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Copper concentration inside Guinier-Preston I zones formed in an Al–Cu alloy

The copper concentration inside a Guinier-Preston (GPI) zone was studied by means of an extended Hückel molecular orbital (EHMO) calculation. The present EHMO calculation revealed that the Cu concentration inside a GPI zone depends on the size of the zone. The GPI zone comprises both Cu and Al in a small GPI zone, whereas the Cu concentration inside the GPI zone increases to nearly 100 at.% Cu in a large GPI zone. A compressive lattice distortion, which is associated with the zone, increases the stability, but when a GPI zone is 5 nm in diameter, the stabilizing effect of the zone is estimated to be not higher than 10 % of the chemical energy due to Cu coalescence.

Keywords: Al–Cu alloy; Guinier-Preston zones; Copper concentration; Extended Hückel MO calculation

1 Introduction

The precipitation behavior is one of the most important issues in an Al alloy study since the phenomenon is widely used in age-hardening Al-base alloys. An Al–Cu alloy is one of the most important precipitation-hardening Al alloys for practical purposes. Many studies have been devoted to clarifying the precipitation behavior in the alloy. Relative to the aging process of the alloy, one widely accepted interpretation holds that several metastable and stable phases appear individually and consecutively in a supersaturated solid solution (ssss) $\rightarrow$ GPI $\rightarrow$ GPII (or θ'') $\rightarrow$ θ' $\rightarrow$ θ . In most studies, the GPI zone is interpreted as a solute aggregate initially formed in an Al matrix [1, 2]. There are, however, disputes on several basic points such as the Cu concentration and structure inside the zone. Some of those points were discussed in a special issue of *Scripta Metallurgica* (1988) [3], but no definitive conclusions were reached there or in successive works.

As far as the precipitation hardening is concerned, the Cu concentration inside a GPI zone is essentially important to consider since the strength of the particle is expected to be closely dependent on the concentration. Gerold [4, 5] proposed a monolayer platelet model comprising only Cu atoms as a GPI, based on an X-ray diffraction experiment. However, some investigations based on X-ray diffraction [6], extended X-ray absorption edge fine structure investigation (EXAFS) [7] and field ion microscopy (FIM) [8] which supported a model containing aluminum as well as Cu atoms were also reported on the GPI zone. Jouffrey and his coworkers [9, 10] recently investigated the composition of the zone by means of high-resolution transmission elec-

tron microscopy (TEM) and energy-dispersive X-ray analysis (EDX) and claimed that the GPI zone contains both Cu and Al.

To investigate the Cu concentration inside the GPI, one of the present authors (M. T.) applied an empirical chemical-bond calculation based on the extended Hückel molecular orbital (EHMO) theory to estimate the stability of the GPI zone and published some of the results in 1992 [11]. According to the calculation done by the group, the GPI zone comprises both Al and Cu atoms. An opposite conclusion, however, resulted from an EHMO calculation by other workers [12]. An important remaining task is to examine the size dependence of the composition of the GPI zone since the previous papers did not explicitly consider this point. Furthermore, such a consideration may also be crucial when any experimental technique is applied to the examination of the Cu concentration inside the GPI zone. The present work aimed at examining the solute composition of the GPI zone by the EHMO calculation taking into account the size of the zone.

2 Fundamental aspects of the EHMO calculation

The method for the present calculation is based on the EHMO theory, which is categorized as an empirical molecular orbital method. The EHMO calculation uses the time-independent Schrödinger equation,

$$H\psi = \varepsilon\psi \quad (1)$$

where H is the Hamiltonian, ε is the eigenvalue of energy, and ψ is the eigenfunction. Because the Schrödinger equation for a cluster model consisting of many atoms cannot be analytically solved, the linear combination of atomic orbital (LCAO) approximation is introduced for a numerical computation. That is,

$$\psi = \sum_{i=1}^N C_i \chi_i \quad (2)$$

where ψ is a molecular orbital and χ_i is an atomic orbital of constituent atoms.

