Materials Transactions, Vol. 52, No. 8 (2011) pp. 1685 to 1688

RAPID PUBLICATION

Deformation of Cu-Be-Co Alloys by Aging at 593 K

T. Hasegawa[1,*1], Y. Takagawa[1,*2], C. Watanabe[2] and R. Monzen[2,*3]

[1]*Division of Mechanical Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan*
[2]*Division of Innovative Technology and Science, Kanazawa University, Kanazawa 920-1192, Japan*

The warping deformation along grain boundaries has been found for thin plates of Cu-1.8 mass%Be-0.2 mass%Co and Cu-1.8 mass%Be-0.2 mass%Co-0.03 mass%Mg alloys aged at 593 K for 3 h after cold rolling to 0% and 20% reduction, but not been detected for the two alloys aged at the same condition after cold rolling to 90% reduction, by surface roughness measurements. The aging produces γ' precipitates in grains and discontinuous precipitation (DP) cells at grain boundaries in the two alloys after 0% and 20% cold-rolling, but no DP cells in the alloys after 90% cold-rolling. The addition of Mg or the increase in cold-rolling rate decreases the width of DP cells, resulting in reduction in the degree of warping deformation. The warping deformation along grain boundaries can be attributed to the difference between the length changes of the DP cell and the grain interior by the aging. [doi:10.2320/matertrans.M2011057]

(Received February 17, 2011; Accepted May 6, 2011; Published June 22, 2011)

Keywords: *copper-beryllium alloy, warping deformation, discontinuous precipitation, magnesium addition*

1. Introduction

Cu-Be-Co alloys containing about 2.0 mass%Be and 0.2 mass%Co exhibit an excellent hardening through aging after solutionizing. The aged Cu-Be-Co alloys have the highest hardness, proof stress and tensile strength among Cu-base alloys, and possess high electrical and thermal conductivities. The alloys, therefore, are widely used for electrical connectors, mechanical parts and injection molds for plastics. The addition of a slight amount of Co to a Cu-Be alloy aims to suppress discontinuous precipitation (DP) reactions.[1)]

It is well known that shape and dimensional changes of thin Cu-Be-Co plates simultaneously occur on aging at about 600 K.[2,3)] Industrially, the shape change of thin plates is suppressed by cold rolling of the plates previous to aging.[3)] Watanabe *et al.*[4)] and Monzen *et al.*[5)] have performed length-change measurements for a Cu-1.8 mass%Be-0.2 mass%Co alloy aged at 593 K after solutionizing or solutionizing and subsequent cold-rolling to 90% reduction, and concluded that the length-change behavior of the Cu-Be-Co specimens during aging is well represented by the combination of expansion due to the depletion of solute Be in the Cu matrix and contraction due to the existence of precipitated phases. It may be easily imagined that the specimen shape change is closely related to the specimen length change. However, the cause for the shape change has not been clarified, as yet.

We have found that aging thin plates of a Cu-1.8 mass%Be-0.2 mass%Co alloy at 593 K for 3 h produces warping deformation along grain boundaries, and adding 0.03 mass%Mg to the alloy or cold rolling prior to aging suppresses formation of DP cells and, as a result, reduces the degree of the warping deformation. In this study, the obtained results of the finding will be reported.

*1 Graduate Student, Kanazawa University. Present address: Nachi-Fujikoshi Corp., Toyama 930-8511, Japan
*2 Graduate Student, Kanazawa University
*3 Corresponding author, E-mail: monzen@t.kanazawa-u.ac.jp

