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Abstract. The microstructure and aging behavior of Cu-1.8wt%Be-0.2wt%Co alloy specimens processed by high-pressure torsion (HPT) at room temperature (RT) and 150°C after solution treatment have been studied. Application of HPT processing at RT and 150°C under an applied pressure of 5 GPa for 10 revolutions at 1 rpm to alloy specimens (RT- and 150°C-specimen) produces an ultra-fine grained structure with a grain size of 70 nm. The hardnesses of the RT- and 150°C-specimens increase with equivalent strain up to 7 and then saturate at constant values of 400 and 430 Hv, respectively. Annealing the RT-specimen at 150°C for 10 min increases the hardness from 400 to 430 Hv. Transmission electron microscopy observations of the 150°C-specimen and the RT-specimen annealed at 150°C reveal that there are no intragranular and intergranular precipitates. It is suggested that the higher hardness of the 150°C-specimen than the RT-specimen is ascribed to the segregation of Be atoms on dislocations during HPT processing at 150°C. The RT- and 150°C-specimens harden rapidly and exhibit maximum values of hardness at 3 min during aging at 320°C. The increase in the hardness is attributed to the precipitation of finely dispersed G.P. zones.

Introduction

In the last two decades, there is considerable interest in the production of ultrafine-grained (UFG) metals whose mean grain size is smaller than 1 μm by the severe plastic deformation (SPD) method [1]. As a consequence of the Hall-Petch relationship, the UFG metals produced by the SPD technics exhibited relatively high strength at ambient temperature.

Recently, several investigations of the aging behavior of age-hardenable alloy systems processed by the SPD technics have been conducted. Reported aging responses after SPD processing are generally different from alloy to alloy. For example, aging such Al-base alloys as Al-Cu [2, 3] and Al-Ag [4] alloys after solution treatment and SPD processing produces no or only slight amounts of hardening, whereas age-hardenable Cu-base alloys, e.g. Cu-Ni-Be [5], Cu-Ni-P [5] and Cu-Ni-Si [6] systems, after SPD processing often exhibit larger amounts of age-hardening than the Al-based alloys. The homologous temperature T_h on SPD processing can be pointed out as one possible reason for the difference in age-hardening behavior between the age-hardenable Al- and Cu-base alloys SPD-processed. The values of T_h at RT for the Al and Cu alloys are about 0.32 and 0.22, respectively. In this study, we investigate the effects of SPD-processing temperature on the microstructure and aging behavior of Cu-1.8wt%Be-0.2wt%Co alloy specimens processed by high-pressure torsion (HPT) after solution treatment. HPT processing was performed at temperatures of RT and 150°C that correspond to respectively $T_h \approx 0.22$ and 0.32 for the Cu-Be-Co alloy.

Experimental Procedure

This study used a extruded bar of a Cu-1.8wt%Be-0.2wt%Co alloy with a diameter of 100 mm. Disks with a thickness of 0.8 mm were cut from the bar. The disks were solution-treated at 820°C for 2h and then quenched into cold water. The solution-treated disks were subjected to HPT under an applied pressure of 5 GPa for 10 rotations with a rotation speed of 1 rpm at RT or 150°C. Hereafter, specimens processed at RT and 150°C will be referred to as RT-specimen and 150°C-specimen, respectively. The RT- and 150°C specimens after HPT were aged at 320°C. 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.

Disks with a diameter of 3 mm were cut from the specimens. The center of the 3-mm disks was at the distance of 3mm from the center of the 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% HNO_3 and 67% of CH_3OH at -30°C by applying 6.5 V. Microscopy was performed by a field-emission transmission electron microscope (JEOL, 2010FEF) operated at 200 kV.

The dislocation density in the RT- and 150°C-specimens was estimated by the Warren–Aberbach method based on the Williamson–Hall plots using the conventional X-ray diffraction data for {111}, {200}, {220} and {311} reflections. A detailed explanation is given in the literature [7].

Results

Microstructure after HPT. Fig. 1 shows (a) a Bright-field and (b) a dark-field image of the RT-specimen. The inset in Fig. 1(a) is the corresponding selected-area diffraction pattern (SADP) taken using a selected-area aperture having a diameter of 2.5 μm. Analyses of many SADPs using dark-field technique revealed that roughly equiaxed grains were separated by a reasonably high fraction of high-angle boundaries. The average grain sizes of RT- and 150°C-specimens were almost the same, about 70 nm. HPT processing till 10 rotations at RT and 150°C gave significant grain refinement from about 50 μm to 70 nm. In grains, deformation twins ({111}/<112> type) were often observed.

