Comparison between Resistivity Changes and Monte Carlo Simulation for GP Zone Formation in Al–Cu Base Ternary Alloys

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The formation behavior of GP zones has not been fully understood because experimental detection of their nucleation and growth is rather difficult especially in the early stage of aging. Monte Carlo simulation is a most powerful method to examine such microscopic events occurring in alloys during phase transformations. The present work aims to investigate the effects of various additional elements to an Al–Cu alloy from both viewpoints of the nucleation and growth behavior of GP zones. Comparisons between the quantitative kinetics determined by the electrical resistivity changes and the microstructural evolution obtained from the simulation provide useful information on both the macroscopic transformation behavior and the detailed formation mechanism of Cu clusters. As is well known so far, addition of Zn or Ag exerts no marked influence on the GP zone formation, whereas addition of Sn or Zr markedly retards the growth rate of GP zones. As for a small addition of Mg, however, slightly complicated effects are revealed; i.e. a characteristic nucleation behavior and a suppressed growth of GP zones. This is well explained in terms of both the extremely increased number density of Mg/Cu/Vacancy complexes and the pronounced decrease in free-vacancies available for Cu diffusion due to the preferential vacancy trapping by Mg atoms. Such situations are directly observed in atom configurations during the simulation.

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I. Introduction

In general, experimental detection of the nucleation behavior of low-temperature precipitates such as GP zones is significantly difficult because of their extremely rapid formation during quenching and/or in the early stage of aging. Therefore, it has been normally regarded that an activation energy for their nucleation is practically almost negligible. However, our recent results\(^{12}\) on the rate of electrical resistivity changes showed that Al–Cu alloys containing substantial amounts of Li exhibit a distinct stage for the GP(1) zone nucleation with an activation energy of 85.5 kJ/mol. Simultaneous small addition of Mg was also found to decrease the activation energy due to the heterogeneous nucleation effect with the aid of Mg/Cu/Vacancy complexes. These results indicate that third additional elements to Al–Cu alloys significantly change the nucleation behavior of GP zones. Therefore, it is important to elucidate the detailed role of additional elements on the formation behavior of GP zones especially from their nucleation point of view.

On the other hand, many investigations have been reported on the growth kinetics of GP zones in Al–Cu alloys containing various trace elements\(^{10}\). As a consequence of hot arguments in the early 1970’s, it is widely believed that the elements having high binding energies with vacancies such as Sn, Cd and In markedly retard the growth rate of GP zones because of the so-called vacancy-trapping effect proposed by Kimura and Hasiguti\(^{10}\). The transition elements having low solubility limits; e.g. Fe, Cr and Zr, are also well-known to suppress the coarsening rate of GP zones due to the increased number density of insoluble compounds that act as vacancy sinks. As for a small addition of Mg, in contrast, Entwistle et al.\(^{15}\) suggested that Al–4 mass%Cu alloys containing Mg higher than 0.1 mass% exhibit an enhanced formation of GP zones resulting in an increased hardness because of accelerated diffusion of Cu atoms with the aid of mobile Cu/Mg/Vacancy groups. Wyss and Sanders, Jr.\(^{16}\) also proposed that an acceleration of the GP zone formation in a naturally aged Al–2.6 mol%Cu–0.18 mol%Mg alloy is attributed to Mg-Vacancy clusters, which significantly enhance the GP zone nucleation by increasing the number of nucleation sites and/or the frequency of nuclei formation. However, these proposed mechanisms do not unfortunately appear to be recognized because of a slightly confusion of both the nucleation and growth behavior of GP zones. The problem relating to the Mg addition, therefore, is still under debate.

