Effect of Precipitates on Recrystallisation Temperature in Cu–Cr, Cu–Zr and Cu–Zr–Cr Alloys*

By Takeshi Nagai**, Zenzo Henmi**, Teruo Sakamoto** and Shigeyasu Koda***

In a previous paper, it was reported that the high recrystallisation temperature of Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys was due to the formation of fine precipitates during recrystallisation, which obstructed dislocation climb, glide and grain boundary migration.

In the present paper, the recrystallisation behaviours in Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys quenched, tempered (at 350, 450, 500, 550 and 700°C), heavily cold worked and annealed at various temperatures were studied by the resistometric method, measurements of mechanical properties and transmission electron microscopy. No fine precipitates were detected at dislocations or sub-boundaries in the low temperature annealing stage, but fine precipitates, which retard recovery, must exist since electrical resistivity decreased during low temperature annealing. The mechanism of retardation of recovery is due to the binding of dislocation jogs by fine precipitates. In the high annealing temperature range, the growth of precipitates and crystal grains was observed by transmission electron microscopy and the effect of precipitates on the retardation of recrystallisation was also detected.

The size of precipitates formed during tempering before cold working did not affect the recrystallisation temperature, because the precipitates were broken up by heavy cold work and were thus made a constant size.

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I. Introduction

In a previous paper(1), it was reported that the recrystallisation temperatures of Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys were higher than that of pure copper by 200~400°C due to the formation of fine precipitates during recrystallisation, which obstructs the climb and glide motion of dislocations and grain boundary migration. It was also predicted from the textures of these alloys that fine precipitates might exist prior to recrystallisation(2).

In the present paper, the recrystallisation behaviours in Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys quenched, tempered, heavily cold worked and annealed at various temperatures were studied by the resistometric method, measurements of mechanical properties and transmission electron microscopy. Then the effect of the state of precipitates on the recrystallisation temperature and the retardation of recrystallisation by precipitates in these alloys were discussed.

II. Experimental Procedures

The chemical compositions of the alloys are shown in Table 1. 8 mmφ bars of each alloy were cut into the length of 300 mm and homogenised as follows. The Cu–Cr and Cu–Zr–Cr alloys were homogenised for 20 min at 970°C and quenched. The Cu–Zr alloy was homogenised for 20 min at 920°C and quenched. One of the quenched bars was left as-quenched, and others were tempered for 1 hr at 350, 450, 500, 550 and 700°C, respectively. Tempered 8 mmφ bars were swaged to 3.5 mmφ bars and then cold drawn to 0.4 mmφ wires or cold roll-flattened to 0.05~5 mm strips (Table 2). The wires (0.4 mmφ×200), strips (0.05×5×100 mm) and blocks (8 mmφ×10) prepared from the bars in the as-quenched state were used as specimens. The specimens were annealed in vacuum for 1 hr from 100°C to 700°C at 50°C intervals and at 800°C.

The electrical resistivity and the tensile strength were measured using 0.4 mmφ wires. The hardness and transmission electron micrographs were obtained with 0.05×5 mm strips and optical micrographs were taken with 8 mmφ×10 blocks.

In order to observe the state of precipitates after each tempering treatment, 0.05~5~100 mm strips of each alloy with the same composition as used in a previous paper(1), were sealed into silica tubes, homo-

<p>| Table 1 Chemical composition (wt.%). |</p>
<table>
<thead>
<tr>
<th>Cu</th>
<th>Cr</th>
<th>Zr</th>
<th>Si</th>
<th>P</th>
<th>Pb</th>
<th>Sn</th>
<th>Fe</th>
<th>Ni</th>
<th>Bi</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cr</td>
<td>99.10</td>
<td>0.83</td>
<td>—</td>
<td>0.019</td>
<td>&lt;0.005</td>
<td>0.002</td>
<td>0.004</td>
<td>0.02</td>
<td>0.002</td>
<td>0.0001</td>
<td>0.0004</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>99.71</td>
<td>—</td>
<td>0.24</td>
<td>0.006</td>
<td>0.021</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>Cu-Zr-Cr</td>
<td>98.81</td>
<td>0.88</td>
<td>0.22</td>
<td>0.043</td>
<td>&lt;0.005</td>
<td>0.001</td>
<td>0.004</td>
<td>0.02</td>
<td>0.002</td>
<td>0.0001</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

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*** School of Science and Engineering, Waseda University, Tokyo, Japan.
(1) Z. Henmi and T. Nagai: Trans. JIM, 10 (1969), 305.
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genised, tempered for 1 hr from 300°C to 700°C at 50°C intervals and at 800°C. Homogenised, quenched and tempered strips were examined by hardness measurements and transmission electron microscopy.