The secular Eq. (3) is obtained from Eqs. (1) and (2).

$$\text{Det } |H - \varepsilon S| = 0 \quad (3)$$

$$H_{ij} = \langle \chi_i | H | \chi_j \rangle \quad (4)$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle \quad (5)$$

Using the further approximations that (i) the Slater-type orbitals are adopted as the bases and Coulomb and resonance integrals are related as (ii) $H_{jj} = -I_j$ (ionization potential),

and (iii) $H_{ij} = K(H_{ii} + H_{jj}) S_{ij}/2$ ($K = 1.75$), the total energy is calculated by

$${}^{\circ}E = \sum n_i \varepsilon_i \quad (6)$$

The cohesive energy is given by

$${}^{\circ}E = \sum n_i \varepsilon_i - \sum N_j I_j \quad (7)$$

In the present study, the difference of the energy ΔE for the clusters with and without a GPI zone is estimated by the following equation,

$$\begin{aligned} \Delta E &= {}^{\circ}E_{\text{GP}} - {}^{\circ}E_{\text{disorder}} \\ &= {}^{\circ}E_{\text{GP}} - {}^{\circ}E_{\text{disorder}} \end{aligned} \quad (8)$$

where ${}^{\circ}E_{\text{GP}}$ is the orbital energy containing a GPI zone and ${}^{\circ}E_{\text{disorder}}$ is the energy of the solid solution. We calculated the E_{disorder} value with an assumption that the value is equal to the arithmetic average of pure Al and pure Cu clusters based on the concentration. In addition, the difference of the energy ΔE is normalized by dividing with the number of constituent atoms (n). Thus, $\Delta E/n$ is finally used for the estimation of the stability of the structure.

$$\Delta E/n = ({}^{\circ}E_{\text{GP}} - {}^{\circ}E_{\text{disorder}})/n \quad (9)$$

It is known that a non-empirical molecular orbital calculation sometimes provides a value more accurate than the EHMO calculation for a small cluster model. In spite of that, the EHMO method has several advantages over other molecular orbital calculation techniques. That is, (i) the EHMO method can deal with a relatively large cluster mod-

el which is essentially important to consider the stability depending on the concentration, and (ii) the EHMO calculation offers the total energy, which can be used as a scale for the stability. Although the energetic scale is rough, the estimation has been successfully applied to consider various aspects of phase stability such as surface absorption [13] and intermetallic phase stability [14]. Thus, the EHMO calculation has already been recognized as a simple but useful technique which gives us information of general tendencies in various phenomena with clear physical insights. In this work, the 2s- and 2p-atomic orbitals of Al and the 4s- and 4p-atomic orbitals of Cu were taken into account. Although no lattice distortion was included in the previous EHMO calculation [9], both cluster models with and without local lattice deformations were considered in the present work. The EHMO calculation can, in principle, easily include local deformations associated with a GPI zone. The lattice parameter of the Al matrix was used for the models ($= 0.406$ nm) with no local distortion model. Since no reliable data of the local deformations were experimentally derived, the present calculation considered compressive distortions up to 10 %, taking the difference of the lattice constants in pure Al and pure Cu bulk crystals into account.

Figure 1 shows an example of cluster models for the present EHMO calculations. All models were constructed with the special attention to reduce an artifact due to the modeling of the structure. Therefore, all the models were built to be as symmetric and spherical as possible. For the same reason, the Cu atoms were also placed on symmetric positions. Figure 2 shows the atomic arrangements in the Cu layer, which have different Cu concentrations. The Cu concentrations inside the zone are estimated as 20.0, 38.5, 55.6 and 100 at.%. Since the present purpose is to examine the stability depending on the Cu concentration inside the monolayer GPI, the center layer containing Cu atoms is sandwiched by several pure Al layers on both sides.

Fig. 1. A GPI zone cluster model for the present EHMO calculation (the central and upper six layers of the model are drawn).

Fig. 2. Atomic arrangements of the central layer comprising different Cu concentrations in at.% (a–d).

3 Results and discussion

3.1 Size dependence of the Cu concentration of the GPI zone

Figure 3 shows the chemical formation energy ($\Delta E/n$) of the GPI zone which was obtained from the present EHMO calculation. The formation energy is dependent on the total number of Cu atoms, and the energy is negatively increased with the number of Cu atoms. It is clearly shown that the curve of the formation energy is minimized at a certain Cu concentration range. If a small number of Cu atoms were

Fig. 3. Formation energy of the GPI zone obtained from the present EHMO calculation.

