Microstructural and mechanical stability of Cu-6 wt. % Ag alloy

M. S. LIM, J. S. SONG, S. I. HONG
Department of Metallurgical Engineering, Chungnam National University, Taedok Science Town, Taejon 305-764, South Korea
E-mail: sihong@cnu.ac.kr

The microstructural and mechanical stability of Cu-6 wt. % Ag alloy obtained by cold rolling combined with intermediate heat treatments have been investigated. The stress-strain responses and fracture behavior of Cu-6 wt. % Ag alloy were examined and correlated with the microstructural change caused by thermo-mechanical treatments. The deformation bands stabilized by silver precipitates were observed in heavily rolled Cu-6 wt. % Ag alloy. The highly deformed microstructure stabilized by silver filament was observed to be unstable at temperatures above 200°C. The strength of Cu-6wt.%Ag alloys were found to decrease remarkably if they were heat-treated above 300°C. The fracture surfaces of Cu-Ag two phase alloys showed typical ductile type fracture. The electrical conductivity did not change appreciably up to the aging temperature of 200 °C and increased rapidly at temperatures above 300°C. The increase of the conductivity and the decrease of the strength can be associated with the microstructural coarsening of heavily deformed linear band structure. The difference of the UTS and the conductivity between the rolling direction and the direction perpendicular to the rolling direction (on the rolling plane) were found to be relatively small.

1. Introduction

Cu-based two-phase composites including Cu-Nb, Cu-Cr and Cu-Ag are of great interest for a wide range of electrical applications because of the outstanding combinations of high strength and electrical and thermal conductivity [1–10]. One of the most demanding applications is for windings of pulsed high-field magnets. The conductor material is required to have high strength to resist electromagnetic forces occurring at high fields and to be highly conductive to suppress Joule heating. The Cu-Ag alloys of most interest for such applications are those containing more than about 20 wt. % Ag, where a second phase (Ag) lamellae and/or filaments appear in addition to the Cu matrix phase [1–3]. Values of ultimate tensile strength and conductivity for these microcomposites depend upon the composition, degree of cold work and intermediate annealing schedules [1–3, 9, 10]. The more general application and use of Cu-Ag two phase alloys are limited by the high cost of the alloys. Recently, the mechanical and electrical properties of the two phase Cu-Ag alloys were found to be improved by the optimization of thermomechanical processing [1–3, 9, 10]. The present study has been carried out to examine the possible ways to improve the physical properties of Cu-Ag alloys with lower silver content. The mechanical and microstructural stability of Cu-6wt.%Ag alloy were examined and correlated with the microstructural change caused by thermo-mechanical treatments.

2. Experimental methods

Electrolytic copper and silver with a purity of 99.9% were used as starting materials. Cu-6wt.%Ag alloy was cast by a vaccum induction melting. Ingots were cold rolled to 0.5 mm (rolling ratio = 98.5%) and 0.3 mm (rolling ratio = 99%) thickness with intermediate heat treatments. Heat treatments during the cold working process were performed between 400–500°C for 1–2 h. Intermediate heat treatments were carried out at the rolling ratio of 40% and 75%. Then, half of the samples were rolled to the final thickness without further heat treatment (IH-2) and the other half were rolled to the final thickness with another intermediate heat treatment at 95% (IH-3). In order to examine the microstructural and mechanical stability after heavy deformation, rolled Cu-6 wt. % Ag alloy sheets were heat treated at 100°C, 200°C, 300°C and 400°C for 1 hr. Longitudinal and transverse sections (perpendicular to the rolling plane) were observed using scanning electron microscope (SEM).

The evaluation of mechanical properties was carried out by tensile testing using a United machine (SFM-10) equipped with an extensometer for accurate strain measurements. All tensile tests were performed at room temperature using a strain rate of 5.5×10^{-4} s^{-1}. In order to examine the effect of the orientation on the mechanical properties, tensile samples were cut in two orientations (parallel and perpendicular to the rolling direction on the rolling planes). The evolution of the microstructure was examined by scanning electron microscope and transmission electron microscope (TEM). TEM specimens parallel to the rolling plane were prepared by double jet-thinning technique. Fracture surfaces of the tensile specimens were examined in a SEM to characterize the fracture behavior. Electrical resistivity measurements were made using a standard four-probe technique.