2. Experimental

Cu-1.8 mass%Be-0.2 mass%Co and Cu-1.8 mass%Be-0.2 mass%Co-0.03 mass%Mg alloys were prepared by melting in an Argon atmosphere. The cast alloys were homogenized at 1130 K for 24 h in a vacuum and then cold-rolled to a 50% reduction in thickness. The rolled strips were solutionized at 1073 K for 20 min in an Argon atmosphere and then quenched into water. The average grain size after the solution treatment was about 12 µm. The solutionized alloys were cold-rolled to a 0%, 20% and 90% reduction in thickness. Plate-like pieces with 0.25 mm in thickness were cut out from the specimens with and without rolling and then aged at 593 K for 3 h in a salt bath. Surface roughness measurements on the pieces unaged and aged were made by a laser microscope. Furthermore, length changes ε_T on aging were examined by measuring, with a micrometer, the distance between two scribed marks, about 15 mm apart for the Mg-added specimen pieces aged at 593 K for 3 h and at 773 K for 6 h. The length change is defined as $\varepsilon_T = (l - l_0)/l_0$, where l_0 and l are the length between the two marks before and after aging. The measurement accuracy of length change is in the order of 10^{-5} in strain. An X-ray analysis also was performed to examine the lattice parameters of the Mg-added pieces before and after aging at 593 K for 3 h and at 773 K for 6 h.

Transmission electron microscopy (TEM) was performed using a JEOL 2010FEF and a Hitachi H-9000NAR microscope at operating voltages of 200 kV and 300 kV, respectively. Thin foils for TEM observations were prepared using a twin-jet polishing method with a solution of 67% methanol and 33% nitric acid in volume fraction at 253 K and 5 V.

3. Results and Discussion

3.1 Hardness change

Figure 1 shows the hardness changes of Cu-1.8%Be-0.2%Co alloy specimens during aging at 593 K up to 10 h (3.6×10^4 s) after the solution treatment at 1073 K for 20 min and subsequent 0, 20 and 90% cold-rolling. For the rolling-free or 20%-rolled specimen, the hardness starts to steeply

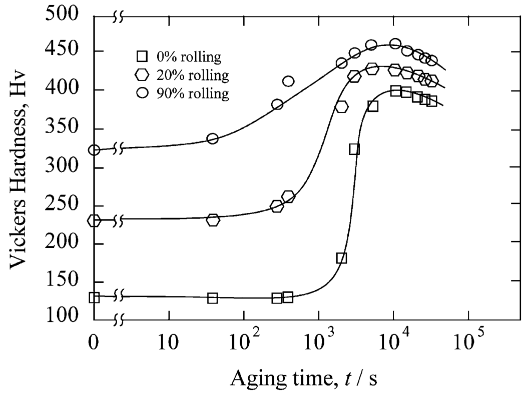

Fig. 1 Age-hardening curves of a Cu-1.8%Be-0.2%Co alloy aged at 593 K after 0%, 20% and 90% cold-rolling.

increase at about 15 or 10 min, exhibits a peak at about 3 h (1.08×10^4 s) or 2 h (0.72×10^4 s) and continues to decrease with further aging. For the 90%-rolled specimen, however, it gradually increases with increasing time and eventually attains a peak at about 3 h. It should be noted that the increase in cold-rolling rate from 0% to 20% decrease the time at which the peak hardness effect occurs, but the increase in rolling rate to 90% inversely increases the time. The increase in the time is caused by a different precipitation process in the 90%-rolled specimen, as will be shown later. The addition of 0.03%Mg to the Cu-Be-Co alloy did not significantly change the microhardness throughout the aging processes. Previous to this work, Miki *et al.*[3)] have showed that the time at which the peak hardness in a Cu-Be-Co alloy occurs decreases with increasing the rolling rate up to 60%.

Monzen *et al.*[6)] and Watanabe *et al.*[4)] have reported from high-resolution (HR) TEM observations that the precipitated phases in Cu-0.9%Be alloy single-crystals aged at 473 to 698 K[6)] and Cu-1.8%Be-0.2%Co alloy polycrystals aged at 593 K[4)] follow a G.P. zone $\rightarrow \gamma'' \rightarrow \gamma_I' \rightarrow \gamma_I + \gamma' \rightarrow \gamma$ sequence with aging time. The disk-shaped G.P. zones consist of monolayers of Be atoms on $\{100\}_\alpha$ of the Cu matrix and transform continuously to the γ_I phase via γ'' and γ_I'. These metastable phases are composed of alternative Be and Cu matrix layers parallel to $\{100\}_\alpha$. The γ' phase transforms successively to the equilibrium γ phase (CuBe intermetallic).