The thin foil specimens were examined using a Hitachi HU-11A electron microscope at 100 kV. The method of preparing thin foils was the same as in a previous paper (1).

III. Experimental Results

1. Changes in hardness and structure observed by transmission electron microscopy after homogenising, quenching and tempering (strips and blocks)

Figure 1 shows changes in hardness of Cu-Cr, Cu-Zr and Cu-Zr-Cr alloys in the form of strips tempered for 1 hr at various temperatures after homogenising and quenching. The Cu-Cr alloy hardened by tempering at 550°C and Cu-Zr-Cr alloy at 500°C. Figure 2 shows changes in hardness of Cu-Cr, Cu-Zr and Cu-Zr-Cr alloys in block form. All of the alloys showed the highest hardness when tempered for 1 hr at 500~550°C and the hardness was in the descending order of Cu-Zr-Cr, Cu-Zr and Cu-Zr alloys. The block specimens of the Cu-Zr alloy hardened a little by tempering, but the strip specimens did not harden at all. The precipitates, however, were observed in the Cu-Zr alloy strip when quenched and tempered (see Photo 6).

Table 3 shows the size of precipitates in strip type specimens after each tempering treatment. Fine precipitates were observed when tempering for 1 hr at 450°C in all alloys, as shown in Photos 1, 2 and 3. Photographs 4 and 5 show grown precipitates in the Cu-Cr alloy tempered for 1 hr at 500 and 550°C, respectively. The large precipitates (ca. 0.3 μ) already existed after homogenising and the small precipitates (ca. 200 Å) were formed by tempering. Photograph 6 shows

![Photo 1](transmission electron micrograph of Cu-Cr alloy tempered for 1 hr at 450°C after quenching)

![Photo 2](transmission electron micrograph of Cu-Zr alloy tempered for 1 hr at 450°C after quenching)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Tempering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As quenched</td>
</tr>
<tr>
<td>Cu-Cr</td>
<td>Undetectable</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>Undetectable</td>
</tr>
<tr>
<td>Cu-Zr-Cr</td>
<td>Undetectable</td>
</tr>
</tbody>
</table>
precipitates along dislocations appeared in the Cu–Zr alloy tempered for 1 hr at 550°C.

2. Changes in hardness after homogenising, quenching, tempering, cold working and annealing

The hardness vs annealing temperature curves for the strip-shaped specimens of these Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys are shown in Figs. 3, 4 and 5, respectively. The tempering temperatures of 350, 450, 500, 550 and 700°C, and are marked on the curves. As shown in Table 3, precipitates were present in each of these alloys. However, the size of precipitates before working did not have a significant effect on the hardness curves. To be more exact, it can be said that the annealing treatment at 550 and 500°C for 1 hr was most effective for increasing the recrystallisation temperature in Cu–Cr and Cu–Zr–Cr alloys, respectively. No difference in the recrystallisation temperature was found in Cu–Zr alloy.

Fig. 3 Changes in micro-hardness of Cu–Cr alloy annealed for 1 hr at various temperatures after roll-flattening.

Fig. 4 Changes in micro-hardness of Cu–Zr alloy annealed for 1 hr at various temperatures after roll-flattening.
3. Changes in tensile strength after homogenising, quenching, tempering, cold working and annealing

The tensile strength vs annealing temperature curves in the wire specimens of the alloys after tempering and drawing are shown in Figs. 6, 7 and 8, respectively. The tempering temperature used were 350, 450, 500, 550 and 700°C, as marked on the curves. The changes of the tensile strength were very similar to those of hardness, and the size of precipitates was thought to have no significant effect. In a strict sense, however, the most effective tempering temperature was 550°C both in Cu–Cr and Cu–Zr–Cr alloys. However, no significant difference in the effect of the tempering temperature could be found in Cu–Zr alloy.

4. Changes in electrical resistivity after homogenising, quenching, tempering, cold working and annealing

The variation of the electrical resistivity with annealing temperature is shown in Figs. 9, 10 and 11 for wire specimens of the Cu–Zr and Cu–Zr–Cr alloys. The increased resistivity in the as-drawn state decreased by precipitation with rise in tempering temperature. The resistivity was also found to decrease...
Fig. 9 Changes in electrical resistivity of Cu-Cr alloy annealed for 1 hr at various temperatures after drawing.