In order to investigate the formation behavior of GP zones, microstructural evolutions should be examined, although it is rather difficult experimentally. Computer simulation using a reliable model is an alternative powerful method to understand the microscopic behavior occurring in alloys. In particular, the simulation using a Monte Carlo method can visualize atomistic events such
as the nucleation and growth of precipitates for arbitrary alloy systems. Soisson et al.\(^7\) performed a Monte Carlo simulation of Cu atom clustering in \(\alpha\)-Fe to follow the microstructural evolutions such as the morphology, composition and size distribution of the precipitates. Ikeda and Matsuda\(^9\) qualitatively ascribed the changes in electrical resistivity of an Al–4.5 mol\%\(\text{Zn}\) alloy to size distributions of Zn atom clusters obtained from a Monte Carlo simulation. Furthermore, Saito and Harada\(^10\) applied the simulation to ordering of the \(\gamma'\) phase in commercial Ni-base superalloys in order to predict the preferential substitution behavior of alloying elements in the multicomponent alloys.

In this work, the effects of third additional elements on the kinetics of the GP zone formation in an Al–1.8 mol\%\(\text{Cu}\) alloy have been experimentally investigated in the temperature range from 278 to 373 K using electrical resistivity measurement. In particular, the effects of Mg addition were examined in detail from both viewpoints of the nucleation and growth of GP zones. A Monte Carlo simulation was performed to examine the microstructural evolution of Cu atom clusters resulting in the GP zone formation. Comparisons between the quantitative kinetics determined by the resistivity changes and the microstructural evolution directly observed in the simulation give important information on both the macroscopic transformation kinetics and the microstructural formation mechanism of Cu clusters in Al–Cu alloys containing various additional elements.

II. Electrical Resistivity Measurement

The alloys used in this work were prepared from high-purity elemental ingots under air atmosphere. The elements added to an Al–1.8Cu (in mol\%) alloy are 0.3Mg, 0.3Si, 0.3Zn, 0.3Ag, 0.3Li, 0.05Zr and 0.01Sn. The chemical compositions of the alloys are listed in Table 1. The concentrations of impurity elements such as Fe and Ti are lower than 0.01 mass\% in all alloys. The ingots were homogenized at 723 K for 36.4 ks and rolled down to 1.6 mm-thick sheets through hot- and cold-rolling. The wires for electrical resistivity measurement were prepared by drawing with dimensions of \(\phi 1.0\text{ mm} \times 300\text{ mm}\). All the wire specimens were solution-treated at 793 K for 1.8 ks followed by water quenching at \(-298\) K. Aging treatments were carried out at temperatures from 278 to 373 K for various aging times. The electrical resistivity was measured during aging by a four-probe potentiometric technique at liquid nitrogen temperature. The overall accuracy of the electrical resistivity was assessed to be within \(\pm 0.02\%\) by using a standard resistor.

The quantitative analysis for the formation kinetics of GP zones was made on the basis of Johnson-Mehl-Avrami equation\(^n\)\(^\text{(9)-(10)}\):

\[
y = 1 - \exp \left[ - (kt)^n \right],
\]

where \(n\) is the power related to the transformation mechanism, and \(k\) is the rate constant at a fixed temperature. In the following analysis, eq. (1) is rewritten below by taking the logarithms:

\[
\ln \left[ 1 / (1 - y) \right] = n \ln t + n \ln k.
\]

In this work, the transformed fraction, \(y\), is defined as

\[
y = (\rho_t - \rho_0) / (\rho_{\text{max}} - \rho_0)
\]

where \(\rho_0\), \(\rho_t\), \(\rho_{\text{max}}\) are the resistivities at the as-quenched state, at time \(t\) and at the maximum, respectively. The definition represented in eq. (3) is sufficiently reasonable because the electrical resistivity during natural aging in an Al–1.8 mol\%\(\text{Cu}\) alloy linearly increases with increasing average diameter of zones, not integrated intensity related to the volume fraction of zones\(^3\), as illustrated in Fig. 1. From the linear relationship indicated by the straight line, a resistivity at arbitrary time, \(\rho_t\), allows a determination of the average number of Cu atoms composed in one plate-like zone with the corresponding diameter. Thus, \(y\) is considered to be the degree of Cu condensation compared with the number of Cu atoms inside one zone providing the maximum resistivity, \(\rho_{\text{max}}\).