The present Cu-1.8%Be-0.2%Co-0.03%Mg alloy aged at 593 K after 0% and 20% cold-rolling showed nearly the same precipitation processes as the Cu-1.8%Be-0.2%Co alloy used in the previous study.[4)] The phases in the present alloys followed a G.P. zone $\rightarrow \gamma'' \rightarrow \gamma_I' \rightarrow \gamma_I + \gamma' \rightarrow \gamma$ sequence with aging time. The continuous transformation from the G.P. zones to the γ_I phase via γ'' and γ_I' in the rolling-free and 20%-rolled alloys did not cause a significant increase in the hardness (Fig. 1). In the previous and present studies, as soon as the metastable γ' phase heterogeneously precipitated on the γ_I phase under a high degree of Be supersaturation, it rapidly grew, resulting in a low supersaturation. Corresponding to the formation, rapid growth and coarsening of the γ' precipitates, the hardness for the rolling-free or 20%-rolled alloys began to rapidly increase on aging for about 15 or 10 min, eventually reached a peak at about 3 or 2 h and then decreased (Fig. 1). Figure 2(a) depicts plate-like γ' precipitates parallel to $(1\bar{1}\bar{2})_\alpha$ or $(1\bar{1}3)_\alpha$ of the Cu matrix in the Cu-Be-Co specimen aged at 593 K for 3 h after solutionizing.

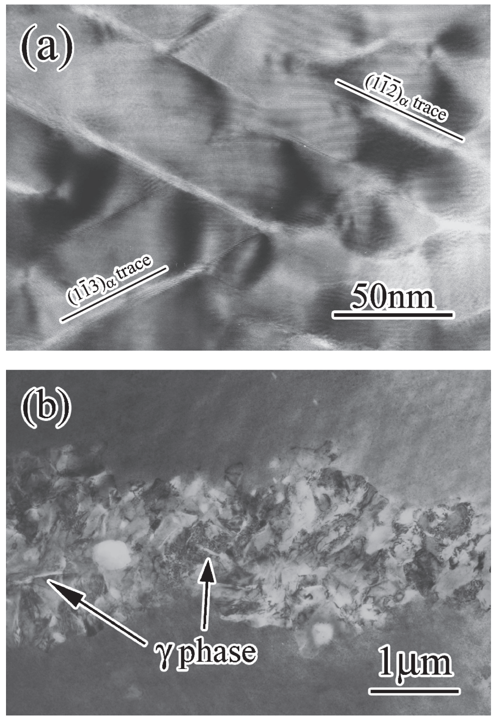

Fig. 2 TEM images of (a) γ' precipitates and (b) a DP cell in a Cu-1.8%Be-0.2%Co alloy aged at 593 K for 3 h after solutionizing. In (a), the zone axis is parallel to $[110]_\alpha$.

On the other hand, HRTEM observations by Monzen *et al.*[5)] of Cu-1.8%Be-0.2%Co specimens aged at 593 K for various periods after 90% rolling revealed complicated precipitation processes. This has been also confirmed for the Mg-added alloy. In the previous work,[5)] as a consequence of the promotion of formation of the G.P. zones by the introduction of dislocations by 90% rolling, the supersaturation of the Cu matrix decreased from the beginning of aging, and thus there coexisted only γ'' and γ_I' precipitates even after aging for 1 h. Aging the Cu-Be-Co alloy for 3 h produced mainly γ'', γ_I' and γ_I precipitates, the volume fraction of which was very large.[5)] The heterogeneous precipitation of γ' on γ_I was rarely noticed. The supersaturation of the Cu matrix in the alloy was already low after aging for 1 h and thus the heterogeneous formation and growth of γ' were suppressed.[5)] These observations have also held for the Mg-added alloy. These observations can explain the gradual increase in hardness with increasing aging time and subsequent attainment of a hardness peak at about 3 h for the 90%-rolled alloys (Fig. 1).

