Effect of Co and P on the Discontinuous Precipitation Behavior in High Concentration Corson Alloy*

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The effects of Co and P on the discontinuous precipitation (DP) behavior of Cu–Ni–Si system alloys have been investigated using Cu–4.5 mass%Ni–1.1 mass%Si alloy (base alloy), Cu–4.0 mass%Ni–0.5 mass%Co–1.1 mass%Si alloy (Co alloy) and Cu–4.0 mass%Ni–0.5 mass%Co–1.1 mass%Si–0.05 mass%P alloy (Co + P alloy) aged at 430, 460 and 490°C. In all the alloys, slightly before attaining peak age-hardening within grains, DP cells nucleated at grain boundaries and grew into the grains ahead of reaction fronts. The growth rates of DP cell for Co alloy were slower than those for Base one. Moreover, the trace addition of P to Co alloy (Co + P alloy) considerably retarded DP reaction. The kinetic analyses of DP using the Turnbull (T) and Petermann and Hornbogen (P-H) models yielded grain-boundary diffusion coefficients for both alloys determined from the P-H model were slightly larger than those obtained from the T model and about 130 kJ mol⁻¹, respectively. The values for both alloys determined from the P-H model were slightly larger than those obtained from the T model and about 130 kJ mol⁻¹. These results strongly suggested that the growth of DP cells in base and Co alloys was controlled by the boundary diffusion of Ni, and Ni or Co in Cu matrix, respectively. The smaller growth rate of DP cells in the Co alloy was ascribed to the higher number density of continuous δ precipitates than that of base one, which successively suppressed the boundary migration. [doi:10.2320/matertrans.MT-M2019152]

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1. Introduction

Copper alloys used for electronic components are required to have high strength, good electrical conductivity and appropriate bend formability to achieve miniaturization and improve the functionality of electronic equipment. Alloys based on the Cu–Ni–Si system, widely known as Corson alloys, have an excellent balance between strength and electrical conductivity. Thus, Corson alloys are used in a wide range of electrical applications. The electrical conductivity of Corson alloys is generally higher than that of Cu–Be and Cu–Ti system alloys, but the strength of Corson alloys is relatively low compared with Cu–Be and Cu–Ti system alloys. Therefore, improvements in the strength of Corson alloys are increasingly essential to attain high-density packaging in electronic devices.

It is well known that the high strength of Corson alloys is caused by the precipitation of a fine δ-Ni₃Si phase. Era et al.¹ and Kuwagaki et al.² have reported that age-hardening in Corson alloys increases with increasing Ni and Si concentration. However, higher amounts of Ni and Si lead to discontinuous precipitation (DP) at the grain boundaries.³

Fine δ-precipitates with sizes of several nanometers formed by continuous precipitation (CP) significantly contribute to age-hardening. Conversely, DP causes the mechanical properties of the alloys to deteriorate because the DP reaction produces coarse rod-shaped precipitates in the DP cells.³ Watanabe et al. reported that the addition of trace P to a Cu–Ni–Si alloy significantly suppressed the DP reaction.⁵ Recently, Izawa et al.⁶ showed that the partial replacement

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200 kV) equipped with an energy dispersive X-ray spectroscopy (EDX) system for chemical composition analysis of the precipitates.

3. Results and Discussion

3.1 Age-hardening behavior

Figure 1 shows the age-hardening curves of the base, Co and Co + P alloys during aging at 460°C. The closed and open symbols represent the hardness obtained from in-grains (CP) and DP cells (DP), respectively. For all the alloys, the maximum hardness was achieved after approximately 3 h. The Co and Co + P alloys exhibited a more rapid initial hardening and higher peak hardness compared with those of the base alloy. The higher peak hardnesses of the Co and Co + P alloys can be ascribed to the higher number density of CP precipitates, as will be discussed in Section 3.3. The DP reaction initiated in each alloy just before peak hardness was attained. It can be seen that the hardness of the DP cells is lower than that within the grains. These results are in good agreement with the literature.3,4)

3.2 Growth kinetics of DP cells

Figure 2 shows optical micrographs of the base, Co and Co + P alloys after aging for 3 h at 460°C. The formation and growth of DP cells (regions with dark contrast) can be seen in all alloys. The DP cells initially formed at grain boundaries and grew toward the adjacent grains with increasing aging time. The reaction fronts only migrated in one direction. The area fraction of DP cells decreased in the order of base, Co and Co + P alloys, as can be seen in Fig. 2. The changes in the area fraction of DP cells upon aging at different temperatures are summarized in Fig. 3. The area fraction of DP cells increased with increasing aging time \( t \), and then saturated. Higher aging temperatures brought about a higher increase in the area fraction.