Fig. 10 Changes in electrical resistivity of Cu-Zr alloy annealed for 1 hr at various temperatures after drawing.

Fig. 11 Changes in electrical resistivity of Cu-Zr-Cr alloy annealed for 1 hr at various temperatures after drawing.

Fig. 7 Transmission electron micrograph of Cu-Cr alloy annealed for 1 hr at 400°C after roll-flattening.

Fig. 8 Transmission electron micrograph of Cu-Zr-Cr alloy annealed for 1 hr at 600°C after roll-flattening.

greatly by annealing. The minimum resistivity was obtained by annealing for 1 hr at 500 and 550°C and then increased with the temperature, which may be ascribed to redissolution of precipitates into the matrix at temperatures above 600°C. The behaviours of the electrical resistivity for the Cu-Cr, Cu-Zr and Cu-Zr-Cr alloys were similar to each other.

5. Effects of the precipitates on each stage of recrystallisation examined by transmission electron microscopy

Transmission electron micrographs of the Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys subjected to the various treatments are shown in Photos. 7, 8, 9 and 10. As seen in Photo. 7 fine precipitates were observed in the Cu–Cr alloy annealed for 1 hr at 400°C after rolling.

Therefore the decrease in electrical resistivity of the alloy during annealing will be due to the fine precipitates. Photograph 8 shows an early stage of recrystallisation of the Cu–Zr–Cr alloy annealed for 1 hr at 600°C after rolling, in which the precipitates
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Table 4 Estimation of amounts of precipitates by decreasing the electrical resistivity in Cu–Cr alloy.

<table>
<thead>
<tr>
<th>Annealing temp. (°C)</th>
<th>As drawn</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical resistivity (μm cm)</td>
<td>3.73</td>
<td>3.72</td>
<td>3.67</td>
<td>3.59</td>
<td>3.49</td>
<td>3.46</td>
<td>3.27</td>
<td>3.27</td>
<td>2.71</td>
<td>2.08</td>
<td>1.94</td>
<td>1.94</td>
<td>1.99</td>
<td>2.05</td>
<td>2.11</td>
</tr>
<tr>
<td>Subtraction (%)</td>
<td>0</td>
<td>0.01</td>
<td>0.06</td>
<td>0.14</td>
<td>0.24</td>
<td>0.27</td>
<td>0.46</td>
<td>0.46</td>
<td>1.02</td>
<td>57</td>
<td>1.65</td>
<td>1.79</td>
<td>1.79</td>
<td>1.74</td>
<td>1.68</td>
</tr>
</tbody>
</table>

IV. Discussion

1. Cu–0.83% Cr alloy

As shown in Fig. 9, the electrical resistivity of the as-drawn specimens decreased as the tempering temperature was raised from 350 to 700°C, because precipitation occurred during tempering. From the changes shown in Fig. 9 and a comparison of Photos. 4 and 5, the highest rate of precipitation was considered to occur at 550°C. The electrical resistivity, on the other hand, greatly decreased after annealing at 500°C, because the precipitation was accelerated by cold work.

It may be assumed that the full precipitation corresponds to the minimum of residual solute atoms in the matrix and to the minimum electrical resistivity. If the latter is considered as 100% of precipitation, the total amount of precipitates can be estimated from the change in electrical resistivity. Then in the present case, the degree of precipitation at each annealing temperature is such as that illustrated in Table 4. It can be seen that the precipitation is 15% after annealing for 1 hr at 300°C. However, the electrical resistivity also changes with the degree of cold work, and the maximum increase may be about 5%; for example, the increase of electrical resistivity in nickel silver is 6% by 97.5% cold drawing(3). Therefore, approximately 10% precipitation was obtained by annealing at 300°C. By annealing for 1 hr at 400°C the cold worked state still remained as shown in Photo. 7, and about 57–52% precipitation was obtained. It can be concluded that fine precipitates were present prior to recrystallisation which would be a factor of the increase in recrystallisation temperature.