3. Results and discussion

Fig. 1A and B show the longitudinal and transverse sections of as-rolled Cu-6 wt. % Ag alloy with three intermediate heat treatments (IH-3). Fig. 1C shows the three dimensional view of as-rolled Cu-Ag sheet (IH-3). The microstructure of two intermediate heat treatments (IH-2) was quite similar to that of IH-3 and will not be shown here. As-rolled microstructure in the longitudinal section appeared highly elongated and continuous. It is quite interesting to observe that the fine microstructure was stabilized in Cu-6wt.%Ag alloy. Actually, the highly elongated microstructure of Cu-6wt.%Ag alloy of the present study appears to be quite similar to that of eutectic Cu-72wt.%Ag alloy with fine silver filaments (see Fig. 4b of Ref. 1). Fig. 2a and b show the EDS spectra from the white and black lines in Fig 1A respectively. EDS spectra as in Fig. 2 showed that silver content in the linear white markings are higher than that in the black area between linear white markings, supporting that silver atoms are segregated along the linear white markings. It is impossible to obtain the exact silver content in linear white markings since the electron beam and specimen interaction volume is much larger than the beam diameter. However it is safe to conclude that silver content in linear white markings is higher than that in the black area between linear white markings. These linear white markings in the transverse section (Fig. 1B) are rather discontinuous. Since the maximum solubility of Ag in Cu is about 7.35 wt.% at high temperatures, the volume fraction of the second phase in Cu-6 wt. % Ag alloy would be very small if there is any [1, 11]. The linear bands parallel to the rolling direction in Fig. 1 are thought to be deformation bands [12–15] stabilized by silver atoms, not silver filaments as in eutectic Cu-Ag alloy. Another interesting observation in Fig. 1A was the presence of shear bands (indicated by arrows) inclined to the rolling plane [12–15].

Fig. 3 shows TEM micrograph and selected area diffraction pattern of as-rolled Cu-6 wt. % Ag alloy parallel to the rolling plane. Linear defects in Fig. 3A appear to be quite similar to the grain boundary phase (GBP) observed in Cu-Zr alloys by Singh *et al.* [16]. Singh *et al.* reported that GBP is rich in zirconium and exhibited fine planar defects in Cu-Zr. In Fig. 3B, the selected area diffraction pattern from the area shown in Fig. 3A indicated the presence of silver phase. The presence of silver was also confirmed by EDS analysis. Silver atoms are likely to be preferentially precipitated in deformation band walls (which are parallel to the TEM foil) like the zirconium rich phases (GBP) at grain boundaries in Cu-Zr.

