Effects of Natural Aging on Age-Hardening Behavior of Cu-Be-Co and Cu-Ti Alloys Processed by High-Pressure Torsion^{*1}

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The microstructural change and aging behavior of Cu-1.8mass%Be-0.2mass%Co and Cu-3mass%Ti alloys severely deformed by high-pressure torsion (HPT) at room temperature were investigated on two-step aging condition; natural aging and subsequent artificial aging. Application of HPT processing under an applied pressure of 5 GPa for 10 revolutions at 1 rpm to the alloys produced ultra-fine grained structures. The hardnesses of the Cu-Be-Co and Cu-Ti alloys increased with equivalent strain up to 7, and then saturated to constant values of 400 and 330 Hv, respectively. Aging the HPT-processed alloys at 293 K gradually decreased the resistivities of the alloys; however, even after the longest natural aging period of 2.59 Ms (1 month), the hardnesses of the alloys remained essentially unchanged. The attained peak hardness of the Cu-Be-Co alloy on subsequent artificial aging at 593 K decreased with increasing natural aging time, while the age-hardening behavior of the Cu-Ti alloy during aging at 623 K was practically unaffected by natural aging at 293 K up to 2.59 Ms. [doi:10.2320/matertrans.MH201502]

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1. Introduction

Lately, many investigators have examined the aging behavior of age-hardenable alloy systems processed by severe plastic deformation (SPD) technics such as accumulative roll-bonding (ARB) and high-pressure torsion (HPT). Reported aging responses after SPD processing were generally different from alloy to alloy. For example, aging Al-base alloys such as Al-Cu¹⁾, Al-Mg-Si²⁾ and Al-Ag³⁾ alloys after solution treatment and subsequent SPD processing produced no or only slight amounts of hardening, whereas age-hardenable Cu-base alloys, e.g. Cu-Ni-Be⁴⁾, Cu-Ni-P⁴⁾ and Cu-Ni-Si⁵⁾ systems, after SPD processing often exhibited larger amounts of age-hardening than the Al-based alloys. However, the cause of the difference in aging responses has not been clarified yet.

Subjecting SPD processes to metallic materials produces not only ultrafine-grained microstructures but also high densities of lattice defects, in particular, very high densities of vacancies. The concentrations of the vacancies are typically close to those of vacancies in thermal equilibrium at the melting points⁶⁾. Gibicza *et al.* reported that, during storage of the SPD-processed Cu even at room temperature (RT), the vacancy concentration reduced significantly, while the dislocation density and the grain size remained unchanged⁷⁾. Excess vacancy concentrations are well-known to have a strong effect on the precipitation kinetics of second phases⁸⁾. Therefore, natural aging of age-hardenable alloys after SPD processing should strongly affect the aging responses of the alloys on subsequent artificial aging treatments.

In this study, we investigated the effects of natural aging treatments on the subsequent artificial aging behaviors of Cu-1.8mass%Be-0.2mass%Co alloy and Cu-3mass%Ti alloy specimens solutionized, and then processed by HPT. G.P.

zones first nucleate when the Cu-Be-Co alloy is solutionized, and then aged at around 573 K. The G.P. zones then transforms continuously to the stable γ phase via meta-stable phases⁹⁾. On the other hand, aging the Cu-Ti alloy at around 623 to 773 K^{10–12)} produces meta-stable β' -Cu₄Ti phase precipitates via spinodal decomposition.

2. Experimental Procedure

This study used a commercial extruded bar of a Cu-1.8mass%Be-0.2mass%Co alloy with a diameter of 100 mm, and a commercial hot-rolled sheet of a Cu-3mass%Ti alloy with a thickness of 1 mm. Disks with a diameter of 10 mm and a thickness of 0.8 mm were cut from the bar and sheet. The disks of the Cu-Be-Co alloy or Cu-Ti alloy were solution-treated at 1093 K for 7.2 Ks or 1273 K for 7.2 Ks, respectively, and then quenched into cold water. The solution-treated disks were subjected to HPT processing under an applied pressure of 5 GPa for 10 rotations with a rotation speed of 1 rpm at RT. The disk specimens were held at 193 K within 120 s immediately after the HPT processing. The HPT Cu-Be-Co and Cu-Ti specimens were then naturally aged at 293 K for various periods up to 1 month. Hereafter, specimens naturally aged at 293 K for 0 s, 1 week (0.61 Ms) and 1 month (2.59 Ms) are referred to as 0s-, 1w- and 1m-specimens. Following the natural aging, the Cu-Be-Co and Cu-Ti specimens were artificially aged at 593 and 523 K, respectively. The Vickers microhardness was measured along 8 radial directions on the mechanically polished surface of the disk-shaped specimens before and after aging. The measurements of microhardness started at the center of the disks and were taken at every 1 mm from the disk center to the edge of specimens.

