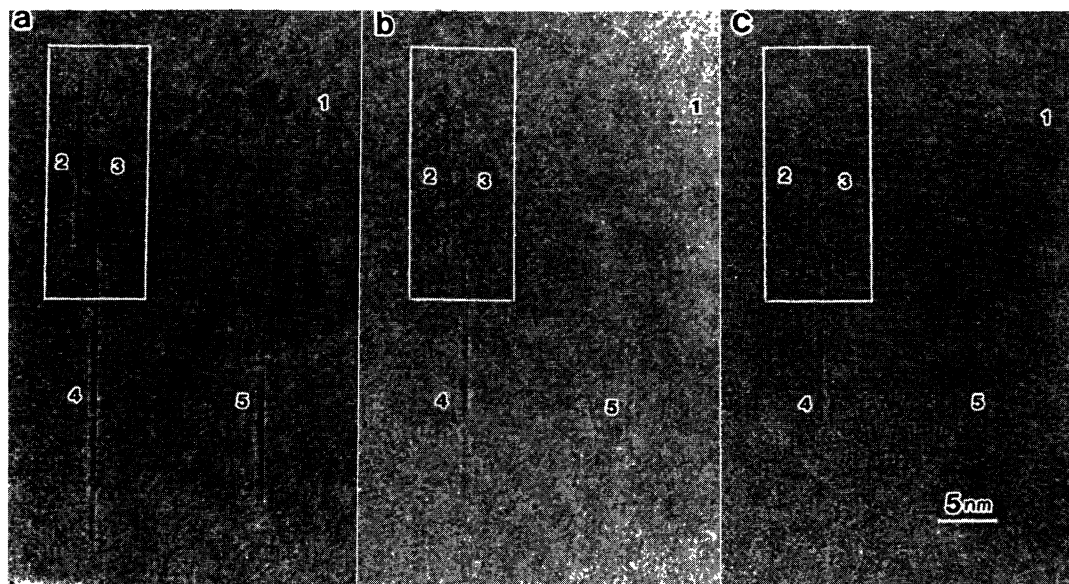


Fig. 2. — Disappearance of G.P.-1 and G.P.-2(3) zones by electron irradiation which was carried out at room temperature for (b) 0.24 and (c) 0.42 ks with a dose rate of about $1 \times 10^{22} \text{e/s.m}^2$ at 300 kV respectively.

phase at room temperature within a multi-layered G.P.-2(2) zone by electron irradiation induced diffusion at 300 kV. Figure 3a 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 $1 \times 10^{22} \text{e/m}^2 \text{ s}$ 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 figure 3b. 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 change so much. 3) After that, a new type of lattice fringes, which is similar to that of θ' -phase, appears in regions where the structure change preferentially occurred, as seen in a region indicated by arrows in figures 3(c) and (d). 4) These structure-change always occur in inner regions of the multi-layered G.P.-2(2) zone, but scarcely occur in peripheral regions.

Figures 4a-d were picked up from the lattice fringes taken in the bulk specimens aged at 523 K for 10.8 ks. In figure 4, micrograph (d) corresponds to a well developed θ' -phase, and each arrow also shows a Cu-rich $\{100\}$ plane. It is to be noted in figure 4c 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 figure 3. 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.

4. A formation mechanism of atom clusters in the alloys.

The author already reported [14] that new three peaks appear by aging in the aluminum $L_{2,3} \text{VV}$ spectrum of Auger valence electron spectroscopy in aged Al-2.2at%Cu alloys. These peaks clearly

