Effect of P Content on Stress Relaxation and Clustering Behavior in Cu-Ni-P Alloys

Yasuhiro Aruga, David W. Saxey, Emmanuelle A. Marquis, Hisao Shishido, Yuya Sumino, Alfred Cerezo, and George D. W. Smith

1. Introduction

Copper alloy sheets are widely used for electrical terminals in automotive applications. Terminals are manufactured by pressing out sheets of the correct shape, and then bending them into box shapes. One of the most important performance requirements of the terminals is that the contact pressure at the point of spring contact is maintained over long periods. Stress relaxation decreases the spring contact pressure with increasing time. The main accelerating factor for the relaxation is the temperature, making it a particularly important material property for connectors used in high temperature environments, such as inside the engine space in automotive applications. In most cases, stress relaxation is measured quantitatively in terms of how much of an initial elastic deflection applied to a material is changed into permanent deformation during heat treatment.

In a recent study, we characterized the ultrafine structures in Cu-P and Cu-Ni-P alloys using three-dimensional atom probe (3DAP) and transmission electron microscopy (TEM), and explored the stress relaxation behavior of these alloys. The results showed that low temperature annealing greatly improved the stress relaxation performance, especially in the Cu-Ni-P alloys. It was revealed that Ni-P clusters were present in the Cu-Ni-P alloys and that the clusters gave rise to significant improvements in the stress relaxation performance, without requiring significant change in the dislocation density. It is known that a binary Cu-Ni alloy shows almost the same rate of decrease of stress relaxation ratio as pure Cu. On the other hand, a Cu-P alloy has an improved stress relaxation performance over pure Cu and the Cu-Ni alloy due to the pinning effect of segregated solute P atoms. In our previous work, we used Cu-0.10P (mass%) and Cu-0.41Ni-0.11P (mass%) alloys, so the segregation of solute P atoms to dislocations within these materials is almost the same. Hence, any differences between the pinning effects of solute P atoms and Ni-P clusters in relation to the stress relaxation behavior have yet to be discussed.

1) In the present paper, we report an extension of the previous work to include a low-phosphorus Cu-Ni-P alloy, and we refine the earlier 3DAP statistical analysis procedures to permit the identification of smaller solute clusters. We analyze the overall improvement in the stress relaxation performance in terms of dislocation pinning, either by solute P or by clusters, within both the Cu-P and Cu-Ni-P alloys.

2) Experimental Procedure

Ingot of three alloys with the chemical compositions shown in Table 1, were manufactured using an air furnace, homogenized at 950°C, hot rolled, and cold rolled down to 0.80 mm thickness. The Cu-P alloy and Cu-Ni-P alloy with low P content (Cu-Ni-P (LP) alloy) were fully recrystallized and solution treated at 600°C for 20 s, and the Cu-Ni-P alloy with high P content (Cu-Ni-P (HP) alloy) was heat-treated at 650°C for 20 s. The average grain size for both alloys was about 20 μm after water quenching. The alloy sheets were given a final cold rolling, with a reduction of 50%, followed by a low temperature annealing at 250°C for up to 1000 s. The reason why 250°C was chosen as the annealing temperature is that the strength of both alloys showed a significant drop after annealing at 300°C or more.

Tensile test specimens (width, 25 mm; gauge length, 50 mm) were made by machining. The longitudinal direction of the test specimens was perpendicular to the rolling direction. Tensile tests were carried out at room temperature using an Autograph manufactured by Shimadzu Corporation (Kyoto, Japan).

Table 1 Chemical composition of alloys (mass%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-P</td>
<td>—</td>
<td>0.10</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cu-Ni-P (LP)</td>
<td>0.39</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>0.41</td>
<td>0.11</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
The electrical conductivity of specimens was calculated by an average cross section method. Stress relaxation testing was carried out in accordance with standard JCBA T309 of the Japan Copper and Brass Association. Specimens for the tests were taken in a direction perpendicular to the rolling direction. Stress relaxation in a cantilever bending state was evaluated as shown in Fig. 1. The test conditions were set so that the maximum surface stress of the specimen was equal to 80% of the room temperature yield stress. The specimens were held in a furnace maintained at a temperature of 150°C for different periods of time up to a maximum of 10^6 s. The displacement due to stress relaxation is measured as the permanent strain \( \delta \) remaining after the initial deflection \( d \) was removed. The stress relaxation ratio, \( RS \) (%), was calculated by the following equation:

\[
RS = \frac{\delta}{d} \times 100
\]

A smaller value of \( RS \) corresponds to a better stress relaxation behavior.