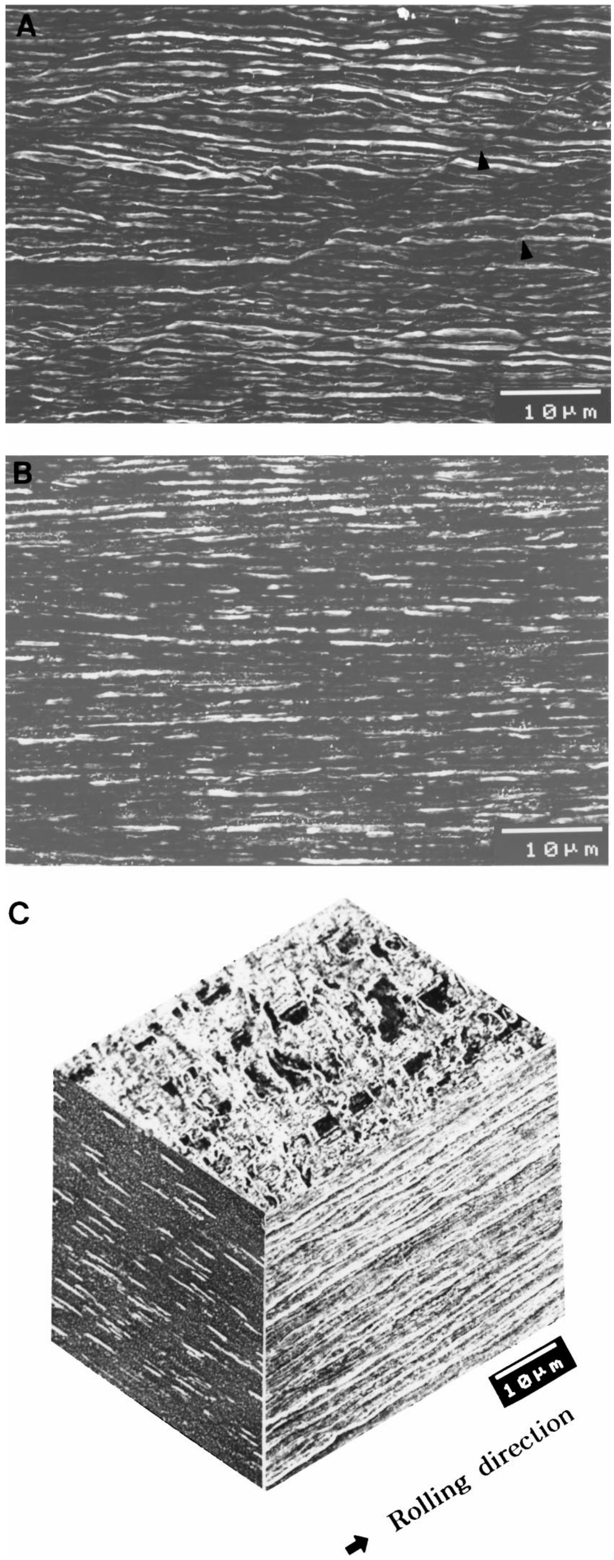

Figure 1 SEM Micrographs of as-rolled Cu-6 wt. % Ag alloy with three intermediate heat treatments (IH-3). Longitudinal (A), transverse (B) sections and three dimensional view (C).

The change of the microstructure was found to be insignificant after heat treatment at 200°C. Fig. 4 shows the microstructure of Cu-6 wt. % Ag alloy (IH-3) heat treated at 400°C for 1 hr. At 400°C, the morphological instability due to break-up of linear band structure was observed. The highly deformed microstructure stabilized by silver atoms may be unstable at temperatures above 200°C because of the increase of the

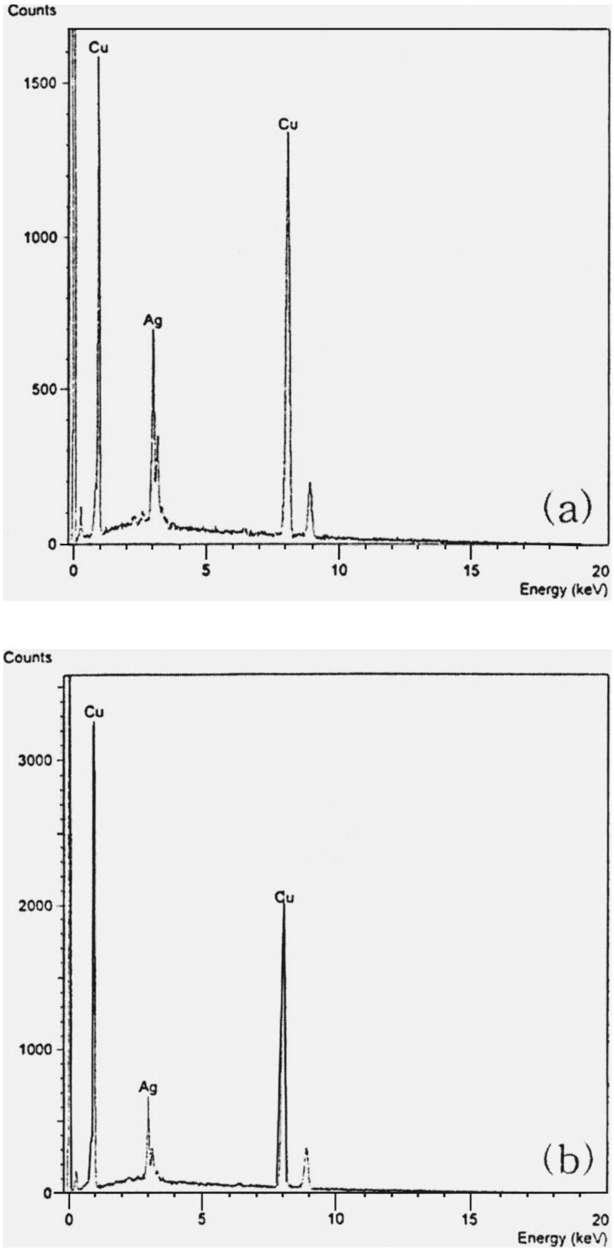

Figure 2 EDS spectra from linear white markings (a) and black areas (b).

diffusivity of silver atoms [2]. The morphological instability observed in this study is consistent with the observation on Cu-24 wt. % Ag in which heavily drawn silver filaments spheroidized at 300°C [2]. This suggestion is compatible with the observation of Hong *et al.* [2, 3] that the stability of the second phase filaments is strongly dependent on the interfacial diffusivity of solute atoms. The observation on the break-up of heavily deformed linear band at 400°C strongly supports that the highly deformed linear band structure in as-rolled sheets is indeed pinned by silver atoms. Heavily deformed structure may degenerate into more stable microstructure if the mobility of silver atoms and instability of linear bands increase at high temperatures.