![Fig. 1 Variations in integrated intensity, \(Q\), and average diameter, \(D\), of GP zones in a naturally aged Al–1.8 mol\%\(\text{Cu}\) alloy with experimentally measured electrical resistivity, \(\rho\).](image-url)
III. Monte Carlo Simulation

Computer simulation was performed on a rigid f.c.c. lattice with 25 × 25 × 25 unit cells by a conventional Monte Carlo method. In this simulation, periodic boundary conditions are also adopted to eliminate a limitation of the simulation size. The lattice sites are first occupied at random by Al atoms, Cu atoms and third elemental atoms with the corresponding alloy compositions. The realistic diffusion of atoms takes place via vacancies with a concentration of \( \sim 1.5 \times 10^{-4} \). The exchange of a randomly selected vacancy with one of its nearest neighbor atoms is allowed if the transition probability, \( W_r \), is greater than a random number, \( x \), between 0 and 1. The values of \( W_r \) are calculated from the symmetrical solution\(^{(18)}\):

\[
W_r = \exp \left( -\frac{\Delta E}{kT} \right) / [1 + \exp \left( -\frac{\Delta E}{kT} \right)],
\]

where \( \Delta E \) is the energy difference between the atom configurations before and after the exchange. In this simulation, nearest neighbor interactions are taken into account for the calculation of \( \Delta E \) values. All the interactions are estimated from known thermodynamic quantities such as the cohesive energy, \( E_{coh} \), the formation energy of a vacancy, \( E_v^F \), in the pure element and maximum solubility limits, \( C_{max} \), in the corresponding binary aluminum phase diagrams.

Pair interactions between same atom species, \( \varepsilon_{ii} \), are estimated by assuming the Lennard-Jones type potential:

\[
\varepsilon_{ii} = \varepsilon_{ii}^{pure} \left[ \left( \frac{r_{ii}^{pure}}{r} \right)^6 - 2 \left( \frac{r_{ii}^{pure}}{r} \right)^{12} \right],
\]

where

\[
\varepsilon_{ii}^{pure} = 2E_{coh}/z.
\]

Figure 2(a) illustrates the variations in \( \varepsilon_{ii} \) with the interatomic distance, \( r_{ii} \), for Al–Al and Cu–Cu pairs. Note that a slightly larger value of \( \varepsilon_{CuCu} \) than the most stable \( \varepsilon_{AlAl} \) is utilized in this simulation for an application to the case of Cu–Cu pairs on Al lattice sites with interatomic distance \( r_{CuCu}^{pure} = 0.2864 \text{ nm} \).

In contrast, pair interactions between different atom species, \( \varepsilon_{ij} \), are obtained from interaction parameters, \( \varepsilon_{dea} \), which can be derived from the equilibrium phase diagram for the \( i-j \) binary alloy, as follows:

\[
\varepsilon_{ij} = \varepsilon_{dea} + (\varepsilon_{ii} + \varepsilon_{jj})/2.
\]

A derivation method of \( \varepsilon_{dea} \) values is described in Appendix.

Furthermore, pair interactions between an atom and a vacancy, \( \varepsilon_{iv} \), are estimated from the assumed potential of the form:

\[
\varepsilon_{iv} = \varepsilon_{iv}^{pure} (r_v / r_{Al}),
\]

where the ‘ghost’ binding energy between an atom and a vacancy in the pure element, \( \varepsilon_{iv}^{pure} \), is calculated from

\[
\varepsilon_{iv}^{pure} = (E_v^F + E_{coh})/z,
\]

as previously derived by Doyama and Koehler\(^{(17)}\). Figure 2(b) illustrates the variations in \( \varepsilon_{iv} \) with the distance between the atom and the vacancy, \( r_v \), for Al-Vacancy and Cu-Vacancy pairs. No repulsive force works between them under this assumption.