3.2 Warping deformation

Figures 3(a) and 3(b) depict the surface appearances of the Cu-Be-Co specimens unaged and aged at 593 K for 3 h after solutionizing and subsequent etching using a solution of water : ammonia water : hydrogen peroxide = 14 : 5 : 1 in volume ratio. The surface roughness profiles along the dotted lines in Figs. 3(a) and 3(b) are also shown at the lower sides. The aging at 593 K for 3 h induces marked unevenness on the surface. The values of the maximum height in Figs. 3(a) and

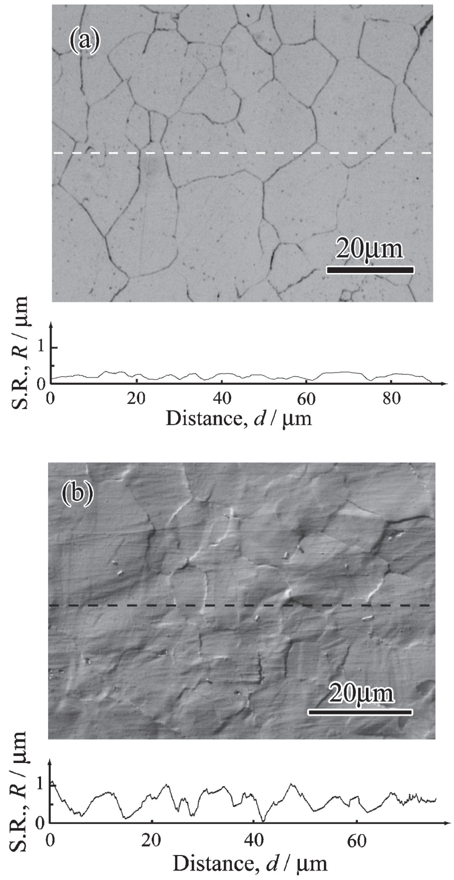

Fig. 3 Optical micrographs showing the surface appearances of a Cu-1.8%Be-0.2%Co alloy (a) unaged and (b) aged at 593 K for 3 h. Also shown are the surface roughness (S. R.) profiles along the dotted lines in (a) and (b).

3(b) are about 0.4 μm and 1.1 μm, respectively. It should be noted in Fig. 3(b) that warping deformation occurs generally at the intersections of the dotted line with the grain boundaries. The warping deformation along the grain boundaries on aging was noticed for the Cu-Be-Co and Mg-added alloys with and without 20% rolling. For the 90%-rolled alloys, however, no grain boundaries were detected before and after aging. In addition, as recognized in Fig. 4, the maximum height values for the 90%-rolled alloys were about 0.4 μm even after aging which is identical to the value of about 0.4 μm for the aging-free alloys (Fig. 3(a)). Thus it is judged that the 90%-rolled alloys exhibit no warping deformation along grain boundaries on aging. Table 1 summarizes the values of the maximum height for the Cu-Be-Co and Cu-Be-Co-Mg specimens aged at 573 K for 3 h after 0%, 20% and 90% rolling. The values of the maximum height before aging are also shown in parentheses. Surface roughness measurements were about 5 times carried out for each specimen. For example, the average values of the maximum height before and after aging the rolling-free Cu-Be-Co specimen were measured as 1.2 ± 0.2 μm and 0.4 ± 0.1 μm, respectively. The addition of Mg or the increase in cold-rolling rate decreases the maximum height, namely, the level of warping deformation. The latter result corresponds to the fact that industrially the shape change of Cu-Be-Co plates caused by aging is suppressed by cold rolling of the plates prior to aging.[3)]

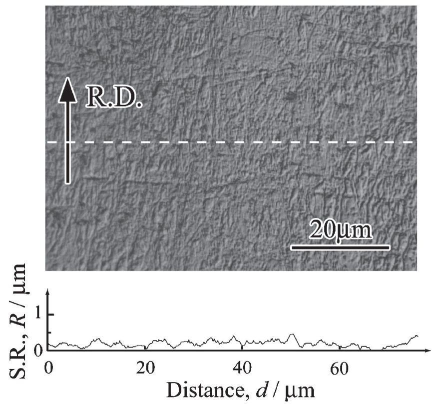

Fig. 4 Optical micrograph showing the surface appearance of a Cu-1.8%Be-0.2%Co alloy aged at 593 K for 3 h after cold rolling to 90% reduction. Also shown is the surface roughness (S. R.) profile along the dotted line. R. D. = rolling direction.