Figure 4 illustrates the cell width \( w \) as a function of \( t \) for the base, Co and Co + P alloys aged at 430 and 490°C. It can be seen that linear relationships exist between \( w \) and \( t \) for all alloys and aging temperatures. A decrease in cell growth rates...
after a certain aging time can be seen for base and Co alloys upon aging at 490°C. It can also be seen that partial replacement of Ni with Co in the base alloy decreased the cell growth rate. Moreover, the addition of trace P to the Co alloy significantly suppressed DP cell growth.

Kinetic analyses of DP cell growth were performed using the Turnbull (T) and Petermann and Hornbogen (P-H) models. Although both of these models were originally developed for binary system alloys, they can be applied to the present alloys under the assumption of a Cu-δ quasi-binary system. According to these models, the growth kinetics can be expressed by\(^5,6\)

\[
s\delta D_h = \frac{x_0}{x_0 - x_e} v \lambda^2 (T) \quad (1)
\]

\[
s\delta D_h = -\frac{RT}{8\Delta G} v \lambda^2 (P-H) \quad (2)
\]

where \(s\) is the segregation factor, \(\delta\) is the grain boundary thickness, \(D_h\) is the grain boundary diffusion coefficient, \(x_0\) is the initial solute concentration, \(x_e\) is the solvus of \(\delta\) precipitates in the Cu matrix, \(v\) is the growth rate of the DP cell, \(\lambda\) is the inter-precipitate spacing of \(\delta\) precipitates in the cell, and \(R\) and \(T\) have their usual meaning. \(\Delta G\) in eq. (2) is the driving force for DP in terms of the overall change in the Gibbs energy, which is described by\(^6\)

\[
\Delta G = -RT \left[ x_0 \ln \frac{x_0}{x_e} + (1 - x_0) \ln \frac{1 - x_0}{1 - x_e} \right] + \frac{2\sigma V_m}{\lambda}. \quad (3)
\]

The first term on the right-hand side of eq. (3) corresponds to the change in chemical energy when the supersaturated solid solution decomposes into the Cu matrix and the \(\delta\) phase (assuming ideal solution behavior). The second term is related to the free energy needed for the formation of the boundaries between the Cu matrix and the \(\delta\) precipitates.\(^7\)

The values of \(x_0\) were calculated from the composition of the alloys under the assumption that all solutes were consumed during formation of the \(\delta\)-phase. The estimates of \(x_0\) are 3353 mol m\(^{-3}\) for the base alloy and 3395 mol m\(^{-3}\) for the Co alloy. \(V_m\) is the molar volume of the \(\delta\) phase and is given by \(V_m = N_A a b c / 12 = 6.55 \times 10^{-6} \text{m}^3\text{mol}^{-1}\), where \(N_A\) is Avogadro’s number and \(a = 0.703, b = 0.499,\) and \(c = 0.372\) nm, which are the lattice constants of the \(\delta\)-Ni\(_2\)Si phase.\(^8\) \(\sigma\) is the incoherent interface energy (0.6 J m\(^{-2}\)) between the Cu matrix and \(\delta\) precipitates.\(^9\)

From the slopes of the linear fits shown in Fig. 4, which were computed using the least-squares method, the cell growth rate \(v\) was obtained for each aging temperature and alloy. The obtained values of \(v\) are listed in Table 1. The values of \(\lambda\) were determined by SEM and TEM. Rod-shaped coarse \(\delta\) precipitates were observed within the DP cell, as previously reported.\(^3\) The rod-shaped \(\delta\) precipitates maintained an almost constant value of \(\lambda\) under isothermal aging conditions. Table 2 summarizes the obtained values of \(\lambda\). The values of \(\lambda\) in the Co alloy were smaller than those in the base alloy for each aging condition.

The solvus \(x_e\) was obtained experimentally according to the coarsening theory modified by Ardell,\(^10\) under the assumption of a Cu-δ quasi-binary system. The concentration of solute in the matrix \(x(t)\) after coarsening time \(t\) is expressed as

\[
x(t) = x_e = k t^{-1/3}, \quad (4)
\]