Fig. 5 shows the stress-strain responses of as rolled and annealed Cu-6 wt. % Ag alloy (IH-3). There was negligible work hardening for Cu-6 wt. % Ag alloy. The total strain to failure was reduced after annealing at 100 and 200°C. The reduction of ductility at 100 and 200°C was associated with a slight increase in UTS.

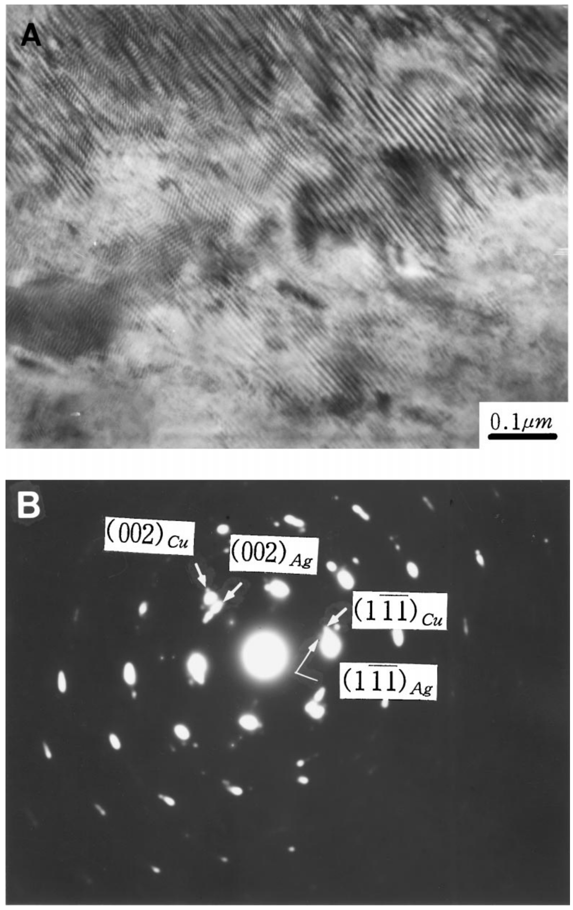

Figure 3 TEM Micrograph and selected area diffraction pattern of Cu-6Ag (IH-3) heat treated at 200 °C. Longitudinal (A) and transverse (B) sections.

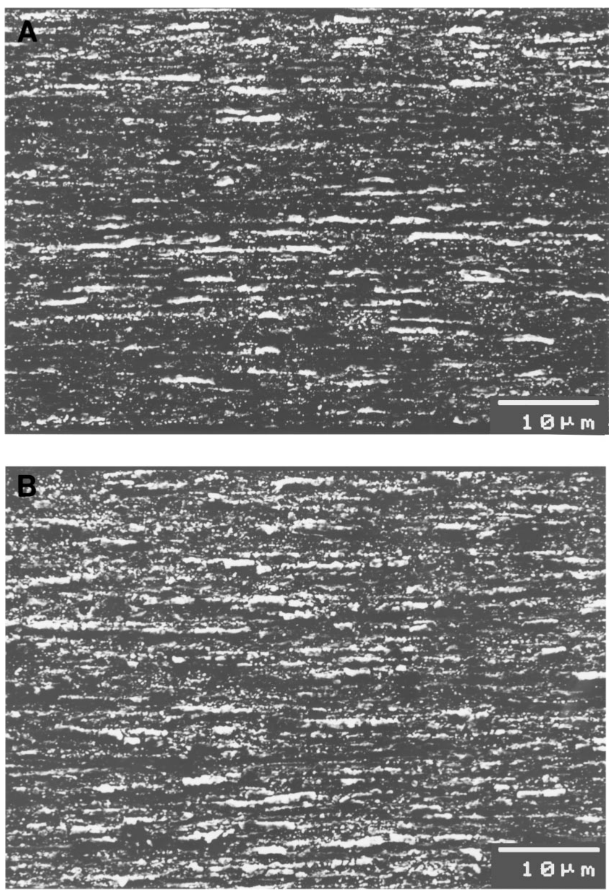

Figure 4 SEM Micrographs of Cu-6Ag (IH-3) heat treated at 400 °C. Longitudinal (A) and transverse (B) sections.