involved, the curve of the formation energy ($\Delta E/n$) would show a large plateau. For example, if five Cu atoms were segregated, the stability would be nearly similar whether the Cu concentration inside the GPI zone was 30 or 100 at.%. The curve of the energy, however, tends to have a narrow plateau and to shift the minimum value towards 100 at.% in Cu concentration when a larger number of Cu atoms is committed in the GPI zone formation. Thus, the result shown in Fig. 3 strongly suggests that the Cu concentration inside the GPI zone is gradually changed and approaches 100 at.% with the growth. Converting the number of Cu atoms involved in the GPI zone into the size of the zone, we find that a GPI zone of approximately 3.5–5.0 nm in diameter is occupied by up to more than 70 at.% Cu. Considering the size dependence of the formation energy, a GPI zone larger than ~5.0 nm in diameter is expected to have 70–100 at.% Cu. It may be noted that this critical size of a GPI zone with a high Cu concentration can be shifted towards a larger value if the configuration entropy gives a significant influence.

3.2 Influence of a lattice compression on the stability of a GPI zone

A bright-field TEM observation often shows that a GPI zone is accompanied by a strain contrast around it. Although the lattice deformation associated with the GPI zone is not easy to be estimated quantitatively by experiments, the effect of a deformation would also be an interesting item to examine using a molecular orbital calculation.

Figure 4 shows a set of curves of the formation energy, which was obtained for cluster models with and without a compressive deformation in the central (001) plane where Cu atoms are segregated. If the GPI zone comprises five Cu atoms, the distortion slightly alters the energy level. The influence of the deformation, however, becomes explicit to the zone which is as large as the one containing 29 Cu atoms. A compressive distortion of 10 % in ratio reduces the formation energy and makes the zone more stable, especially for a GPI zone with a large diameter. The difference of the forma-

Fig. 4. Influence of lattice distortions inside the GPI zone on the formation energy of the zone.

Fig. 5. Influence of lattice distortions vertical to GPI zone.

tion energy is approximately 10 % in the total energy for a GPI zone consisting of 29 Cu atoms. Thus, the stability of the GPI zone is mainly due to the chemical effect of solute coalescence for a zone > 5 nm in diameter.

Figure 5 shows the formation energy of a GPI zone vertically distorted at Al layers adjacent to the central layer of the GPI zone. Two sets of curves, which are drawn in the upper and lower parts of the figure, show the energy for a GPI zone comprising 13 and 29 Cu atoms with and without a compressive distortion, respectively. In both cluster sizes, a slight difference in energy is visible between the curves for the models with and without the vertical distortion. Therefore, the vertical distortion does not effectively work for a GPI zone stability. It should be noted that this result does not directly suggest that vertical distortion is not introduced during GPI zone formation. Contrarily, the present authors suppose that a small difference in the energy could cause a vertical distortion which is similar to the distortion associated with a Frank dislocation loop.

The present EMO calculation leads to the conclusion that the Cu concentration of the GPI zone is changed from low to high with the growth of the zone. Referring to the experimental conditions of previous studies, we found that there was a tendency to use aging treatments at low temperatures for short durations in the work that concluded there was a mixture of the constituent atoms in the GPI zone [6–10], whereas those who supported the pure Cu GPI model used treatments at higher temperatures for longer periods [4, 5]. The present EMO calculation has successfully provided a reason for the fact that contradictory conclusions were experimentally presented, although the previous works hardly recognized the alteration in Cu concentration due to the growth.

There are several possible solutions based on similar theories. We adopted a measuring scale [i. e., Eq. (9)] which was used in the previous studies by the present authors. Yamamoto et al. [12] adopted cohesive energy and relaxation time to estimate the stability of the state. Further investigation is necessary to clarify this point. The present paper stresses that a critical size should be taken into account when further examination of the Cu concentration is undertaken in future experiments.

4 Conclusions

The present EMO calculation examined the size dependence of the Cu concentration inside a monolayer GPI zone formed in an Al–Cu alloy. The formation energy of a GPI zone depends on the size of the zone. When the GPI zone is small, the curves of the formation energy show a minimum energy of ~40 at.% Cu, and the stability of the zone is almost similar in the range 35–100 at.% Cu. When the GPI zone grows large, the range of the minimum energy becomes narrow and limited to near 100 at.% Cu. The size dependence of the Cu concentration inside the GPI zone is a possible explanation for the controversial results that have been obtained in experiments. A compressive distortion among the Cu atoms positively affects the increase in the stability of the GPI zone with a large diameter. A vertical distortion at Al layers adjacent to the central layer can occur, but the distortion has a slight influence on the zone stability.

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