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Mechanical properties of Cu-Ni-Be system alloys

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Abstract. The effects of addition of 0.17wt%Zr, 0.1wt%Mg and 0.1wt%Co on the mechanical properties of a Cu-1.2wt%Ni-0.2wt%Be alloy have been investigated. Adding Zr, Co or Mg to the Cu-Ni-Be alloy brings about the improvement in strength and stress relaxation property. The Zr, Co or Mg addition decreases the inter-precipitate spacing of γ'' precipitates, resulting in the increase in strength. The higher resistance to the stress relaxation of the Zr- or Co-added alloy is attributed to the lower density of mobile dislocations. The improvement of stress relaxation property by the Mg addition is explained by the viscous glide motion of dislocations dragging Mg atoms, in addition to the lower density of mobile dislocations.

1. Introduction

Copper-base alloys are used for electrical parts such as connectors and lead frames because the electrical conductivity of the alloys is very high. The high strength of the copper-base alloys is also required for small devices used in microelectronics. Most of the alloys are usually of the precipitation-strengthened types and are dilutely alloyed with elements of very low solubility to preserve high levels of conductivity. Cu-Ni-Be alloys containing usually about 2wt%Ni and 0.4wt%Be are one of such precipitation-hardenable copper-base alloys. Recently, a Cu-1.27wt%Ni-0.22wt%Be alloy, which contains smaller amounts of Ni and Be than the standard Cu-Ni-Be alloys, has been developed. The strength and electrical conductivity of the Cu-1.27wt%Ni-0.22wt%Be alloy and a standard Cu-2.05wt%Ni-0.35wt%Be alloy aged at 360 to 500 °C after cold rolling have been examined [1]. The former alloy exhibits a lower strength and a higher electrical conductivity than the latter alloy. Both alloys are hardened by disk-shaped coherent precipitates of γ'' phase.

In this study, we investigate the strength and stress relaxation property of Cu-1.2wt%Ni-0.2wt%Be alloys with and without 0.17wt%Zr, 0.1wt%Mg or 0.1wt%Co aged at 450 °C. It has been reported that the addition of Mg to a Cu-Ni-Si alloy [2] and Zr to a Cu-Cr alloy [3] enhances the strength and resistance to stress relaxation of the Cu-base alloys, and the addition of Co to a Cu-Ni-Be alloy increases the strength of the alloy [4]. This is the reason why Zr, Mg and Co were selected as added elements.

2. Experimental

Cu-1.2%Ni-0.2%Be, Cu-1.2%Ni-0.2%Be-0.17%Zr, Cu-1.2%Ni-0.2%Be-0.1%Co and Cu-1.2%Ni-0.2%Be-0.1%Mg alloys were prepared by melting in an argon atmosphere. The cast alloys were homogenized at 1000 °C for 24h in a vacuum, cold-rolled by 50% reduction in thickness and then spark-cut into specimen strips. All the specimen strips were solution-treated at 1000 °C for 8h in a

vacuum, quenched into water, cold-rolled to 40% reduction in thickness and then aged at 450°C for various times in an argon atmosphere. The solution-treated specimens had a grain size of 80µm.

Microhardness tests were carried out using the Vickers method. Tensile tests were performed using a static Instron-type testing machine with a constant strain rate of 10^{-3} s^{-1} at room temperature. Electrical resistivity measurements were made by a Hocking AutoSigma 3000 electrical conductivity tester at 20°C. According to the literature [5], cantilever stress relaxation tests were performed at 180°C for 24h in a nitrogen atmosphere. Transmission electron microscopy (TEM) was carried out using a HITACHI H-9000NAR microscope at an operation voltage of 300kV. Thin foils for TEM observations were prepared by slicing the aged specimens with a spark cutter and by electropolishing using a solution of 67% methanol and 33% nitric acid at -30 °C and 6.5 V in a twin-jet electropolisher.

3. Results and discussion

3.1. Effect of Zr, Mg and Co on strength

The hardness curves on aging at 450°C for Cu-Ni-Be alloys with and without Zr, Mg and Co showed that the peak hardness effect occurred after aging for 2h. Aging the alloys at 450°C for 2h after cold rolling to 40% reduction produced disk-shaped precipitates in the Cu matrix of α phase. An analysis of high-resolution TEM (HRTEM) images of the precipitates revealed that the disk-shaped precipitates were a γ'' -NiBe phase, which consisted of a two Be-layer structure separated by a Ni layer parallel to the $\{100\}_\alpha$ plane [1]. No other precipitates were observed in Cu-Ni-Be alloys with Zr, Mg and Co.