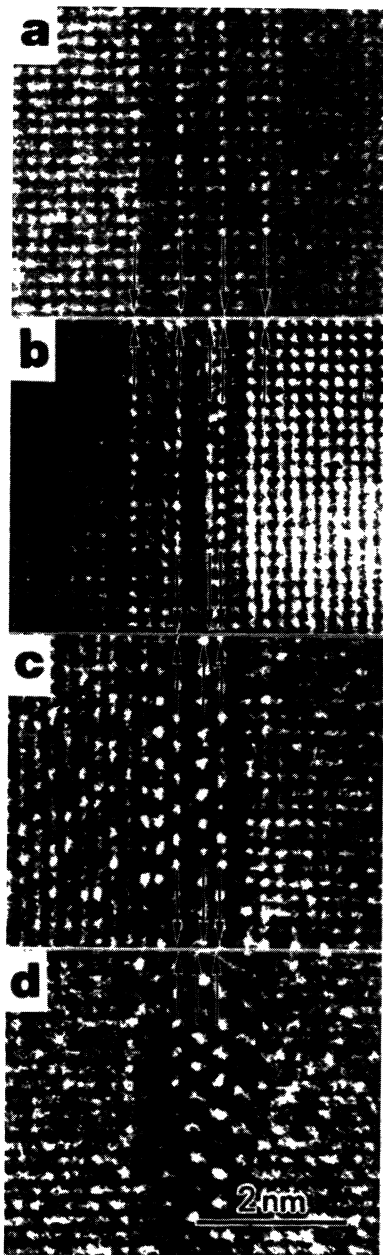


Fig. 3. — Multi-layered G.P.-2(2) zone to θ' -phase transition induced by electron irradiation at 300 kV. Each arrow in the micrograph shows a Cu-rich $\{100\}$ plane. Electron irradiation was carried out for (b) 0.42, (c) 0.8 and (d) 0.9 ks with a dose rate of about $1 \times 10^{22} \text{e/s.m}^2$, respectively.

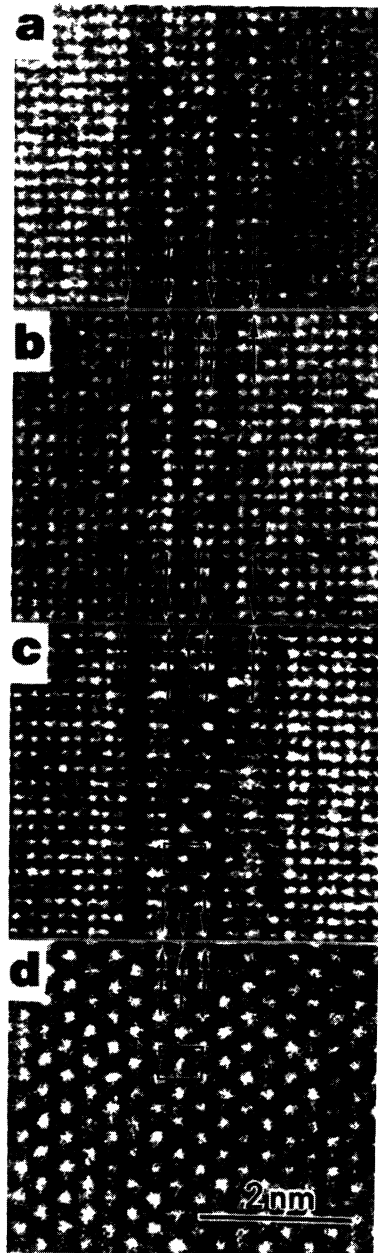


Fig. 4. — Formation of θ' -phase in inner regions of a multi-layered G.P.-2(2) zone by aging at 523 K. Micrograph (d) shows many-waves lattice fringes of a well-developed θ' -phase.

appear at the beginning of aging, and each energy level of them is almost 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

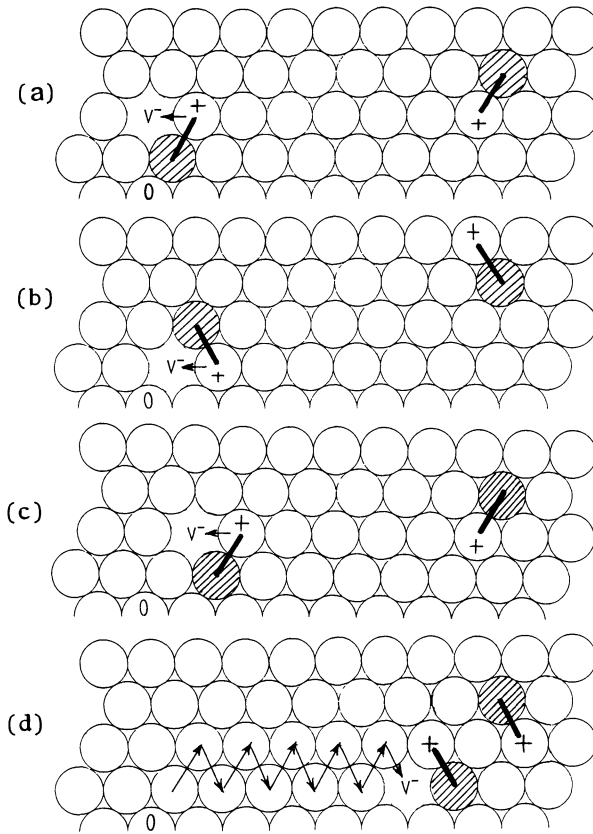


Fig. 5. — Formation mechanism of a Cu-atom cluster by interaction between mobile (left) and immobile (right) electric dipoles.