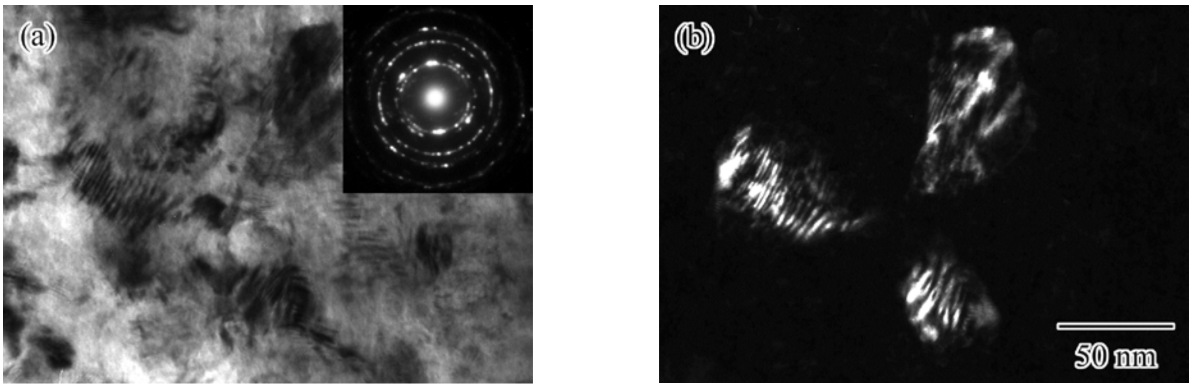

Fig. 1 (a) Bright-field and (b) dark-field TEM images of a Cu-Be-Co specimen HPT-processed till 10 rotations at RT under a compression stress of 5 GPa. The applied rotaion speed was 1 rpm.

Microhardness measurements. In Fig. 2, the Vickers microhardness is plotted against equivalent strain introduced by HPT processing for 10 rotations at RT and 150°C. The equivalent strain ε was calculated using the following equation: [8]

$$\varepsilon = \ln[(2+\gamma^2+\gamma\sqrt{4+\gamma^2}/2]\Big/\sqrt{3} \quad , \tag{1}$$

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

$$\gamma = \frac{2\pi r N}{h} \ . \qquad (2)$$

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 specimens processed at RT and 150°C increase with increasing equivalent strain up to 7, and then saturate to constant values of about 400 and 430 HV, respectively.

In Fig. 3, the age hardening curves of the RT- and 150°C-specimens aged at 320°C are shown. The microhardness was measured at a position of distance of 3 mm from the center of specimens ($\varepsilon \approx 11$). The 150°C-specimen after HTP processing exhibits a larger value of hardness than the RT-specimen after HTP processing. The hardnesses of the RT- and 150°C-specimens continuously increase during aging for 3 min, reach maximum values of 470 and 460 Hv, respectively, and then decrease. The microhardnesses of both specimens in over-age conditions are nearly identical.

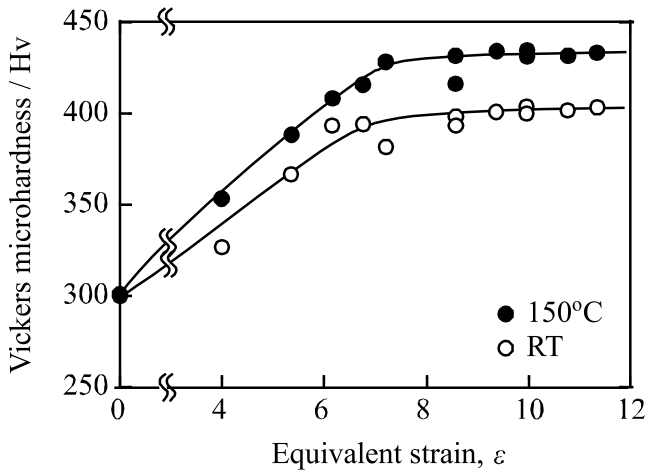

Fig. 2 Change in Vickers microhardness of Cu-Be-Co specimens with introduced equivalent strain ε by HPT processing at RT and 150°C under a compression stress of 5 GPa.