Table 1 summarizes the tensile properties and electrical conductivity of the present alloys aged at 450°C for 2h. The addition of Zr, Mg and Co causes an increase in 0.2% proof stress and tensile strength.

Table 1. 0.2% proof stress, tensile stress, elongation and electrical conductivity, and volume fraction, radius, thickness, number density and average inter-tip spacing of disk-shaped γ'' precipitates for Cu-Ni-Be system alloys aged at 450°C for 2h after 40% cold-rolling.

Specimen (wt%)	0.2% proof stress (MPa)	Tensile stress (MPa)	Elongation (%)	Electrical conductivity (%IACS)	Volume fraction	Radius (nm)	Thickness (nm)	Number density ($\times 10^{23}/\text{m}^3$)	Inter-tip spacing (nm)
Cu-1.2Ni-0.2Be	490	570	7	65	0.013	5.6	0.5	2.7	15
Cu-1.2Ni-0.2Be-0.17Zr	560	640	7	60	0.016	4.0	0.5	6.3	11
Cu-1.2Ni-0.2Be-0.1Co	510	600	6	60	0.014	5.0	0.5	3.7	13
Cu-1.2Ni-0.2Be-0.1Mg	530	620	6	62	0.014	4.6	0.5	4.6	12

It has been reported that the yield stress of Cu-Ni-Be alloys containing γ'' precipitates at room temperature is controlled by the Orowan mechanism at peak-age and over-age conditions [1]. The Orowan stress is inversely proportional to the inter-precipitate spacing λ . The increase in strength due to the addition of Zr, Mg and Co can then be discussed by estimating λ . Nie and Muddle considered the statistical evaluation of the average spacing λ_{ave} between plate tips assuming that the precipitates form as circular disks and arrived at the following expression [6]:

$$\lambda_{\text{ave}} = \sqrt{\frac{\sqrt{3}}{2} \frac{1}{\sqrt{2 \sin \theta \cdot N \cdot r}} - \frac{\pi r}{4} - \frac{\sqrt{3}}{2} \frac{h}{\sin \theta}} \quad (1)$$

Here N is the number density of precipitates per unit volume, r is the radius of precipitates, h is their thickness and θ is the dihedral angle between the plate and the $\{111\}_\alpha$ slip plane. For $\{001\}_\alpha$ precipitate plates, $\theta=54.74^\circ$. The diameter and thickness of γ'' precipitates were measured from HRTEM images. To obtain statistically reliable data, more than 100 precipitates were analyzed for

each alloy. The volume fraction f for the Cu-Ni-Be alloy was determined by applying the values of electrical resistivity, before and after aging at 450°C for 2 h, to the experimental data regarding the dependence of electrical resistivity on Ni or Be concentration [7]. For the Cu-Ni-Be alloys with 0.17%Zr, 0.1%Mg and 0.1%Co, all of the trace atoms were assumed to be dissolved in the matrix. Then f was calculated after the resistivity increment caused by 0.17%Zr, 0.1%Mg or 0.1%Co addition was removed. Table 1 lists the values of r and f for the present alloys. The number density N of γ'' precipitates was obtained from r , h and f using the equation of $N=f/(\pi r^2 h)$. The estimated values of N and λ_{ave} also are listed in table 1. The values of N for the Zr, Mg and Co-added alloys are larger than that for the Cu-Ni-Be alloy, indicating that the Zr, Mg and Co solutes promote the formation rate of γ'' precipitates. Moreover, it is stated that the increase in N or decrease in λ_{ave} by adding Zr, Mg and Co results in an increase in $\sigma_{0.2}$ due to the Orowan looping mechanism.

3.2. Effect of Zr, Mg and Co on stress relaxation property

Table 2 lists the stress relaxation rate for the present alloys tested at 180°C for 24 h. The stress relaxation rate is defined as the ratio of the deflection upon unloading to the deflection upon loading on a cantilever [5]. A lower stress relaxation rate means a higher resistance to stress relaxation. The addition of Zr, Mg and Co to the Cu-Ni-Be alloy enhances the stress relaxation resistance, and the effect is pronounced for the alloys with Zr and Mg.

Table 2. Stress relaxation rate for Cu-Ni-Be system alloys aged at 450°C for 2 h. Stress relaxation tests were performed at 180°C for 24h.