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 atomic structure to each other. In the previous report [14], 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 [15]. 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 the Al-atom is transferred to the 4s level of an 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. This is an important character of the electric dipole.

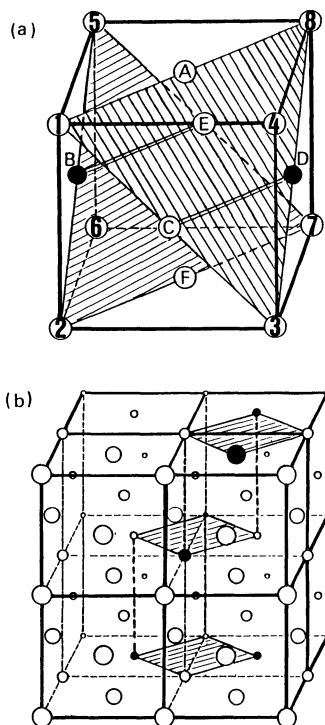


Fig. 6. — A schematic illustration of formation process of a pre-G.P. zone. In these figures, open and close circles also show Al- and Cu-atom positions respectively, and these atom positions on different $\{100\}$ planes are illustrated with different sizes of circles in (b).

As mentioned above, the atom-pair is polarized as an electric dipole in Al-Cu alloys. The electric dipole strongly interact with a vacancy (V^{-1}) nearby which is negatively charged, as seen in figure 5. Namely, the host Al-atom(+) of electric dipole in figure 5a is dragged with the vacancy, but the guest Cu-atom (hatched one), which is negatively charged, is pushed out by electrostatic force of the vacancy. And thus, the guest Cu-atom interacts with another surrounding host Al-atom to form a new electric dipole when the Al-atom of an old partner moves toward the vacancy, as seen in figure 5b [12]. 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 figure 5. Therefore, the mobile electric dipole migrates toward the immobile one to couple with each 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, as seen in figure 5d. This is a formation process of Cu-atom clusters. When the electronegativity difference between host- and guest-atoms reverses, the guest-atom is dragged with the vacancy to form guest-atom clusters in the same manner.

5. Formation mechanisms 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 figure 5, and thus each electric dipole, such as B-E and C-D in figure 6, 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 25at% 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 figure 6a. As a result, the unlike electric dipoles couple on one of the $\{100\}$ planes with each other, as recognized from figure 6a. 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 figure 6b. This stage probably corresponds to the formation of pre-G.P. zones.

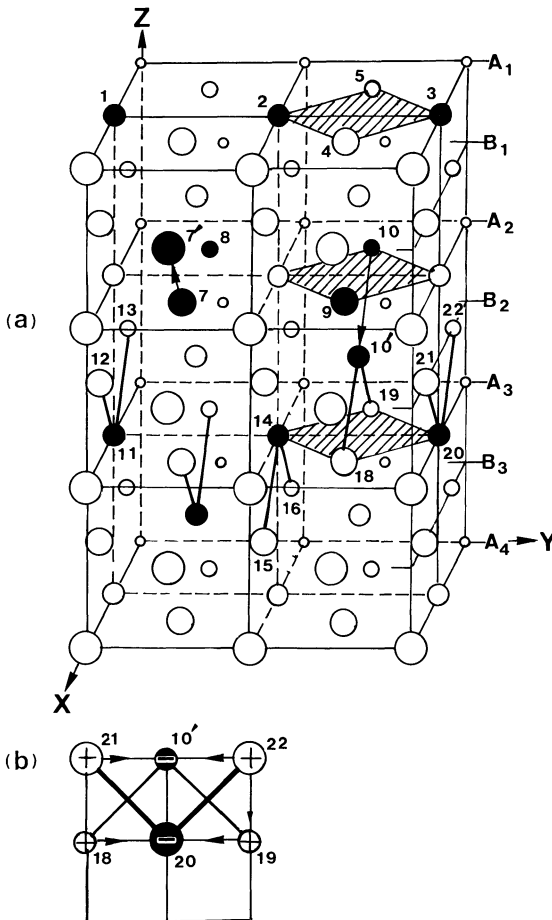


Fig. 7. — A schematic illustration of formation process of a G.P.-2(3) zone. An arrow in (a) shows a diffusion path of Cu-atom in aging. In (b), coupling of electric dipoles 20-21 or -22 and 10'-18 or -19 is stabilized by the resonance between bonding 20-21 and 20-22 and between 10'-18 and 10'-19 respectively.