The experimental values of \( E_{coh} \), \( E_v^F \) and \( r_{vi}^{pure} \) are summarized in Table 2\(^{(28)(39)}\), the parameters utilized in this simulation in Table 3. All pair interactions are assumed to be independent of both the temperature and composition of alloys. As for Li having b.c.c. structure and Sn having b.c.t. structure, the coordination number, \( z \), is regarded as not 8 but 12 because the interatomic distance between second nearest neighbor atoms is rather close to that between nearest neighbor atoms, as previously assessed by Doyama and Koehler\(^{(17)}\). The simulation for the Si-added alloy was not performed because of an open question as to whether a pair interaction between Si–Si atoms estimated from a diamond structure, \( \varepsilon_{SiSi}^{pure} \), can be utilized as a Si–Si pair interaction in Al. The simulation for the Zr-added alloy was not also performed because continuous decrease in the vacancy concentration, indispensable to a description of the vacancy-sink mechanism, is not taken into account in this simulation.

Three structural parameters characterizing the simulation microstructures were followed as a function of Monte Carlo steps (MCS), which is a normalized unit of total attempt times to exchange nearest neighbor pairs by the number of vacancies. In this work a cluster was defined as a solute atom aggregate containing two or more than two solute atoms. Therefore, residual solute concentration in the matrix, \( C_\infty \), is estimated as a concentration...
Table 2   Experimental values of cohesive energy, $E_{coh}$, formation energy of a vacancy, $E_{v}^f$, and interatomic distance, $r_{ij}^{true}$, in pure elements(Ref.1).

<table>
<thead>
<tr>
<th>Elements</th>
<th>$E_{coh}$ [kJ/mol]</th>
<th>$E_{v}^f$ [eV]</th>
<th>$r_{ij}^{true}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-327</td>
<td>0.67</td>
<td>0.2864</td>
</tr>
<tr>
<td>Cu</td>
<td>-336</td>
<td>1.28</td>
<td>0.2556</td>
</tr>
<tr>
<td>Mg</td>
<td>-145</td>
<td>0.58</td>
<td>0.3197</td>
</tr>
<tr>
<td>Li</td>
<td>-158</td>
<td>0.48</td>
<td>0.3040</td>
</tr>
<tr>
<td>Zn</td>
<td>-130</td>
<td>0.54</td>
<td>0.266</td>
</tr>
<tr>
<td>Ag</td>
<td>-284</td>
<td>1.11</td>
<td>0.288</td>
</tr>
<tr>
<td>Sn</td>
<td>-303</td>
<td>0.51</td>
<td>0.302</td>
</tr>
</tbody>
</table>

Table 3   Simulation parameters utilized in this work (in kJ/mol).

<table>
<thead>
<tr>
<th>$e_{ux}$, $e_{uy}$</th>
<th>Al, Cu, Mg, Li, Zn, Ag, Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{ux}$</td>
<td>54.5, -49.3, -34.5, -37.9, -36.4, -49.6, -47.4</td>
</tr>
<tr>
<td>$e_{uy}$</td>
<td>-48.5, -32.2, -35.7, -33.4, -45.5, -46.6</td>
</tr>
<tr>
<td>$e_{ux}$</td>
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</tr>
<tr>
<td>$e_{uy}$</td>
<td>-24.4, -20.3, -47.3</td>
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<tr>
<td>$e_{ux}$</td>
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</tr>
<tr>
<td>$e_{uy}$</td>
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<tr>
<td>$e_{ux}$</td>
<td>-11.8, -6.03, -14.8, -24.2</td>
</tr>
<tr>
<td>$e_{uy}$</td>
<td>-6.03, -14.8, -24.2</td>
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<tr>
<td>$e_{ux}$</td>
<td>-14.8, -24.2</td>
</tr>
<tr>
<td>$e_{uy}$</td>
<td>-24.2</td>
</tr>
</tbody>
</table>

of the isolated solute atoms surrounded by Al atoms, and number density of clusters, $N$, in the unit of m$^{-3}$ is obtained from the number of clusters in the simulation cells. Average size of clusters, $n$, is defined as the number of Cu atoms inside one cluster.