Table 1 Values of the maximum height, obtained from surface roughness measurements for Cu-1.8%Be-0.2%Co and 0.03%Mg-added alloys aged at 593 K for 3 h after 0%, 20% and 90% cold-rolling. Also shown are those of the maximum height before aging in parentheses.

Specimen	Maximum height (μm)		
	0%	20%	90%
Cu-Be-Co	1.2 (0.4)	0.7 (0.4)	0.4 (0.4)
Cu-Be-Co-Mg	1.0 (0.4)	0.6 (0.4)	0.4 (0.4)

Table 2 Values of the width of DP cells in Cu-1.8%Be-0.2%Co and 0.03%Mg-added alloys aged at 593 K for 3 h after 0%, 20% and 90% cold-rolling.

Specimen	Cell width (μm)		
	0%	20%	90%
Cu-Be-Co	2.8	1.7	—
Cu-Be-Co-Mg	1.1	0.5	—

Chiba *et al.*[7)] have shown the presence of DP cells at grain boundaries in an under-aged Cu-1.91%Be-0.21%Co alloy industrially produced. In the rolling-free and 20%-rolled alloys aged at 593 K for 3 h, DP cells also were observed at grain boundaries as exemplified in Fig. 2(b). The DP cell is composed of lamellae of the equilibrium γ phase and solute-depleted α phase (Cu-rich solid solution). In the 90%-rolled alloys, however, no DP cells were formed. Table 2 lists the values of the average width of cells in the Mg-free and -added specimens aged at 573 K for 3 h after 0%, 20% and 90% rolling. Although the addition of Mg or the increase in cold-rolling rate decreased the cell width, it did not significantly change the size and volume fraction of γ precipitates in cells. The decrease in cell width by the Mg addition is in agreement with the report by Monzen *et al.*[8)] that the addition of a small amount Mg to a Cu-1.8%Be-0.21%Co alloy suppresses formation of DP cells. The strength of cells is evidently lower than that of in-grains, since the γ precipitates in cells are much coarser than the γ' precipitates in grains as seen in Figs. 2(a) and 2(b). It may thus be expected that the decrease in cell width by the addition of Mg or by the increase in cold-rolling rate leads to reduction in the level of warping deformation. This holds true as revealed in Tables 1 and 2.

Table 3 Values of the length change for Cu-1.8%Be-0.2%Co[4,9] and 0.03%Mg-added specimens containing γ' precipitates in grains on aging at 593 K for 3 h after 0% and 20% rolling, and for Cu-Be-Co[4,9] and Mg-added specimens composed of DP cells containing γ precipitates on aging at 773 K for 3 h and 6 h, respectively, after 0% and 20% rolling.

Specimen	Precipitate	Length change ($\times 10^{-3}$)	
		0%	20%
Cu-Be-Co	γ'	−1.9	−2.0
	γ	−1.2	−1.1
Cu-Be-Co-Mg	γ'	−1.9	−1.9
	γ	−1.0	−1.0

As mentioned above, aging the Cu-Be-Co and the Mg-added specimens at 593 K for 3 h after 0% and 20% cold-rolling produces γ' precipitates in grains and DP cells at grain boundaries which contain γ precipitates. Watanabe *et al.*[4] have carried out length-change measurements for Cu-1.8%Be-0.2%Co alloy polycrystals aged at 593 and 773 K after solutionizing. The length change of the alloy aged at 593 K exhibits a decrease from about 30 min and a constant value from about 3 h. The contraction is caused by precipitation of the γ' phase. The length change of the alloy aged at 773 K also shows a gradual decrease with the proceeding DP reaction and a constant value from about 2 h. However, these constant values of length change are different from each other (Table 3). It may thus be predicted that such a difference in length change between the DP cell and the in-grain which contains the γ' phase is closely related to the occurrence of the warping deformation along grain boundaries.