2. Cu–0.24% Zr alloy

The change in electrical resistivity of the Cu–Zr alloy were similar to those of the Cu–Cr alloy, as seen from Fig. 10. However, the electrical resistivity in the Cu–Zr alloy was lower as a whole, which is thought to be due to the lower solute atom content compared with the Cu–Cr alloy. In the rolled specimen, precipitates with the diameter of about 200 Å were observed in the matrix after annealing for 1 hr at 500°C. However, in the homogenised specimen precipitates were observed on dislocations after tempering for 1 hr at 550°C (see Photo. 6), but fine precipitates in the matrix were not be observed in contrast with Cu–Cr alloy (Photos. 4 and 5).

Several factors are now known to control solubility in alloy systems: the crystal structure of the alloying elements, the relative size of the atoms, the electronegativity of one element with respect to the other, and the concentration of valence in the alloy(4). When all these factors are different for the matrix and the solute, the solid solubility in the alloy system is small. The smaller is the solubility the higher is the binding

energy between a solute atom and a vacancy. Such solute atoms have low diffusion coefficients and migrate slowly\(^{(5)}\). Several phase diagrams for the Cu–Zr system have been reported and their solid solubility of Zr in Cu was small\(^{(6)–(9)}\). Since vacancies in the Cu–Zr system which easily combine with solute atoms cannot diffuse very quickly and the rate controlling factor of the climb of dislocation is the high mobile vacancy density, the recovery and recrystallisation processes may be obstructed. This is one of the reasons why the recrystallisation temperature was higher in the Cu–Zr alloy than that in the Cu–Cr alloy. However, the electrical resistivity decreased during annealing above 300 °C, as shown in Fig. 10. Therefore, the main cause of the shift of recrystallisation to a high temperature may be due to the fine precipitates as in the Cu–Cr alloy.

3. Cu–0.22%/Zr–0.88%/Cr alloy

The electrical resistivity of the Cu–Zr–Cr alloy was high, as if it were a sum of the resistivities of the Cu–Cr and Cu–Zr alloys, as shown in Fig. 11. This implies that the solute atom content after homogenising corresponds to that obtained by adding the solubility of Cr in Cu and that of Zr in Cu. The amount of precipitates in the Cu–Zr–Cr alloy was larger than those in the Cu–Cr and Cu–Zr alloys. For example, Photos. 11, 12 and 14 in a previous paper\(^{(1)}\) show precipitates in the Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys after annealing for 2 hr at 700 °C. The recrystallisation temperature in the Cu–Zr–Cr alloy was higher than those of the Cu–Cr and Cu–Zr alloys. One of reasons is that the solute Cr and Zr atoms simultaneously trap vacancies obstructing dislocation climb. However, the main causes may be due to fine precipitates increased by annealing at low temperatures and to the amount of precipitates increased as the annealing temperature is raised.

4. Recrystallisation of supersaturated solid solution

Recently, Hornbogen et al.\(^{(10)}\) reviewed systematically the recrystallisation of supersaturated solid solution. According to this review, the recrystallisation of supersaturated solid solutions can be classified into: (1) recrystallisation which is driven by discontinuous precipitation, that is, the main driving force for recrystallisation is the chemical driving force of the so-called grain boundary reaction, e.g. in Cu–Be alloy\(^{(11)}\)\(^{(12)}\), Ni–Be alloy\(^{(13)}\) and Fe–Ni–Cr–Ti alloy\(^{(14)}\), etc., and (2) recrystallisation which is driven by release of stored energy by dislocation annihilation, and is obstructed by fine precipitates, e.g. in Al–Fe alloy\(^{(15)}\), Cu–Co alloy\(^{(16)}\), Ni–Al alloy\(^{(17)}\) and Nb–Ag permalloy\(^{(18)}\). It can be seen that the classification is substantially deduced from the phase diagrams for the alloy systems. Precipitation hardening alloys have a range of solid solubilities whose limits decrease with decreasing temperature; e.g. Cu–Be, Ni–Be and Fe–Ni–Cr–Ti alloys in (1) have a limited solid solubility, and the solid solubilities in the Al–Fe, Cu–Co, Ni–Al and Nb–Ag permalloy systems in (2) are very small. The Al–Cu alloy falls between (1) and (2)\(^{(19)}\) and Cu–Cr, Cu–Zr and Cu–Zr–Cr alloys are classified in (2).