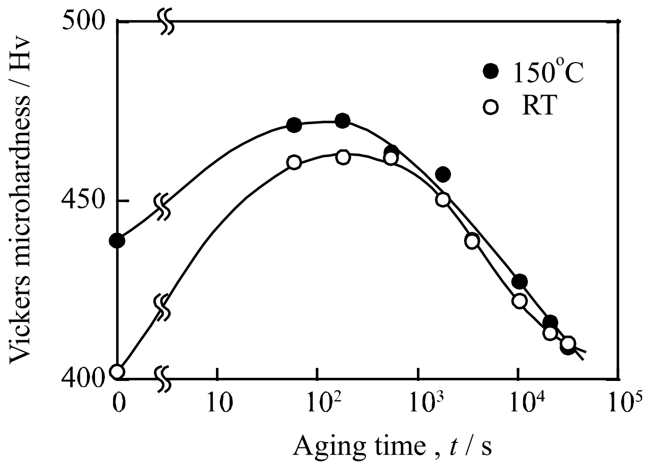

Fig. 3 Change in Vickers microhardness of Cu-Be-Co specimens processed by HPT at RT and 150°C during aging at 320°C. The measured portion is a distance of 3mm from the center of specimens.

Microstructure after aging treatment. A TEM observation was conducted using the RT- and 150°C-specimens peak-aged at 320°C for 3 min. Aging the specimens at 320°C for 3min did not significantly change the average grain size, about 70 nm. Finely dispersed precipitates were observed within grains. Fig. 4 (a) depicts a TEM image of precipitates in the RT-specimen. The beam axis is parallel to $[001]_m$ of the Cu matrix. The precipitates are parallel to $(100)_m$ and $(010)_m$, and have an average diameter of about 4 nm. Fig. 4(b) also shows a high-resolution (HR) TEM image of a precipitate taken using an incident beam of $[110]_m$. According to the literature [9], the precipitates observed are determined as G.P. zones consisting of a mono-layer Be atoms parallel to $\{001\}_m$ plane. These G.P. zones were also found in the 150°C-specimen aged at 320°C for 3 min.

Fig. 5 depicts a bright-field TEM image of the RT-specimen aged at 320°C for 100 h. The average grain size is about 150 nm, which is about twice larger than that of the RT-specimen without aging. Although the growth of grains took place during aging, fine grains were well retained even after prolonged aging at 320°C. In-grain precipitates were not essentially observed, but a small number of coarse precipitates existed on grain boundaries, indicated by the arrows in Fig. 5. From analyses of the SADPs, the coarse precipitates were identified as a stable γ (CuBe) phase with a B2 structure.

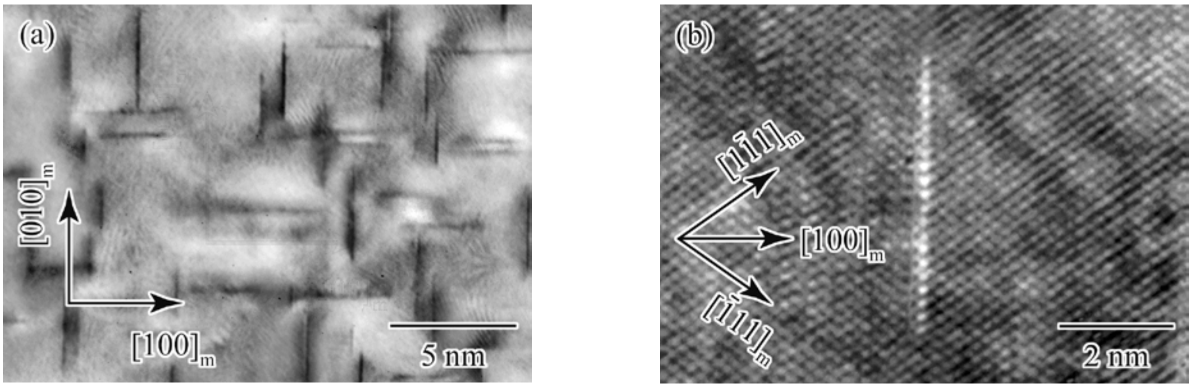

Fig. 4 (a) Bright-field TEM image of disk-shaped G.P. zones and (b) HRTEM image of a G.P. zone in a Cu-Be-Co specimen processed by HPT till 10 rotations at RT, and then aged at 320°C for 3min. The zone axes are parallel to (a) $[001]_m$ and (b) $[110]_m$.

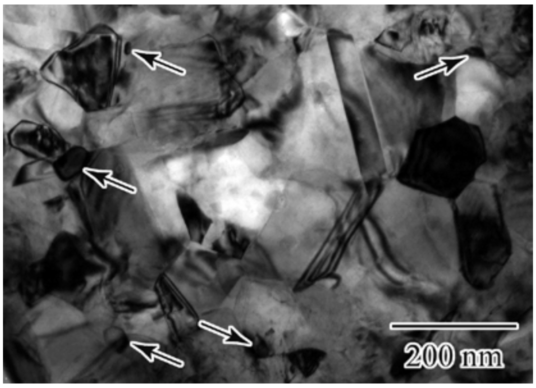

Fig. 5 Bright-Field TEM image of a Cu-Be-Co specimen processed by HPT till 10 rotations at RT, and then aged at 320°C for 100h.