Table 3 lists the values of the length change for the solutionized Cu-1.8%Be-0.2%Co[4,9] or 0.03%Mg-added specimens on aging at 593 K for 3 h after 0% and 20% rolling, and the Cu-Be-Co[4,9] or Mg-added specimens entirely covered with DP cells on aging at 773 K for 3 or 6 h after 0% and 20% rolling. The addition of Mg or the increase in rolling rate does not significantly affect the values of the length change, but the values for the specimens containing the γ' precipitates in grains are different from those for the specimens composed of DP cells containing the γ precipitates. In principle, the specimen length change by aging is the sum of expansion based on the loss of Be solute atoms in the Cu matrix and contraction due to the existence of γ' precipitates in grains or γ precipitates in cells.[4] The γ' and γ phases have different negative misfit strains.[4] The amount of the specimen contraction depends on the misfit strains and the volume fraction of the γ' and γ phase. The addition of Mg or the increase in rolling rate did not essentially influence the volume fraction of the γ' phase in grains and the γ phase in cells, and the expansion due to the loss of Be solute atoms, estimated from the lattice parameters before and after aging following 0% and 20% rolling in the previous[4,9] and present studies. As a result, the addition of Mg or the increase in rolling rate does not significantly affect the specimen length change. The difference in length change between the specimens containing the γ' or γ precipitates in Table 3 is mainly based on the difference between the misfit strains of γ' and γ.[4] In principle, length changes of a DP cell and an in-grain adjacent to the cell by the aging at 593 K for 3 h in this study are identical to those of the specimens containing the γ and γ' precipitates in Table 3. Moreover, the strength of cells is lower than that of in-grains as described before. Therefore it is concluded that the difference in length change between the DP cell and the in-grain brings about the warping deformation along grain boundaries.

4. Conclusions

(1) Cu-1.8%Be-0.2%Co and Cu-1.8%Be-0.2%Co-0.03%Mg alloys aged at 593 K after 0%, 20% or 90% cold-rolling show nearly the same age-hardening behavior. When aged at 593 K after 0% or 20% cold-rolling, the hardness starts increasing rapidly after a time and reaches a maximum at 3 h or 2 h, whereas in case of 90% cold-rolling, it exhibits a gradual increase with increasing time and attains a peak at a relatively long time of 3 h.

(2) Surface roughness measurements of thin plates of the two alloys aged at 593 K for 3 h after cold rolling to 0% and 20% reduction reveal the occurrence of warping deformation along grain boundaries. However, the warping deformation is not detected for the two alloys aged at the same condition after 90% rolling.

(3) γ' precipitates in grains and discontinuous precipitation (DP) cells at grain boundaries are formed in the two alloys with and without 20% cold-rolling prior to aging at 593 K for 3 h, but no DP cells are produced in the 90%-rolled alloys.

(4) The addition of Mg or the increase in cold-rolling rate brings about reduction in the width of DP cells and, as a result, decreases the amount of warping deformation. The difference between the dimensional changes of the DP cell and the in-grain by the aging contributes to the warping deformation along grain boundaries.

Acknowledgement

A part of this work was conducted in the Kyoto-Advanced Nanotechnology Network, supported by the "Nanotechnology Network" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES

1) D. B. Williams and E. P. Butler: Int. Met. Rev. **26** (1981) 153–183.
2) K. Murakawa and T. Ota: J. JRICu **17** (1978) 89–91.
3) M. Miki, K. Morita, S. Ishikawa, Y. Natsume and K. Suzuki: J. JRICu **38** (1999) 139–146.
4) C. Watanabe, T. Sakai and R. Monzen: Phil. Mag. A **88** (2008) 1401–1410.
5) R. Monzen, T. Hasegawa and C. Watanabe: Phil. Mag. Lett. **89** (2009) 75–85.
6) R. Monzen, T. Seo, T. Sakai and C. Watanabe: Mater. Trans. **12** (2006) 2925–2934.
7) H. Chiba, N. Muramatsu and M. Takeda: J. JRICu **45** (2006) 76–80.
8) R. Monzen, T. Hosoda, Y. Takagawa and C. Watanabe: J. Mater. Sci. **46** (2011) 4284–4289.
9) T. Sakai: Master Thesis, Kanazawa University (2007).