Electrical resistivity measurements were performed by the standard 4-terminal measurement technic at 293 K using a DC resistance meter with a constant current of 1 A. The specimens for resistivity measurements were cut into strips with a gage dimension of $0.5^t \times 2.0^w \times 6.0^l$ mm³ from the HPT specimens. The length and width of the strips were measured with

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Fig. 1 Change in the Vickers microhardness of Cu-Be-Co and Cu-Ti specimens with equivalent strain $\varepsilon_{\text{equiv}}$ introduced by HPT processing at room temperature (RT) under a compression stress of 5 GPa.

a vernier caliper, and the thickness with a micrometer. The center of the strips was at the distance of 3 mm from the center of the HPT specimens. Terminals of Cu wires were directly welded on the specimen surface. The accuracy of measurements was approximately a magnitude of 0.001 m Ω , that is, 0.17 n Ω m in resistivity.

Disks with a diameter of 3 mm were cut from the disk-shaped HPT-specimens before and after aging. The center of the 3-mm disks was at the distance of 3 mm from the center of the HPT specimens. The 3-mm disks were mechanically ground down to a thickness of 0.2 mm. Thin foils for transmission electron microscopy (TEM) observations were prepared by electro-polishing using a solution of 33% HNO₃ and 67% of CH₃OH at 243 K by applying 6.5 V. TEM observations were performed by a field-emission transmission electron microscope (JEOL, 2010FEF) operated at 200 kV.

Lattice constants of the specimens before and after aging were analyzed by X-ray diffraction (XRD) analysis using the Cu-K α radiation in a scanning step of 0.02°, and were calculated using the standard $\cos\theta/2\theta$ method. The XRD profiles were obtained from a region distance of 3 mm from the center of HPT specimen.

3. Results

3.1 Microstructure and microhardness after HPT processing

Figure 1 shows the Vickers microhardness, plotted against equivalent strain introduced by HPT processing at RT. The equivalent strain $\varepsilon_{\text{equiv}}$ was calculated using the following equation:¹³⁾

$$\varepsilon_{\text{equiv}} = \ln \left[\left(2 + \gamma^2 + \gamma \sqrt{4 + \gamma^2} \right) / 2 \right] / \sqrt{3}, \quad (1)$$

where γ represents the amount of shear-deformation introduced by HPT and is expressed by

$$\gamma = 2\pi rN/h. \quad (2)$$

Here, r is the distance from the disk center, N is the number of rotations and h is the thickness of the specimen after HPT processing. The microhardnesses of the Cu-Be-Co and Cu-Ti specimens increase with increasing equivalent strain up to 7,

Fig. 2 Bright-field TEM image of a Cu-Be-Co specimen processed by HPT at RT for 10 revolutions under a compression stress of 5 GPa. The inset is the corresponding SADP taken using a selected-area aperture having a diameter of 2.5 μ m.

Fig. 3 Change in the Vickers microhardness and resistivity of a Cu-Be-Co specimen processed by HPT during natural aging at 293 K.

and then saturate to constant values of about 400 and 330 Hv, respectively.

Figure 2 presents a Bright-field image of the Cu-Be-Co specimen subjected to 10 HPT revolutions. The inset in Fig. 2 is the corresponding selected-area diffraction pattern (SADP) taken using a selected-area aperture having a diameter of 2.5 μ m. An analysis of many dark field images revealed the formation of roughly equiaxed, very fine grains with an average size of approximately 50 nm. The average size of grains in the Cu-Ti specimen subjected to 10 HPT revolutions was approximately 70 nm, slightly larger than that of the Cu-Be-Co specimen.

3.2 Change in resistivity and microhardness during natural aging

Figures 3 and 4 show the change in the resistivity and microhardness of the Cu-Be-Co and Cu-Ti specimens subjected to 10 HPT revolutions during natural aging at 293 K, respectively. The data of microhardness shown in Figs. 3 and 4 were obtained from portions apart from 3 mm from the center of the HPT specimens. The resistivities of both specimens gradually decreased with increasing natural aging time t , whereas the microhardnesses of the specimens exhibited almost no change with t . A TEM observation revealed that the grain sizes of both specimens remained essentially unchanged, and that no precipitated phases were formed in the specimens,

Fig. 4 Change in the Vickers microhardness and resistivity of a Cu-Ti specimen processed by HPT during natural aging at 293 K.