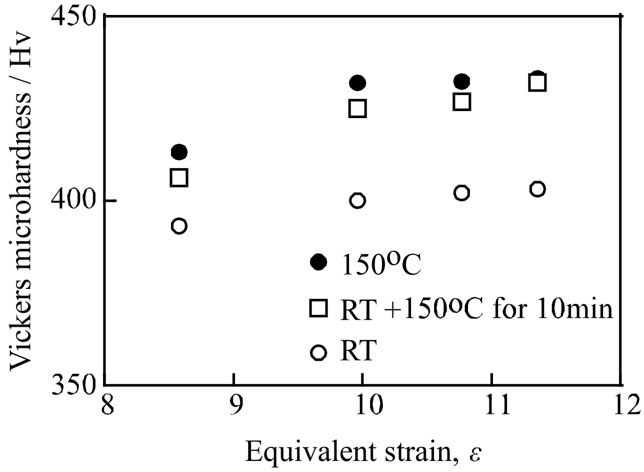

Fig. 6 Change in Vickers microhardness of Cu-Be-Co specimens HPT-processed at RT and 150°C, and HPT-processed at RT and then annealed at 150°C for 10min with equivalent strain.

Discussion

It is well known that dynamic recovery of the lattice defect introduced by plastic deformation occurs during the deformation, and thus the strength of heavily deformed materials generally decreases with increasing processing temperature. In fact, the dislocation density of the RT-specimen after HPT process, $(3.8 \pm 1.2)\text{x}10^{15}$ m^{-2}, is slightly higher than that of the 150°C-specimen, $(3.5 \pm 1.1)\text{x}10^{15}$ m^{-2}. These dislocation densities were obtained by conventional X-ray diffraction. However, as seen in Fig. 2, the hardness of 150°C-specimen is larger than that of RT-specimen. TEM observations revealed that no intragranular and intergranular precipitates existed in both specimens after HPT. Thus the larger hardness of 150°C-specimen cannot be attributed to precipitation hardening during HPT process at 150°C.

One possible reason for this discrepancy in hardness between the RT- and 150°C-specimens is the segregation of solute Be atoms to dislocations during HPT at 150°C. Nishijima et al. reported that annealing a Cu-Ni-Be alloy at a relatively low temperature of 200°C for a short time after peak-aging followed by cold rolling enhanced mechanical properties of the alloy [10]. The improvement of mechanical properties of the alloy by annealing was understood through the locking of dislocations by Cottrell atmosphere of solute atoms. According to them, we have examined change in microhardness of the RT-specimen by annealing at 150°C for 10 min. The annealing temperature and time are determined from the conditions of HPT processing to 10 rotations at 150°C. Fig. 6 shows the microhardness of RT-specimens before and after annealing at 150°C and of 150°C-specimen. Annealing the RT-specimen increases notably the hardness, resulting in almost the same hardness as the 150°C-specimen. Of course, no precipitates are found in the RT-specimen annealed at 150°C by HRTEM. Therefore, the larger hardness of the 150°C-specimen can be ascribed to the segregation of Be atoms on dislocations during HPT processing at 150°C.

Another reason for the difference in hardness between the RT- and 150°C-specimens is that clustering of Be atoms may take place during HPT processing at 150°C. Ringer and Hono [11] have reported that, in age-hardenable Al alloys such as Al-Cu-Mg, Al-Mg-Si, Al-Zn-Mg alloys, solute clustering occurs prior to formation of G.P. zones or precipitation of metastable phases, and these clusters lead to age-hardening effect called clustering hardening. Although the G.P. zones are readily observed by TEM, a clear observation of solute clusters is not possible even with HRTEM. To clarify whether Be clusters exist in the 150°C-specimen or not, an analysis of clustering of Be atoms using 3D atom probe microscopy is now in progress.

Recently, HRTEM observations of precipitated phases in Cu-0.9wt%Be alloy single crystals containing only the G.P. zones on the $(001)_\alpha$ plane have revealed that the phases follow a G.P. zone → γ'' → γ_I' → $\gamma_I + \gamma'$ → γ sequence with increasing aging time [9]. The G.P. zones transform continuously to the γ_I phase via γ'' and γ_I' phase. These metastable phases are composed of alternative Be and Cu matrix layers parallel to {100}m. The metastable γ' phase heterogeneously precipitates on the γ_I phase and transforms successively to the stable γ phase.