5. The recrystallisation of the alloys in which fine precipitates are present

It is stated in IV. 1, 2 and 3 that the electrical resistivity decreases during annealing for 1 hr at 300 °C, and the decrease is too large to be caused only by dislocation annihilation. It is, therefore, concluded that the fine precipitates, which cause a decrease in the electrical resistivity but are not visible by transmission electron microscopy, retard recrystallisation. Now, the reason for the retardation of recrystallisation by fine precipitates will be discussed.

Formation of fine precipitates during low temperature annealing, e.g. 1 hr at 300 °C, may be caused as follows. Vacancies introduced by cold working combine with solute atoms, diffuse to relieve the stress due to dislocations and grain boundaries, and form fine precipitates on dislocations and grain boundaries. Since the Zr atom is much larger than the Cu atom and the Cr atom is the same size as the Cu atom, Zr atoms are preferentially precipitated on dislocations or grain boundaries. Since vacancies can easily combine with solute atoms and diffuse slowly, the dislocation climb may be retarded and the recovery temperature may be much higher than that of pure copper. As one of the reasons for the retardation of recovery in these alloys, that the vacancies which are necessary for the dislocation climb are partly used for the formation of fine precipitates. Moreover, if fine precipitates occur on dislocations, or dislocations catch fine precipitates during the climb motion an excess energy may be required to free the dislocations by the interchange of vacancies and fine precipitates by which their dissolution occurs. It is thought that the climb motion may

\(^{(5)}\) H. Kimura: Private communication.
\(^{(11)}\) Z. Henmi and T. Nagai: Trans. JIM, 10 (1969), 166.
\(^{(12)}\) J. Greven and B. Scholz: Metall, 22 (1968), 1119.
\(^{(15)}\) I. Miki and H. Warlimont: Z. Metallk., 59 (1968), 408.
\(^{(17)}\) E. Hornbogen: Practical Metallography, 7 (1970), 349.
\(^{(19)}\) W. Köster and E. Hornbogen: Z. Metallk., 59 (1968), 792.
be obstructed by this requirement for the excess energy for dissolution and then the recovery may be retarded. When the annealing temperature reaches a level for the beginning of recrystallisation, the precipitates will be integrated by pipe diffusion, etc. and grow up. Photograph 8 shows this stage. Some of the precipitates in the grain pin dislocations, obstructing their mutual annihilation and thus recrystallisation appears to be retarded.

On increasing the annealing temperature, the grain growth begins. The grain growth is caused by grain boundary migration and there are many factors controlling the rate of migration\(^{(20)}\). It is shown by transmission electron microscopy that the operative factors are different from one alloy to another. Close examination of Photo. 9 reveals that the precipitates inside the grain are dissolved into the grain boundary when the grain boundary migrates, and precipitated again after the grain boundary has passed. Since some amount of energy has to be involved in the formation and dissociation of precipitates, the migration of the grain boundary may in turn be obstructed and consequently the growth may be retarded. This behaviour is similar to the phenomenon found in Ni–2.8\%Al alloy\(^{(17)}\). In the Cu–Zr alloy the precipitates on the grain boundary and dislocation are thought to obstruct grain the boundary migration, since the precipitates pin and bend the grain boundary and dislocation (Photo. 10). Since the precipitate density is low near the grain boundary in the Cu–Zr–Cr alloy, the precipitates dissolve into the grain boundary during growth as in the Cu–Cr alloy, and the precipitates on the grain boundary obstruct the grain boundary migration as shown in Photo. 8. Thus, for the recrystallisation in these alloys, an excess energy may be required to overcome the obstacles of various types in each stage of recrystallisation, i.e. recovery, primary recrystallisation and grain growth, resulting in an increase of the recrystallisation temperature.

On the other hand, the size of precipitates formed by tempering prior to cold working does not affect the increase of the recrystallisation temperature. It is also shown that the precipitates are sheared to such a small size that their initial size does not affect the annealing behaviour.

V. Conclusions

1. No fine precipitates are detected at dislocation or sub-boundaries during low-temperature annealing by transmission electron microscopy, but fine precipitates, which retard recovery, must exist, since the electrical resistivity is decreased by low-temperature annealing. The mechanism of retardation of recovery may be due to the binding of dislocation jogs by fine precipitates.

2. In the high annealing temperature range the growth of precipitates and crystal grains is observed by transmission electron microscopy, and the effect of precipitates on the retardation of recrystallisation is also detected.

3. The size of precipitates formed during tempering before cold working does not affect the recrystallisation temperature, because the precipitates are sheared by heavy cold work and become a constant size.

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