Fig. 5 Age hardening curves of Cu-Be-Co specimens artificially aged at 593 K after HPT processing and then natural aging for 0 s (0s), 1 week (0.61 Ms; 1w) or 1 month (2.59 Ms; 1m).

even after the longest period of natural aging (= 2.59 Ms).

3.3 Aging response and microstructure after natural aging

Figure 5 displays the age-hardening curves of the Cu-Be-Co specimens during artificial aging at 593 K for various periods after natural aging for 0 s, 1 week (0.61 Ms) and 1 month (2.59 Ms). The microhardness of each specimen initially increased, eventually attained a peak, and then decreased continuously. It is interesting that, with increasing natural aging time, the peak hardness decreased, and the artificial aging time to attain the peak hardness increased. In contrast, the Cu-Ti specimens did not show any notable change in aging response irrespective of the natural aging time, as shown in Fig. 6.

TEM observations were conducted using the Cu-Be-Co 0s-, 1w- and 1m-specimens peak-aged at 593 K. Figure 7 exemplifies a bright field TEM image of a grain in the 0s-specimen aged at 593 K for 180 s. The beam axis is parallel to $[001]_m$ of the Cu matrix. Finely dispersed, disk-shaped precipitates with an average diameter of about 4 nm, parallel to $(100)_m$ and $(010)_m$ of the Cu matrix, were observed within the grain. According to the literature⁹⁾, the observed precipitates are determined as G.P. zones consisting of a monolayer Be atoms parallel to $\{001\}_m$ plane. The G.P. zones having nearly identical diameters were also observed in the 1w- and

Fig. 6 Age hardening curves of Cu-Ti specimens artificially aged at 623 K after HPT processing and then natural aging for 0 s (0s), 1 week (0.61 Ms; 1w) or 1 month (2.59 Ms; 1m).

Fig. 7 Bright-field TEM image of disk-shaped G.P. zones in a Cu-Be-Co specimen processed by HPT and then aged at 593 K for 180 s. The zone axis is parallel to $[001]_m$ of the Cu matrix.

1m-specimens peak-aged at 593 K. Peak-aging all the Cu-Be-Co specimens at 593 K did not significantly change their grain sizes, about 50 nm.

Figure 8(a) displays a bright-field image of the Cu-Ti 0s-specimen peak-aged at 623 K for 1.08×10^4 s. Figures 8(b) and 8(c) are the SADP corresponding to Fig. 8(a) and the schematic illustration of Fig. 8(b), respectively. The average grain size was almost unchanged by peak-aging. As can be seen in Fig. 8(a), there exist nearly spherical fine precipitates with an average diameter of approximately 5 nm. Analyses of several SADPs of the precipitates revealed that the precipitates were β' -Cu₄Ti phase having BCT structure¹⁰⁻¹²⁾. The β' precipitates in the three Cu-Ti specimens peak-aged at 623 K had almost the same average size of approximately 5 nm.

4. Discussion

As described in Section 3.2, the resistivities of both Cu-Be-Co and Cu-Ti specimens gradually decreased during natural aging after HPT processing; however, the microhardnesses and grain sizes of both specimens remained almost unchanged even after the longest natural aging time of 1 month (2.59 Ms). Moreover, TEM observations revealed that no precipitation occurred upon natural aging of both specimens. These results

Fig. 8 (a) Bright-Field TEM image taken from a Cu-Ti specimen processed by HPT and then aged at 623 K for 10.8 Ks, (b) SADP corresponding to (a), and (c) schematic illustration of (b).

strongly suggest that recovery of a portion of lattice defects, introduced by HPT processing, occurred during natural aging. Gibicza *et al.* reported that, during storage of the SPD-processed pure Cu even at RT, the vacancy concentration decreased significantly while the dislocation density and the grain size remained unchanged⁷⁾. Although the dislocation densities of the specimens before and after natural aging were not measured, the main contributor to the decrease in resistivity during natural aging (Figs. 3 and 4) seems to be decrease in the vacancy concentration during natural aging, because of significantly smaller contribution to the resistivity by dislocations (≈ 0.8 to $2.3 \times 10^{-13} \Omega \text{m}^3$ ¹⁴⁾) than that by a vacancy ($= 1.5 \times 10^{-6} \Omega \text{at}\%^{-1}$ ¹⁵⁾).

As shown in Fig. 5, the age-hardening behavior of the Cu-Be-Co specimen on artificial aging after HPT processing and subsequent natural aging is strongly affected by the period of natural aging. It is widely known that the concentration of vacancies strongly influences the nucleation of precipitates.

Table 1 Lattice parameters a of Cu matrix and volume fractions f of G.P. zones for Cu-Be-Co specimens processed by HPT (as HPT) and Cu-Be-Co specimens peak-aged at 593 K after HPT processing and subsequent natural aging for 0 s (0s), 1 week (0.61 Ms; 1w) or 1 month (2.59 Ms; 1m).