Specimens for 3DAP were cut from the sheets and electropolished using the standard two-stage method. Initial electropolishing was performed using a double layer technique with a solution of 10 vol% orthophosphoric acid in water at 4–20 V AC at room temperature. This was followed by electropolishing using a solution containing 10 g Na_2CrO_4·4H_2O in 100 ml acetic acid at 5 V DC at room temperature.

3DAP analyses were carried out with a LEAP™ 3000HR instrument (Imago Scientific Instruments, Madison, WI) at the University of Oxford. The analyses were performed at a specimen temperature of 50 K, a voltage pulse fraction (pulse voltage/steady-state voltage) of 20%, and a pressure in the specimen chamber below 10^-8 Pa. Visualization and quantitative evaluation of the 3D atom-by-atom datasets were performed with IVAS (Imago Scientific Instruments, Madison, WI) and PoSAP (Oxford nanoScience Ltd., Oxford, United Kingdom) software packages. Three separate experimental runs were carried out for each material and heat treatment, and consistent results were obtained between runs.

3. Results

3.1 Strength and electrical conductivity

Figure 2 shows the change in tensile strength in the Cu-P and Cu-Ni-P alloys after low-temperature annealing at 250°C. Some of the data in Fig. 2 have been already published. Increasing the annealing time causes a gradual decline in the strength in every material. The Cu-Ni-P (HP) alloy has the highest strength among the three materials and the values are higher than those of the Cu-Ni-P (LP) alloy by about 80 MPa. The annealing-time dependence of the electrical conductivity of the two alloys is shown in Fig. 3. Some of the data in Fig. 3 have been already published. The electrical conductivity of Cu alloys is expressed in terms of %IACS (International Annealed Copper Standard). The conductivity of the Cu-Ni-P (LP) alloy is much higher than the other materials. It is evident that the electrical conductivity shows almost no change as annealing time increases.

3.2 Stress relaxation behavior

Figure 4 shows the stress relaxation ratio against the exposure time at 150°C for each material. Figure 4 includes some of the data in the previous work. Figure 4(a) is for the Cu-P alloy. The stress relaxation ratio increases as the exposure proceeds. In other words, increasing the exposure time leads to deterioration in the stress relaxation performance. Low temperature annealing prior to testing tends to improve the stress relaxation performance progressively with increasing annealing time. As a result, the specimen annealed at 250°C for 1000 s shows the highest stress relaxation resistance.
The stress relaxation behavior of the Cu-Ni-P (LP) alloy is shown in Fig. 4(b). A similar beneficial effect of low temperature annealing on the stress relaxation performance in the Cu-P alloy is observed. After heating for $10^6$ s, the stress relaxation ratios of as-rolled Cu-P alloy and Cu-Ni-P (LP) alloy are 58% and 52% respectively. On the other hand, the ratios of the two alloys annealed at 250°C for 1000 s are 50% and 35% respectively. Thus, the Cu-Ni-P (LP) alloy shows a one-third improvement in the stress relaxation ratio by annealing at 250°C for 1000 s followed by a test exposure time of $10^6$ s, while the Cu-P alloy undergoes an improvement of just one seventh after an equivalent treatment. This indicates that the efficacy of the annealing for the Cu-Ni-P alloy is much greater compared with the Cu-P alloy.

The stress relaxation behavior of the Cu-Ni-P (HP) alloy is displayed in Fig. 4(c). The efficacy of the annealing is almost the same as for the Cu-Ni-P (LP) alloy, as measured by the absolute change in the stress relaxation ratio. However, because the stress relaxation ratios of the Cu-Ni-P (HP) alloy are overall lower than those of the Cu-Ni-P (LP) alloy by approximately 20%, the relative improvement in performance is much greater—by a factor of two third, instead of a factor of one third, after annealing at 250°C for 1000 s followed by a test exposure time of $10^6$ s.

Unless otherwise stated all subsequent references to “annealed” specimens refer to those annealed at 250°C for 1000 s, for both the Cu-P and Cu-Ni-P alloys.