Specimen (wt%)	Stress relaxation rate
Cu-1.2Ni-0.2Be	0.15 ± 0.02
Cu-1.2Ni-0.2Be-0.17Zr	0.10 ± 0.02
Cu-1.2Ni-0.2Be-0.1Co	0.13 ± 0.02
Cu-1.2Ni-0.2Be-0.1Mg	0.10 ± 0.02

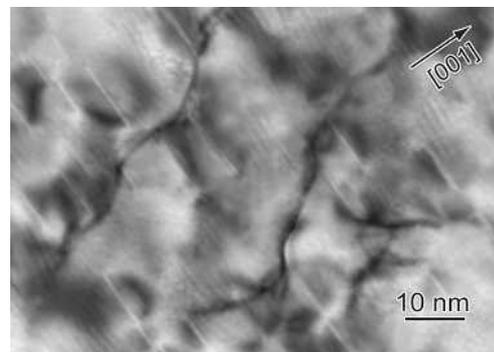


Figure 1. TEM image of disk-shaped γ'' precipitates in a Cu-1.2%Ni-0.2%Be alloy aged at 450°C for 2 h after 40% cold-rolling. The zone axis is $[110]_{\alpha}$.

Since stress relaxation tests were performed at a relatively low temperature of 180°C in the present study, the stress relaxation is likely to occur by logarithmic creep caused by the relatively short range motion of dislocations [8]. Thus, the stress relaxation depends on the mobility and density of mobile dislocations.

It is well known that the mobility of dislocations decreases when they are dragging their atmospheres of solute atoms behind them. Then the improvement of the stress relaxation property of the Cu-Ni-Be alloy by the addition of Zr, Mg or Co in table 2 might be expected to be attributable to the drag of atmosphere of Zr, Mg or Co atoms. However, we found that the addition of 0.17%Zr and 0.1%Co to pure Cu did not change the stress relaxation rate, although the addition of 0.1%Mg decreased it. There existed no precipitates in the Cu-Zr, Cu-Mg and Cu-Co alloys examined. Thus, it is necessary to discuss another factor responsible for the decrease in stress relaxation rate by the addition of Zr, Mg and Co.

In a previous paper [9], we have found that the present Cu-1.2%Ni-0.2%Be alloy exhibits better stress relaxation property than Cu-1.2%Ni and Cu-0.2%Be alloys. It has been concluded that this result is probably because atoms caused by pairs of Ni and Be chemical bonding are dragged by moving dislocations. Thus, the amounts of Ni and Be atoms dissolved in the Cu matrix affect the

stress relaxation property. It may thus be inferred that the development of the stress relaxation property by the addition of Zr, Mg and Co is caused by the increase in amounts of Ni and Be in the Cu matrix. However, it is seen from table 1 that the addition of each element increases the value of f : that is, it decreases the amounts of Ni and Be atoms in the Cu matrix.

As mentioned before, the stress relaxation should be affected by the density of mobile dislocations. In order to examine this, stress relaxation tests were carried out at 180°C for 24h, using pure Cu with and without 20% cold-rolling after annealing. The stress relaxation rates of Cu with and without 20% cold-rolling were 0.5 and 0.42, respectively. It is said that a higher density of mobile dislocations brings about a lower resistance to stress relaxation. Therefore, it may be expected that the addition of Zr, Mg or Co lowers the density of mobile dislocations and, as a result, the stress relaxation rate decreases. TEM observations of the present alloys aged at 450°C for 2 h after 40% cold-rolling revealed that γ'' precipitates formed preferentially on dislocations, as exemplified in figure 1. As shown in table 1, the number density of the precipitates increases by the element addition. This increase in number density should cause an increase in the number density of the γ'' precipitates preferentially formed on dislocations, resulting in a decrease in the density of mobile dislocations. This explains the development of the stress relaxation property due to the addition of each element.

As mentioned before, the addition of 0.1%Mg to pure Cu improved the stress relaxation property. In the previous paper [2], we have reported that the increase of stress relaxation resistance by the addition of 0.1%Mg to a Cu-2.0%Ni-0.5%Si alloy is caused by the Mg-atom-drag effect on dislocation motion. Therefore, the decrease in stress relaxation rate by adding Mg to the Cu-Ni-Be alloy is attributable to the drag effect of Mg atoms on dislocation motion, in addition to the decrease in the density of mobile dislocations due to the increase in the number density of the γ'' precipitates preferentially formed on dislocations.

4. Conclusions

We have found that 0.17wt%Zr, 0.1wt%Co or 0.1wt%Mg added to a Cu-1.2wt%Ni-0.2wt%Be alloy enhances the strength and stress relaxation property of the Cu-Ni-Be alloy. The increase in strength by the addition of each element is ascribed to the decrease in inter-tip spacing of γ'' precipitates. The improvement of stress relaxation property by the addition of Zr and Co is explained by the decrease in the density of mobile dislocations due to the increase in the number density of γ'' precipitates preferentially formed on dislocations. The increase in stress relaxation resistance by the Mg addition is attributed to the viscous glide motion of dislocations dragging Mg atoms, in addition to the decrease in the density of mobile dislocations.

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