(B) G.P.-1 and G.P.-2(3) zones: When the content of Cu-atoms increases more than about 25at% 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 figure 7a, with host Al-atoms on the 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 figure 7a, 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 figure a. And thus, these Cu-richmost planes are separated with three Al-rich planes, as shown in figure 7a.

Here it should be noted in figure 7b 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. Namely, the torque moment (\uparrow) between dipoles 20–21 and 10'–18 is canceled with that between 20–22 and 10'–19. In this process, each Cu-atom (10' or 20) of the coupled electric dipoles (20–21 and 10'–18 or 20–22 and 10'–19) is considered to promote the charge transfer between adjacent Al-atoms (21 and 22 or 18 and 19) around a Cu-atom of the other dipole 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 50at% and 25at% on the Cu-richmost {100} plane and its first nearest planes respectively.

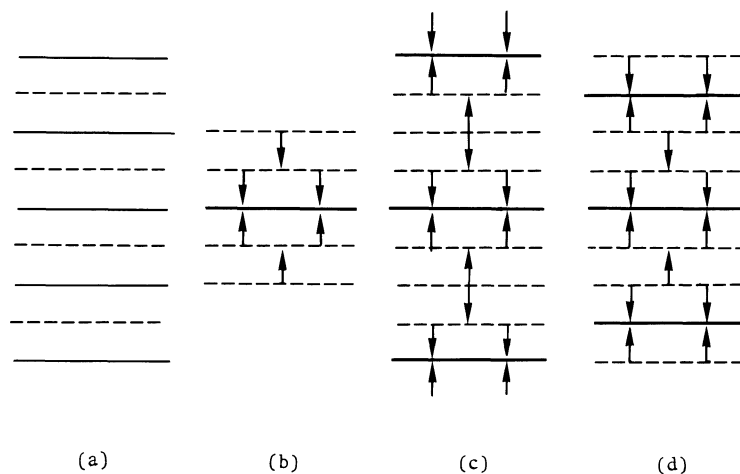
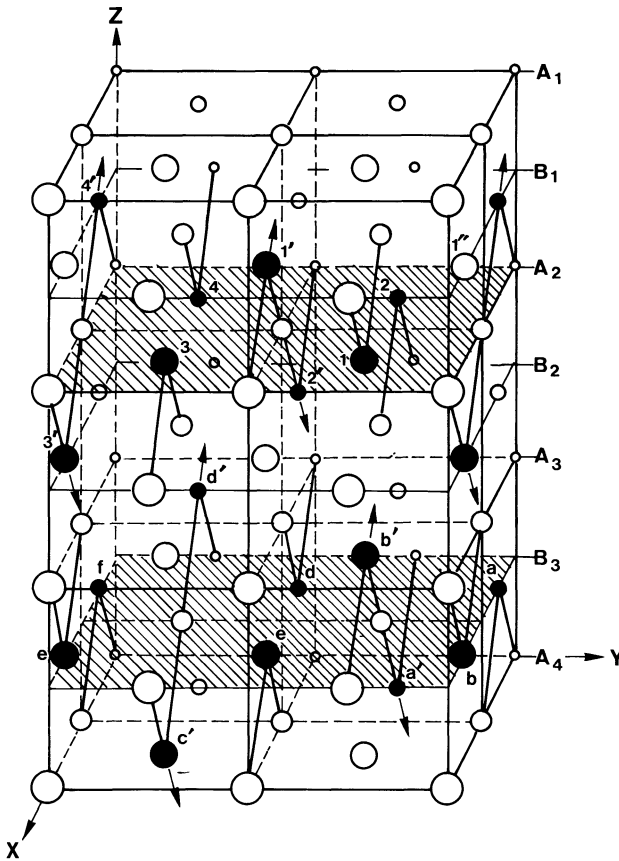


Fig. 8. — Movement of Cu-atoms in transitions among different G.P. zones. (a) shows a distribution of Cu-atoms in pre-G.P. zones, (b), (c) and (d) show transition processes from pre-G.P. zones to G.P.–1, G.P.–2(3) and G.P.–2(2) zones, respectively. Broad and dotted lines in the figures show Cu- and Al-rich {100} planes respectively, and arrows diffusion paths of Cu-atoms along the $\langle 110 \rangle$ directions.

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 figure 7a, a G.P.–1 zone is formed around a single Cu-richmost plane, i.e., A_2 plane in figure 7a. In this case, the content of Cu-atoms on the Cu-richmost {100} plane is expected to be less than 50at%, and that of the first nearest {100} planes is about 25at% or less, as expected from figure 7a. Namely, Cu-atoms on Cu-rich planes in pre-G.P. zones migrate



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Fig. 9. — A schematic illustration of 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.