From the obtained structural parameters, the calculated increments in electrical resistivity, $\Delta \rho_{cat}$, can be estimated as follows:

$$\Delta \rho_{cat} = \sum C_i \rho_i^0 + N g(n)$$

(10)

where $\rho_i^0$ and $g(n)$ refer to contributions to electrical resistivity by residual solute atoms per 1 mol% and by one cluster with average size $n$, respectively. Here, we adopted $\rho_i^0$ values of 8.0 for Cu(24), 4.6 for Mg(21), 2.4 for Zn(22), 13.4 for Ag(23), 8.38 for Li(24) and 9.0 for Sn(25) (in n$m^2$/mole). As for the function $g(n)$, furthermore, the following relationship is assumed:

$$g(n) = (2.1 \times 10^{-35}) n^{0.8}$$

(11)

from the experimental results for plate-like GP zones in Al–Cu alloys(26).

IV. Results and Discussion

1. Electrical resistivity changes

The increments in electrical resistivity from the as-quenched values during aging at 278 K are illustrated in Fig. 3 for the Al–Cu, Mg–, Si–, Zn–, Ag–, Sn–, Zr– and Li–added alloys. From just after quenching all alloys display a monotonic increase in $\rho$ due to a rapid formation of GP(1) zones, then a gradual decrease to show a maximum resistivity, $\rho_{max}$. From a comparison between the rates of resistivity-increase in the early stage of aging, Mg is found to obviously retard the GP zone formation as well as Sn and Zr.

The retardation of the GP zone formation in the Mg-added alloy is confirmed by the quantitative analysis using Johnson-Mehl-Avrami equation. Figure 4 illustrates the variations in $\ln \ln [1/(1-y)]$ with $\ln y$ derived from the electrical resistivity changes in Fig. 3. The corresponding straight lines through plotted points provide almost identical tangents; i.e., $n = -0.35$, indicating that the same transformation mechanism works in all alloys. On the other hand, the rate constants, $k$, for the Mg-, Sn- and Zr-added alloys are significantly smaller than those for the Al–Cu, Zn– and Ag-added alloys as revealed by their intercepts on the $\ln \ln [1/(1-y)]$ axis. This implies that small amounts of Mg, Sn and Zr markedly suppress the GP zone formation, whereas Zn and Ag additions exert almost no influence on the phase transformation kinetics of Al–Cu alloys. It is further shown in Fig. 4 that additions of Si and Li also show a weak tendency to suppress the GP zone formation as previously reported(25). The similar results are obtained for other aging temperatures lower than 373 K.

In general, the plots of $\ln k$ against reciprocal aging temperatures, $1/T$, provide an apparent activation energy for the precipitate formation, $Q^*$, according to the following relationship:

$$k = A \exp \left(-\frac{Q^*}{RT}\right),$$

i.e.,
Cu, Zn- and Ag-added alloys, 70.8 kJ/mol for the Mg-added alloy and 84.6 kJ/mol for the Sn-added alloy, respectively. Although these values are slightly larger than previously reported activation energies for the growth of GP zones; *i.e.* 48.2 kJ/mol (0.5 eV) for an Al-4 mass% Cu alloy and 67.5–77.2 kJ/mol (0.7–0.8 eV) for an Al-4 mass% Cu–0.025 mass%Sn alloy, it can be concluded that Mg is also classified to be an element which markedly retards the GP zone formation besides well-known Sn. However, two questions still remain unsolved; *i.e.* which stage of the nucleation and growth attributes to the retardation of the GP zone formation and why the contradictory results were reported on the effect of Mg addition. Monte Carlo simulation is likely capable of providing alternative useful suggestions to them.

2. **Simulation results**

Figure 6(a)–(c) illustrates the evolution of Cu atom distributions on one atom layer of (001) plane in the Al–Cu alloy simulated at 273 K. At the beginning of the simulation, Cu atoms, indicated by solid circles, are homogeneously distributed throughout the Al matrix, indicated by open circles, then gradually constitute an extensive volume fraction of Cu clusters due to a positive value of $\varepsilon_{\text{AlCu}}$. In this simulation, the morphology of Cu clusters are not disk-shaped but unshaped close to spherical, unlike GP zones observed in Al–Cu alloys, because an elastic effect induced by the difference in atomic radii between Al and Cu atoms is not considered. This simplification, however, is reasonable enough because the formation of GP zones is generally believed to be governed by the rate of the diffusion-controlled growth rather than
that of the interface-controlled growth. In fact, the $Q^*$ value for the Al–Cu alloy, $\approx 54$ kJ/mol, is in agreement with reported activation energies for the migration of vacancies, 42–67 kJ/mol\textsuperscript{[27–31]}. Therefore, the difference in the shape of Cu clusters considered to play no noteworthy part here in the kinetics of the GP zone formation.