### 3.3 3DAP experiments

Experimental 3DAP maps are shown in Fig. 5 for the Cu-P alloy, and in Figs. 6 and 7 for the Cu-Ni-P alloys. The P and Ni atoms are depicted by points and no Cu atoms are shown.
so as to illustrate the distribution of solute P and Ni atoms more clearly. There is no immediate visual evidence of distinct clusters in the images. Thus, a statistical method known as a compositional frequency distribution \(^5\) was employed to identify any non-randomness of P and Ni atoms in the data. Compositional frequency distributions were calculated from the 3DAP data using a block size of 100 atoms, and with the \(\chi^2\) test used to identify any non-randomness in the data. The value of \(\chi^2\) is a measure of the probability that the degree of deviation from the binomial distribution could occur by random fluctuations. Results from

the compositional frequency distribution analysis in the Cu-P and Cu-Ni-P alloys are shown in Table 2. \(\chi^2\) values and probabilities of random distribution in both the cold-rolled and annealed conditions of Cu-P alloy give no evidence for any statistically significant non-random variations of P, either immediately after cold rolling or when annealed. The distribution of both the P and Ni atoms appears to be homogeneous in the cold-rolled condition in the Cu-Ni-P (LP) alloys, whereas some indication of the non-randomness of the both atoms is observed in the annealed condition. Regarding the Cu-Ni-P (HP) alloys that higher \(\chi^2\) values implies non-randomness of the both atoms in the cold-rolled condition, and significantly increased \(\chi^2\) values clearly show

Fig. 6 Atom maps showing the 3D elemental distribution of P and Ni atoms in the Cu-Ni-P (LP) alloy (a) in the as-rolled state, (b) annealed at 250°C for 1000 s.

Fig. 7 Atom maps showing the 3D elemental distribution of P and Ni atoms in the Cu-Ni-P (HP) alloy (a) in the as-rolled state, (b) annealed at 250°C for 1000 s.
the non-randomness in the annealed condition. A contingency table analysis was also carried out to test whether there is a correlation in the distributions of Ni and P atoms in the Cu-Ni-P alloys. The results of these statistical analyses revealed that clustering of Ni and P atoms occurred in the Cu-Ni-P alloys. The results of these statistical analyses revealed that clustering of Ni and P atoms occurred in the Cu-Ni-P alloys, as discussed in our previous work.

In order to make reasonably accurate measurements and allow comparisons of the atomic-scale microstructural changes, the maximum separation method was used to select discrete regions enriched in solute. This was done by grouping together solute Ni and P atoms within a given distance \( d_{\text{max}} \) of one another (\( d_{\text{max}} = 0.6 \text{ nm in the present study} \). Then by removing all the groups that contained less than \( N_{\text{min}} = 5 \) solute atoms, a map of solute-rich regions was obtained. \( N_{\text{min}} \) and \( d_{\text{max}} \) values were chosen so that no solute clusters were observed in a simulated random solid solution of the same composition. This was tested by randomly assigning identities to the atomic positions in the data and testing different \( N_{\text{min}} \) and \( d_{\text{max}} \) values on this randomized data. Using these values, the distribution of the clusters was identified and the number density of the clusters was quantified. The 37% efficiency of the 3DAP measurement was considered in calculating the number of clusters in a unit volume. The test was previously carried out using \( N_{\text{min}} = 10 \) in our earlier work, whereas value of \( N_{\text{min}} = 5 \) is applied in the present study in order to examine the possible existence of ultra-small atom clusters because P content in the Cu-Ni-P (LP) alloy is very low.

Table 3 shows the number densities and volume fractions of clusters in the Cu-P alloy and Cu-Ni-P alloys, obtained by applying the maximum separation method using \( N_{\text{min}} = 5 \). The volume fraction of the clusters can be calculated using equations given in our previous work.

The data gives no clear evidence for any clusters, either immediately after cold rolling or when annealed, in the Cu-P alloy. In addition, it appears that no clusters are dispersed in the as-rolled state in the Cu-Ni-P (LP) alloy, whereas a significant amount of clusters are formed by annealing. The number densities and volume fractions of clusters in the Cu-Ni-P (HP) alloy in both the cold-rolled and annealed conditions are higher than in the annealed Cu-Ni-P (LP) alloy. The spatial distributions of Ni-P clusters that are identified by the maximum separation method are shown in Fig. 8 for the Cu-Ni-P (LP) alloy in the annealed condition, and in Fig. 9 for the Cu-Ni-P (HP) alloys.