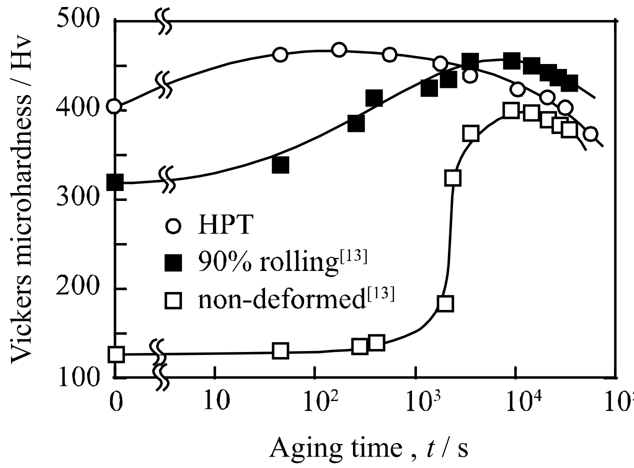

Fig. 7 Age-hardening curves of Cu-Be-Co alloys processed by HPT at RT, cold-rolled to 90% [13] and then aged at 320 °C. Also shown is an age-hardening curve of the alloy aged at 320 °C after solution treatment [13].

It has also been reported that cold-rolling to a 90% reduction prior to aging at 320°C affects the precipitation process in a Cu-1.8wt%Be-0.2wt%Co alloy [12]. In the cold-rolled Cu-Be-Co alloy, a γ_m phase with a body-centered monoclinic lattice transformed continuously from γ'' phase was newly found. Moreover, since the promotion of nucleation of the G.P. zones by dislocations induced by 90% cold-rolling lowered the supersaturation of Be atom in the early stage of aging, the transformation from the G.P. zones to γ' via γ'', γ_I' and γ_I was retarded during subsequent aging in comparison with that for the non-deformed alloy. At a peak-age condition at 320°C, the coexistence of γ'', γ_I' and γ_I was observed in the cold-rolled alloy, but the γ' precipitates mainly formed in the non-deformed alloy. Contrary to this observation, only the G.P. zones are noticed in the specimen HPT-processed and then peak-aged at 320°C, as depicted in Fig. 4. Although the dislocation density in the Cu-Be-Co alloy after 90% rolling was not measured in the literature [13], the dislocation density in the specimen processed by HPT is expected to be much larger than that of the cold-rolled specimen. A higher dislocation density in the HPT specimens may result in a higher number density of the G.P. zones than those of non-deformed and cold-rolled specimens. Fig. 7 shows the age-hardening curves of the Cu-Be-Co alloy aged at 320°C after non-deformation and 90% cold-rolling in the literature [13] together with that of the present alloy aged at 320°C after HTP processing at RT. The aging time to reach a maximum microhardness becomes shorter with increasing the amount of plastic deformation. It should be noted that the peak-aging effect is achieved at 3min by precipitation of the G.P. zones in the RT-specimen aged at 320°C, whereas no hardening of the non-deformed specimen and an small amount of hardening of the cold-rolled specimen were seen at an aging time at which only the G.P. zones exist [13]. This result supports the above expectation that the number density of G.P. zones in the specimen processed by HPT is much higher than that in the cold-rolled specimen. However, the influence of the number of rotations, i.e. introduced amount of plastic deformation, and processing temperature of HPT on the precipitation behavior of the alloy is still unclear. Further study is necessary to make a conclusive statement on this point.

Conclusions

An investigation of the microstructure and aging behavior of Cu-1.8wt%Be-0.2wt%Co alloy specimens processed by high-pressure torsion (HPT) at room temperature (RT) and 150°C after solution treatment has yielded the following conclusions:

(1) An ultrafine-grained structure with an average size of 70 nm is obtained through application of HPT process at RT and 150°C under an applied pressure of 5 GPa for 10 rotations.

(2) Microhardnesses of the alloy specimens processed at RT and 150°C (RT- and 150°C-specimens) increase with increasing strain, and saturated to a constant level of 400 and 430 Hv, respectively. It is suggested that the higher hardness of the specimen processed at 150°C is ascribed to the segregation of Be atoms on dislocations during HPT processing at 150 °C.

(3) Microhardnesses of the RT- and 150°C-specimens increase rapidly and reach maximum values at 3 min during aging at 320°C. This age hardening is caused by a fine dense dispersion of G.P. zones within ultra-fine grains.

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