where \(k\) is the kinetic parameter of coarsening. This theory predicts that the solute concentration decreases in proportion to \(t^{-1/3}\). Figure 5 shows plots of the solute concentration in the matrix against \(t^{-1/3}\), which should be linear according to eq. (4). The solute concentration \(x(t)\) in the Cu matrix was estimated from the specific resistance of the alloys. The resistivity change of the alloys was assumed to be caused only by the change in the solute concentration in the Cu matrix due to the precipitation of the \(\delta\) phase. The experimentally obtained specific resistivities were converted to solute concentrations based on the contribution to the resistivity of solute Ni, Si, and Co in the Cu matrix (\(\Delta \rho_{\text{Ni}} = 11 \text{nΩ m at}\%^{-1}, \quad \Delta \rho_{\text{Si}} = 31 \text{nΩ m at}\%^{-1}, \quad \Delta \rho_{\text{Co}} = 58\)).
linear relationships between solute concentration and decreased at the beginning of the aging period, and then the nucleation and growth stage, and the coarsening stage of concentration and the linear relation correspond to the values obtained after a certain aging time, as would be using the least-squares method and are listed in Table 3. The values of $Q_b$ obtained using the models of Turnbull (T) and Petermann-Hornbogen (P-H) for Base and Co alloys. were 125 ± 1 and 130 ± 2 kJ mol$^{-1}$ using the T and P-H models, respectively, and the corresponding values for the Co alloy were 124 ± 1 and 133 ± 11 kJ mol$^{-1}$. The values calculated using the P-H model are slightly larger, but no significant differences were found between the alloys. It is well known that the activation energy of grain boundary diffusion is about one half to two thirds of the activation energy of impurity diffusion ($Q_{b,\text{Ni}} = 225$ kJ mol$^{-1}$,$^{13}$ $Q_{b,\text{Co}} = 214$ kJ mol$^{-1}$,$^{14}$ and $Q_{b,\text{Si}} = 172$ kJ mol$^{-1}$). The $Q_b$ values obtained from the T and P-H models are considerably smaller than $Q_{b,\text{Si}}$, and about half those of $Q_{b,\text{Ni}}$ and $Q_{b,\text{Co}}$. This strongly suggests that the DP cell growth is controlled by grain boundary diffusion of Ni in the base alloy and Ni and/or Co in the Co alloy. The values of $Q_b$ are nearly identical for both alloys, although it should be noted that there exists a difference in the DP cell growth rates (Fig. 4).

### 3.3 Influence of CP on DP cell growth

It is well known that the existence of fine precipitates within grains affects the growth behavior of DP cells. The causes of this effect are a lowering of the degree of supersaturation of the solute by the CP reaction, which reduces the driving force of DP cell growth, and also pinning effects due to the movement of advanced grain boundaries (reaction fronts) by finely dispersed CP precipitates.$^{15,16}$ It can be seen from Fig. 1 that the CP behavior is different between the base and Co alloys. Compared with the base alloy, the hardness of the Co alloy increased more rapidly in the early stages of aging and the attained peak hardness of the alloy was higher. To quantitatively discuss the difference in CP behavior between the base and Co alloys, the size and number density of CP precipitates before the formation of DP cells occurred were investigated. Figure 8 shows a representative high-resolution TEM image of the Co alloy aged at 430°C for 1 h. The incident direction of the electron beam was parallel to the [100]$_a$ plane. Disk-shaped fine precipitates with a habit plane parallel to the [110]$_a$ planes of the Cu matrix were visible. From the analyses of selected area diffraction patterns, these fine precipitates were determined to be the $\delta$ phase. The following orientation

### Table 3 Values of equilibrium solubility of $\delta$ phase in the Cu matrix of Base and Co alloys.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T$ [°C]</th>
<th>$x_e$ [mol m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>430</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>133</td>
</tr>
<tr>
<td>Co</td>
<td>430</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>111</td>
</tr>
</tbody>
</table>

nΩ m at%$^{-1}$.$^{112}$). For the Co alloy, compositional analysis of the rod-like precipitates in the DP cell was performed using EDX, as shown in Fig. 6. The Ni/Co ratio in the precipitate was nearly constant (11:1), regardless of the aging temperature. Thus, $\text{(Ni}_{0.92},\text{Co}_{0.08})_2\text{Si}$ was used as the composition of the $\delta$ precipitates in the Co alloy.

As can be seen in Fig. 5, the solute concentration rapidly decreased at the beginning of the aging period, and then linear relationships between solute concentration and $r^{-1/3}$ were obtained after a certain aging time, as would be expected from eq. (4). The rapid decrease in solute concentration and the linear relation correspond to the nucleation and growth stage, and the coarsening stage of the $\delta$ precipitates,$^{10}$ respectively. The values of $x_e$ were evaluated directly by extrapolation to $r^{-1/3} = 0$ ($t \to \infty$) using the least-squares method and are listed in Table 3. The values of $x_e$ for the Co alloy are smaller than those for the base alloy at each aging temperature. These results agree well with previous investigations.$^{4}$