Figure 7 shows variations in residual solute concentrations in the matrix, $C_s$, during dynamical evolution for the Al–Cu, Ag- and Mg-added alloys simulated at 273 K. Although an incidental formation of dimer and trimer clusters slightly decreases the initial solute concentrations, the net Cu concentrations are almost identical in the three alloys. As Monte Carlo step (MCs) proceeds, the Ag-added alloy displays a monotonous decrease in residual Cu concentration at the same rate as the Al–Cu alloy, whereas the Mg-added alloy exhibits an obvious retardation of Cu atom condensation. The similar simulation results are obtained for other alloys; i.e. the Zn-added alloy can be classified in the former group, the Sn- and Li-added alloys in the latter one. This is well consistent with the experimental results of the resistivity changes described above. Thus, it is concluded that small amounts of Mg and Li suppress the formation of Cu clusters as is the well-known case of Sn, whereas additions of Zn and Ag exert no marked influence on the phase transformation kinetics of Al–Cu alloys. The pronounced retardation of the Cu cluster formation by Mg, Sn and Li additions is simply explained in terms of the decreased diffusion rate of Cu atoms due to the preferential vacancy trapping by the third elemental atoms. Such situations can be frequently observed in atom configurations during the simulation. Therefore, Mg and Li are also found to be elements showing the so-called vacancy-trapping effect\textsuperscript{[6]} besides Sn.

Figure 8 shows the variations in number density, $N$, and average size, $n$, of clusters during dynamical evolution of the Al–Cu, Ag- and Mg-added alloys simulated at 273 K. The difference in the initial $N$ values between the Al–Cu and the ternary alloys arises from dimer and trimer clusters containing third additional elements which are formed by chance at the beginning of the simu-
lation. With increasing Monte Carlo steps (MCs), $N$ of the Mg-added alloy increases more slowly than those of the Al-Cu and Ag-added alloys, then gradually decreases to show a higher maximum due to the competitive growth among the clusters. The average size of Cu clusters is also significantly smaller in the Mg-added alloy than those of the Al-Cu and Ag-added alloys. The similar classification is valid for other additional elements; i.e., Zn and Ag have almost no effect to change the microstructural evolution of Al-Cu alloys, whereas Mg, Sn, and Li are regarded as the elements which markedly suppress the growth rate of Cu clusters. As for the site occupation behavior of third additional elements, however, the Mg-added alloy alone exhibits an extremely increased number density of clusters containing Mg atoms (and/or some vacancies) compared with those of other alloys, as suggested by higher decrease-rate of residual Mg concentration in Fig. 7. This implies that a small amount of Mg in Al-Cu alloys significantly affects the nucleation behavior of GP zones, for example, due to the heterogeneous nucleation effect with the aid of Mg/Cu/Vacancy complexes. This Mg/Cu/Vacancy complex mechanism is directly observed during the simulation, as illustrated in a solute atom distribution of the Mg-added alloy simulated at 273 K for $5 \times 10^4$ MCs (Fig. 6(d)). Note that Mg atoms, indicated by shaded circles, have a strong tendency to coexist with Cu atoms inside clusters due to a relatively high Cu-Mg interaction. This tendency is smaller in the Li-added alloy and smallest in the Zn-, Sn- and Ag-added alloys.