Specimen	a (nm)	f
As HPT	3.6280	—
0s	3.6128	0.080
1w	3.6135	0.076
1m	3.6138	0.074

Generally speaking, the nucleation rate of precipitates increases with increasing excess vacancies⁸⁾. It can thus be said that the initial age-hardening rate of the Cu-Be-Co specimens on the artificial aging decreases with increasing natural aging time, since the vacancy concentration decreases as the natural aging time increases.

Ota *et al.* reported that the precipitation strengthening by G.P. zones is controlled by the precipitate shearing mechanism¹⁶⁾. According to the shearing mechanism, the amount of precipitation strengthening $\Delta\sigma$ is expressed as¹⁷⁾

$$\Delta\sigma \propto \sqrt{\bar{r}f}, \quad (3)$$

where $\bar{r}$ is the average size of precipitates and f is the volume fraction of precipitates. As described in Section 3.3, the average diameters of G.P. zones are nearly identical in the three Cu-Be-Co specimens peak-aged at 593 K after natural aging for three different periods. Therefore, the differences in the amount of age-hardening between the three specimens can be discussed by estimating f . To obtain values of f of G.P. zones, the lattice constants a of the three specimens before and after natural aging and subsequent peak-aging were measured using XRD technique. The measured lattice constants are listed in Table 1. The values of f were determined by applying the measured lattice constants to the experimental data regarding the dependence of the lattice constant on the Be concentration in the literature ($\approx -3.17 \times 10^{-11} \text{ m at}\%^{-1}$)¹⁸⁾. The disk-shaped G.P. zones are assumed to have a thickness of 0.226 nm, equal to the diameter of Be atoms¹⁹⁾. The calculated values of f are also summarized in Table 1. The value of f decreases with increasing natural aging time. This explains why the amount of age-hardening by artificial peak-aging decreases with increasing natural aging time. It seems that the volume fraction of G.P. zones decreases with increasing natural aging time, since the nucleation rate of G.P. zones decreases as the vacancy concentration decreases. In addition, the growth rate of G.P. zones should also be affected by the vacancy concentration. Thus, it calls for further study on the effects of natural aging on the growth kinetics of G.P. zones.

As shown in Fig. 6, in contrast to the results of Cu-Be-Co specimens (Fig. 5), the difference in natural aging period does not essentially affect the age-hardening behavior of the Cu-Ti specimens on subsequent artificial aging. As discussed above, the change in vacancy concentration by natural aging strongly influences the age-hardening behavior of the Cu-Be-Co specimens, since a nucleation process is necessary for the formation of G.P. zones. On the other hand, the β' precipitates responsible for age-hardening of the Cu-Ti specimens were formed via spinodal decomposition^{10–12)} without nucleation

process. Thus, it can be said that the age-hardening behavior of the Cu-Ti specimens is not influenced by the natural aging. An age-hardening curve of the present Cu-Ti alloy aged at 623 K after solution treatment at 1273 K and subsequent cold-rolling to a reduction of 90% in thickness is also shown in Fig. 7. There are little differences in the amount of age-hardening at peak-aging and the aging time to attain the peak hardness between the HPT and the 90% rolling specimens. In the Cu-Ti alloy, prior mechanical processing (HPT or cold-rolling) and natural aging time have small impact on the age-hardening behavior of the alloy.

5. Conclusions

Our investigation of the effects of prior natural aging on the subsequent artificial aging behavior of Cu-1.8mass%Be-0.2mass%Co and Cu-3mass%Ti alloys severely deformed by high-pressure torsion (HPT) yielded the following conclusions:

(1) The resistivities of both alloys processed by HPT decrease with increasing natural aging time; however, the microhardnesses of the alloys are almost unchanged even after the longest natural aging time of 2.59 Ms. The decrease in resistivity of the alloys can be ascribed to decrease in the excess vacancies introduced by the HPT processing during natural aging.

(2) On artificial aging at 593 K of the Cu-Be-Co alloy after natural aging, the attained peak-hardness decreases and the aging time till peak-hardness increases as natural aging time increases. However, natural aging time does not essentially affect the age-hardening behavior of the Cu-Ti alloy on subsequent artificial aging.

(3) The difference in the effects of natural aging on subsequent artificial aging behavior between the two alloys are associated with the different formation mechanisms of strengthening precipitates, that is, direct formation of G.P. zones in the Cu-Be-Co alloy and formation of β' -Cu₄Ti phase in the

Cu-Ti alloy via spinodal decomposition.

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