The $\bar{s}D_b$ values at each aging temperature for the base and Co alloys were calculated from eqs. (1), (2), and (3) using experimentally obtained values of $x_e$, $\lambda$, and $v$. Figure 7 presents the Arrhenius plots of the sets of $\bar{s}D_b$ data derived using the T and P-H models. For all temperatures, the values of $\bar{s}D_b$ for the base alloy are larger than those for the Co alloy. Although only three sets of data points for each alloy were available, the activation energy $Q_b$ of grain-boundary diffusion was determined from the slope of the straight lines fitted to each $\bar{s}D_b$ dataset. The values of $Q_b$ for the base alloy

\[ Q_b = 172 \text{ kJ mol}^{-1} \]

were 125 ± 1 and 130 ± 2 kJ mol$^{-1}$ using the T and P-H models, respectively, and the corresponding values for the Co alloy were 124 ± 1 and 133 ± 11 kJ mol$^{-1}$. The values calculated using the P-H model are slightly larger, but no significant differences were found between the alloys. It is well known that the activation energy of grain boundary diffusion is about one half to two thirds of the activation energy of impurity diffusion ($Q_{b,\text{Ni}} = 225$ kJ mol$^{-1}$,$^{13}$ $Q_{b,\text{Co}} = 214$ kJ mol$^{-1}$,$^{14}$ and $Q_{b,\text{Si}} = 172$ kJ mol$^{-1}$). The $Q_b$ values obtained from the T and P-H models are considerably smaller than $Q_{b,\text{Si}}$, and about half those of $Q_{b,\text{Ni}}$ and $Q_{b,\text{Co}}$. This strongly suggests that the DP cell growth is controlled by grain boundary diffusion of Ni in the base alloy and Ni and/or Co in the Co alloy. The values of $Q_b$ are nearly identical for both alloys, although it should be noted that there exists a difference in the DP cell growth rates (Fig. 4).
relationship was found between the Cu matrix and the δ precipitate:

\[ [100]_\delta // [001]_\text{Cu}; (011)_\delta // (010)_\text{Cu}. \]

This orientation relationship is in agreement with that previously reported in the literature.\(^\text{17}\) It was confirmed that the morphology and orientation relationship of the δ precipitates in the base alloy were identical to those in the Co alloy. Table 4 lists the diameter \(d\), thickness \(h\), number density \(N_v\), and volume fraction \(f_p\) of the disk-shaped δ precipitates in the alloys. The specimen thickness was measured by the TEM observation, and the thickness was estimated. The sizes of CP precipitates in the Co alloy were larger than those in the base alloy. On the other hand, the volume fraction and number density of CP precipitates in the Co alloy were larger than those in the base alloy. Therefore, it can be concluded that migration of the reaction fronts was effectively prevented by pinning effects, leading to a reduced DP cell growth rate in the Co alloy.

### Table 4 Diameter \(d\), thickness \(h\), number density \(N_v\), and volume fraction \(f_p\) of δ precipitates within grains in Base and Co alloys aged at 430°C for 1 h.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(d) [nm]</th>
<th>(h) [nm]</th>
<th>(N_v[10^{24} \text{m}^{-3}])</th>
<th>(f_p) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>3.1 ± 0.9</td>
<td>2.5 ± 0.8</td>
<td>1.7 ± 0.1</td>
<td>3.2 ± 1.1</td>
</tr>
<tr>
<td>Co</td>
<td>2.4 ± 0.8</td>
<td>1.9 ± 0.7</td>
<td>4.8 ± 0.8</td>
<td>4.2 ± 1.2</td>
</tr>
</tbody>
</table>

### 4. Conclusions

The effects of Co and P on discontinuous precipitation (DP) behavior in Cu–Ni–Si alloys were investigated using Cu–4.5 mass%Ni–1.1 mass%Si alloy (base), Cu–4.0 mass%Ni–0.5 mass%Co–1.1 mass%Si alloy (Co), and Cu–4.0 mass%Ni–0.5 mass%Co–1.1 mass%Si–0.05 mass%P (Co + P) alloys. The findings of the investigation can be summarized as follows:

1. The partial replacement of Ni with Co in the base alloy decreased the growth rate of DP cells. The growth rate was further decreased by the addition of trace P into the Co alloy.

2. Grain boundary diffusion data were determined by kinetic analysis of DP using the Turnbull model\(^5\) as well as the Peterman and Hornbogen model.\(^6\) The activation energies for diffusion in the base alloy estimated by the Turnbull model and the Peterman and Hornbogen model were 125 and 130 kJ mol\(^{-1}\), respectively. For the Co alloy, the corresponding values were 124 and 133 kJ mol\(^{-1}\). Replacing Ni with Co did not significantly influence the grain boundary diffusivity. The obtained activation energies were about half that of the volume diffusion of Ni or Co in Cu. Transport of Ni in the base alloy, and transport of Ni and/or Co in the Co alloy within DP cells seem to occur through the boundaries.

3. The decrease in DP cell growth rate due to the presence of Co was ascribed to the suppression of reaction front migration by the increased number density of δ precipitates formed within the grains.

### REFERENCES