In general, changes in electrical resistivity during GP zone formation are believed to arise from the superimposition of the increases in both size and number density of zones, and the decrease in residual solute concentrations in the matrix. From the structural parameters obtained from the simulation, therefore, the calculated increments in electrical resistivity, $\Delta \rho_{\text{rel}}$, can be estimated using eq. (10). Except for the Zn-added alloy, the changes in $\Delta \rho_{\text{rel}}$ illustrated in Fig. 9 are well consistent with the experimental results in Fig. 3. Although the cause of the discrepancy in the Zn-added alloy is not fully understood, one of the possible reasons is a change of the function $g(n)$ due to additions of third elements. In fact, Hiraoka et al. reported that a scattering power of one GP zone in Al-Zn alloys is slightly changed by third additional elements. As for the other alloys, however, it can be concluded as follows from the simulation results obtained in this work. A small addition of Ag to Al-Cu alloys exerts no marked influence on the formation kinetics of GP zones due to no significant interaction between Ag and Cu atoms, as revealed by the similar microstructural evolution to the Al-Cu alloy. On the other hand, additions of Mg, Sn and Li markedly suppress the growth rate of GP zones because of the so-called vacancy trapping mechanism, resulting in a slower increase in electrical resistivity. Only in the Mg-added alloy, however, an extremely increased number density of clusters containing Mg atoms (and/or some vacancies) are formed due to a considerably high Cu-Mg interaction. This implies that a small amount of Mg in Al-Cu alloys significantly affects the nucleation behavior of GP zones, for example, due to the heterogeneous nucleation effect with the aid of Mg/Cu/Vacancy complexes.

V. Conclusions

The effects of third additional elements on the formation behavior of GP zones were investigated for an Al-1.8Cu (in mol%) alloy aged at temperatures from 278 to 373 K. The elements added to the binary alloy are 0.3Mg, 0.3Si, 0.3Zn, 0.3Ag, 0.3Li, 0.05Zr and 0.01Sn. Comparisons between the quantitative kinetics determined by the electrical resistivity changes and the microstructural evolution during Monte Carlo simulation give important information on both the macroscopic transformation behavior and the detailed formation mechanism of Cu clusters. The obtained results are as follows:

1. Small additions of Mg and Li to the Al-Cu alloy markedly retard the GP zone formation as is the well-known case of Sn. This is because that these additional atoms preferentially trap free-vacancies available for Cu diffusion to form clusters; i.e., the so-called vacancy-trapping mechanism, due to their relatively high interactions with vacancies. Such situations can be frequently observed in atom configurations during the simulation.

2. In contrast, additions of Ag and Zn exert no marked influence on the kinetics of the GP zone formation in Al-Cu alloys. This is explained by no significant interactions between these elemental atoms and Cu atoms, resulting in a similar microstructural evolution of Cu clusters to the binary alloy.

3. Only in the Al-Cu alloy containing Mg, however, an extremely increased number density of clusters containing Mg atoms (and/or some vacancies) are observed during the simulation. This implies that a small amount of Mg in Al-Cu alloys significantly affects the nucleation behavior of GP zones, for example, due to the heteroge-
neous nucleation effect with the aid of Mg/Cu/Vacancy complexes.

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REFERENCES


Appendix

In general, under a regular solution approximation the free energy change on mixing, $\Delta G_{mix}$, in an A-B binary alloy is expressed as follows:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

$$= \Omega x_A x_B + RT (x_A \ln x_A + x_B \ln x_B)$$

where

$$\Omega = N_A z_e.$$  \hspace{1cm} (14)

Here, $x_A$ and $x_B$ refer to molar fractions of A and B atoms, *i.e.* $x_A + x_B = 1$, $\epsilon$ is an interaction parameter and $N_A$ Avogadro's number, respectively.

For a condition of maximum solubility, $C^*_{max}$, at the corresponding temperature, $T^*_{max}$, in the equilibrium diagram for the A-B binary alloy, a following relationship can be approximately assumed:

$$d \Delta G_{mix} / dx_A = \Omega (x_B - x_A) + RT (\ln x_A - \ln x_B) = 0.$$ \hspace{1cm} (15)

Therefore, the interaction parameter, $\epsilon_{dis}$, between A and B atoms derived from the diagram is expressed as follows:

$$\epsilon_{dis} = \frac{RT (\ln x_A - \ln x_B)}{z_A (x_A - x_B)} = \frac{RT^*_{max} (\ln (1 - c^*_A) - \ln c^*_A)}{z_A (1 - 2c^*_A)}.$$ \hspace{1cm} (16)