### Table 2
Results from the compositional frequency distribution analysis in the Cu-P and Cu-Ni-P alloys, block size of 100 (stated errors represent 1 standard error on the bases of 2 measurements per sample).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Low temperature annealing condition</th>
<th>Element</th>
<th>( \chi^2 )</th>
<th>Probability of random distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-P</td>
<td>as-rolled</td>
<td>P</td>
<td>0.03 ± 0.01</td>
<td>90.0</td>
</tr>
<tr>
<td>Cu-P</td>
<td>250°C, 1000 s</td>
<td>P</td>
<td>0.65 ± 0.15</td>
<td>90.0</td>
</tr>
<tr>
<td>Cu-Ni-P (LP)</td>
<td>as-rolled</td>
<td>Ni</td>
<td>2.47 ± 0.05</td>
<td>90.0</td>
</tr>
<tr>
<td>Cu-Ni-P (LP)</td>
<td>250°C, 1000 s</td>
<td>P</td>
<td>7.34 ± 2.57</td>
<td>10.0</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>as-rolled</td>
<td>P</td>
<td>42.59 ± 23.31</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>250°C, 1000 s</td>
<td>Ni</td>
<td>25.33 ± 12.19</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>250°C, 1000 s</td>
<td>Ni</td>
<td>120.86 ± 7.49</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

### Table 3
Number density and volume fraction of clusters in the Cu-P and Cu-Ni-P alloys (stated errors represent 1 standard error on the bases of 3 measurements per sample).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Low temperature annealing condition</th>
<th>Number density of clusters ( (10^2 / \text{m}^3) )</th>
<th>Volume fraction of clusters ( (10^{-4}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-P</td>
<td>as-rolled</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu-P</td>
<td>250°C, 1000 s</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu-Ni-P (LP)</td>
<td>as-rolled</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu-Ni-P (LP)</td>
<td>250°C, 1000 s</td>
<td>1.2 ± 0.12</td>
<td>1.2 ± 0.23</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>as-rolled</td>
<td>2.1 ± 0.19</td>
<td>2.2 ± 0.37</td>
</tr>
<tr>
<td>Cu-Ni-P (HP)</td>
<td>250°C, 1000 s</td>
<td>7.6 ± 0.13</td>
<td>8.0 ± 0.50</td>
</tr>
</tbody>
</table>

Fig. 8 Atom map showing the 3D elemental distribution of Ni (brown) and P (blue) atoms found to be clustered in the Cu-Ni-P (LP) alloy annealed at 250°C for 1000 s.

(a) (b)
4. Discussion

The stress relaxation is considered to occur by logarithmic creep caused by a relatively short-range motion of dislocations.\textsuperscript{10,11} It is thought that stress relaxation is influenced by grain size, dislocation density, solute contents and solute clusters within the specimen. In this study, it can be considered that there is no difference in diffusional creep between materials because the grain sizes within all specimens are almost the same. In our previous study it was found that the dislocation density is not a major factor in the stress relaxation reduction and that Ni-P clusters improve the stress relaxation performance of Cu alloys.\textsuperscript{1} The effect of the amount of Ni on the stress relaxation has already been examined using pure Cu and a Cu-Ni alloy after 40% cold rolling.\textsuperscript{22} According to that work, the stress relaxation is affected very little by the addition of Ni to Cu. Dislocation pinning by solute Ni is not expected to occur in Cu alloys. The influence of the pinning effect of solute P on the stress relaxation behavior is yet to be shown.

In the present study, no clusters are observed in either the cold-rolled or annealed conditions of the Cu-P alloys, or in the cold-rolled condition of the Cu-Ni-P (LP) alloy. In other words, all P and Ni atoms are in a purely solute condition in these materials. The solute P content in the Cu-P alloys is approximately 20 times larger than that in the Cu-Ni-P (LP) alloy, in atomic percent. However, the difference in the stress relaxation ratio of Cu-P material tested at 150°C for 10\textsuperscript{6}s with or without annealing is just 8%. On the other hand, the difference in the stress relaxation ratio between the cold-rolled and annealed conditions of the Cu-Ni-P (LP) alloys is 17% (a factor of two higher than for the Cu-P alloy). The 3DAP results show that Ni-P clusters with a number density of \(1.2 \pm 0.12 \times 10^{23}/\text{m}^3\) are dispersed in the annealed condition of the Cu-Ni-P (LP) alloy (the error represents 1 standard error on the basis of 3 measurements). Even though the number density is quite low due to low P content in the alloy, their effect on the stress relaxation ratio is quite large. Therefore, we can conclude at this point that the pinning effect of solute P has much less impact on the stress relaxation behavior in Cu alloys than the effect of the clusters.