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 figures 8b and c.

(C) G.P.-2(2) zones: when the aging temperature increases so that the average density of the coupled electric dipoles, i.e., the pseudo-triatomic molecules, approaches to that of θ' -phase, diffusion of Cu-atoms occurs asymmetrically in a pre-G.P. zones, as shown in figure 8d, to form a G.P.-2(2) zone. Figure 9 shows an atomistic structure of the G.P.-2(2) zone. In this process, shift of the electric dipole is also considered to occur along one of the $\langle 110 \rangle$ directions. As a result, the content of Cu-atoms on A₂ and B₃ planes becomes 50at%, and those on B₁, B₂, A₃ and A₄ planes 25at% respectively, as estimated from the experimental results obtained by using electron irradiation effects [12, 13].

(D) θ' -phase: When parts of the electric dipoles in figure 9 are shifted further along the $\langle 110 \rangle$ directions, as shown by arrows in figure 9 and with a pair of single and double arrow in figure 10a, the atomistic structure of multi-layered G.P.-2(2) zones transforms to that of θ' -phase, as illustrated at the center region of figure 10b which consists of α , β and γ planes. By this movement

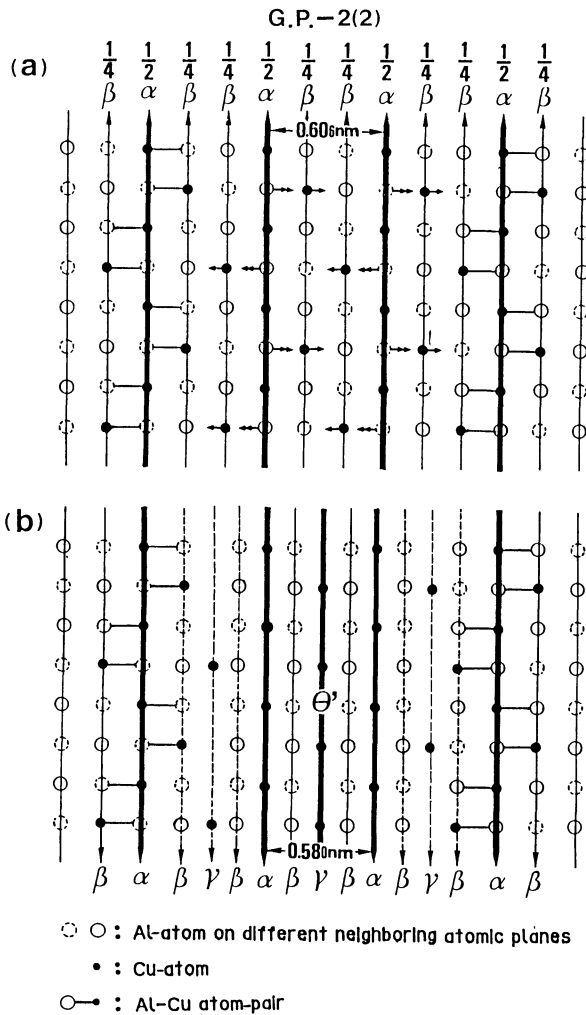


Fig. 10. — Schematic illustration of change of atomistic structure in the transition from a multi-layered G.P.-2(2) to θ' -phase. θ' -phase is formed in the center region of each multi-layered G.P.-2(2) zone, and G.P. zone-like buffer layers are usually retained in the vicinity of the coherent interfaces 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.

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, 100at% Cu-planes, whose atomic density is a half of that of an Al {100} plane, and 100at% Al-planes are formed alternately. This is the formation process of θ' -phase of Al_2Cu .

6. Conclusions.

Up to date, many models have been proposed on the formation of such atom clusters as G.P. zones. In case each solute atom is assumed to simply occupy the substitutional and/or interstitial site of

the matrix crystal, those models are difficult to explain these diffusion phenomena, because the lattice distortion around each individual solute atom causes the repulsive force against the other solute atoms which have the strain fields in the same sign. Practically, however, the chemical, e.g., electronegativity, and the physical, e.g., the Fermi energy which is sensitive to the atomic size difference, properties are different in solute and solvent atoms. The differences cause the charge transfer between these two kinds of atoms so that the electric dipoles are formed, and thus the attractive interaction occurs even among the same solute atoms.

In the present work, the formation of various G.P. zones and transition from G.P. zones to θ' -phase in Al-Cu alloys were well explained in terms of the electric dipoles. Furthermore, it was also shown that the formation of a new crystal structure is closely related to the formation of a pseudo-multiatomic molecule resulting from the resonance among the electric dipoles.

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