Dispersed clusters may pin individual dislocations and inhibit the recovery process. The strengthening effect depends on the force needed to shear the obstacles (clusters). Several strengthening mechanisms need to be considered: (i) order strengthening and stacking fault strengthening, (ii) chemical hardening and (iii) modulus hardening. Recently, Starink and his coworkers\textsuperscript{12} have reported that Cu-Mg clusters are present after natural aging in Al-Cu-Mg based alloys. According to their work it is concluded that the clusters have no internal long-range order, as selected area diffraction of the alloys does not show any distinct evidence of additional diffraction effects. Thus, it is believed that long-range order strengthening or stacking fault strengthening can not occur at the early stage of clustering. However, there will almost certainly be some degree of short range order in almost any kind of cluster and this will be reduced if a dislocation cuts through it. Strengthening due to short range order of dissolved atoms is given by:

\[
\tau_{\text{SRO}} = \frac{c(1 - c)}{3b^3} A_{\text{SRO}}
\]  \hspace{1cm} (2)

where \(c\) is the solute concentrations, \(b\) is the Burgers’s vector and \(A_{\text{SRO}}\) is a parameter depending on nearest neighbor interaction parameters and Warren-Cowley parameters, details of the calculations of these parameters are presented in Ref. 13, 14.

Chemical hardening occurs when the cutting of precipitates by a dislocation creates additional matrix-precipitate interface area. This mechanism can be analyzed if there is a well defined matrix-precipitate interface with a clearly-defined interfacial energy, but cluster-matrix interfaces are diffuse and their interfacial energy is probably very small. Starink \textit{et al.}\textsuperscript{12} argued on the basis of the examination of a range of published data on Al-Cu-Mg alloys,\textsuperscript{15} that it is reasonable to assume that chemical hardening is relatively small, and also their experimental data reported that short range order strengthening is very limited. Gomiero \textit{et al.}\textsuperscript{13} modeled different contributions to hardening, which give a theoretical yield stress in a good agreement with measured values in Al alloys. In the paper they indicated that short range order hardening is substantially smaller than modulus hardening. Therefore, we wish to focus on modulus hardening only.

Modulus hardening is fairly well understood conceptually,\textsuperscript{16-18} but very few descriptions have been quantitatively compared with experimental data. A recent study\textsuperscript{12} reported that a description in which modulus hardening increases with increasing radius of the clusters, such as that suggested in Ref. 16), seems to be inappropriate. At present we adopt the very much simplified treatment by Cartaud \textit{et al.}\textsuperscript{19} and later applied in several works in Al alloys.\textsuperscript{15,20,21} The strengthening from clusters due to a difference in shear modulus is approximated by:

\[
\tau_{\text{cl}} = \frac{\Delta G}{4\pi \sqrt{2}} \sqrt{f_{\text{cl}}}
\]  \hspace{1cm} (3)

where \(\Delta G\) is the difference between the shear moduli of the matrix and the clusters. \(f_{\text{cl}}\) is the volume fraction of the clusters.

\[\text{Fig. 10} \quad \text{Square root of the volume fraction of the clusters and the stress relaxation ratio tested at 150°C for 10^6 s in the Cu-Ni-P alloys (stated errors represent 1 standard error on the basis of 3 measurements per sample).}\]
clusters; hampering of dislocation movement by the presence of clusters is proportional to the square root of the volume fraction of the clusters. In Fig. 10, the square root of the volume fraction of the clusters and the stress relaxation ratio tested at 150°C for 10⁶ s in the Cu-Ni-P alloys are plotted, which shows that a linear relationship \((R^2 = 0.997)\) is found between them. These results emphasize that clusters play a key role in the stress relaxation in Cu alloys and that the stress relaxation performance can be related to the volume fraction of the clusters within the limits of this experiment.

5. Conclusions

The stress relaxation behavior and cluster distributions in a Cu-P alloy and two Cu-Ni-P alloys with different P content have been investigated by means of 3DAP. No clusters were observed in the Cu-0.10P (mass%) alloys, in either the cold-rolled and annealed conditions, nor in the Cu-0.39Ni-0.006P (mass%) alloy in the cold-rolled condition. The three materials showed similar stress relaxation performance, although dislocation pinning by solute P can be expected to occur in the Cu-P alloys. On the other hand, the Cu-Ni-P alloy formed a low density of Ni-P clusters during annealing in spite of low P content, and showed a greater improvement in stress relaxation resistance than the Cu-P alloy. Therefore, it is concluded that the pinning effect of solute P has much less impact on the stress relaxation behavior in Cu alloys than the effect of the clusters.

Furthermore, hampering of dislocation movement by the presence of the clusters has been discussed based on a modulus hardening mechanism. The experimental result indicates that a linear relationship exists between the square root of the volume fraction of the clusters and the stress relaxation ratio in the Cu-Ni-P alloys with different P content. It is shown that clusters play a key role in stress relaxation in Cu alloys and that the stress relaxation performance is related to the volume fraction of the clusters.

REFERENCES