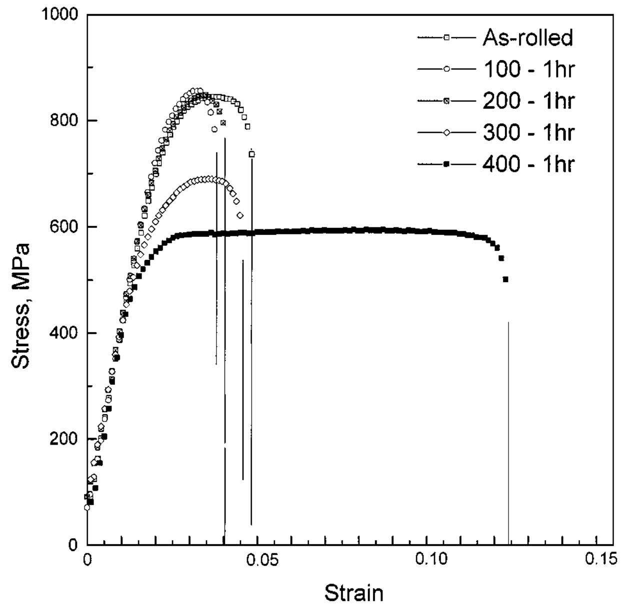

Figure 5 Stress-strain responses of as rolled and annealed Cu-6 wt. % Ag alloy (IH-3).

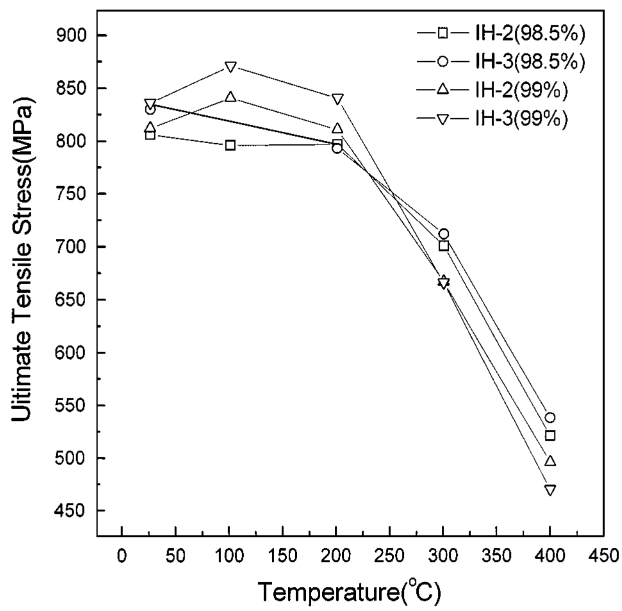

Figure 6 Variation in ultimate tensile strength of Cu-6 wt. % Ag alloys (IH-2 and IH-3) after annealing.

Fig. 6 shows the variation in ultimate tensile strength of Cu-6 wt. % Ag alloys (IH-2 and IH-3) after the heat treatment at 100°C, 200°C, 300°C and 400°C for 1 hr. It is seen that slight increase of the strengthening was obtained by aging at 100°C, and above 300°C, the strength levels fell rapidly. This observation is consistent with that of Benghalem and Morris [1] on Cu-6 wt.% Ag wires. The slight increase of ultimate tensile stress of Cu-6 wt.% Ag alloy heat treated at low temperatures suggests that some silver precipitated during heat treatment at low temperatures as suggested by Hong and Hill [2]. They [2] also observed the slight increase of the strength in Cu-24wt.%Ag microcomposites heat treated at 100 and 200°C. They also suggested that the significant decrease of the ductility by aging in the 100–200°C range was promoted by the presence of shearable precipitates. As shown in Fig. 6, the strength of the as-rolled Cu-6 wt. % Ag increased by 50–60 MPa with increasing rolling ratio from 98.5 to 99%. However, the strength of Cu-6 wt. % Ag alloy with higher rolling ratio (99%) dropped more rapidly at higher aging temperatures (above 250°C) and became lower than that of Cu-6 wt. % Ag alloy with lower rolling ratio (98.5%). This observation suggests that the driving force for microstructural change is higher in Cu-6 wt. % Ag alloy with higher rolling ratio, resulting in softer microstructure with lower internal energy.

The tensile strength of Cu-6 wt. % Ag (830 MPa) with lower rolling ratio (98.5%) in the present study was found to be smaller than that of Cu-24 wt. % Ag (924 MPa). However, the difference is relatively small. Since the deformation band structure was observed in Cu-6 wt. % Ag alloy, the strength can be determined by the spacing between deformation band walls and described by the following Hall-Petch equation:

$$\sigma = \sigma_0 + k\lambda^{-1/2} \tag{1}$$

where σ_0 is the intrinsic friction stress, k is the Hall-Petch coefficient, and λ is the spacing between the filaments. The intrinsic friction stress, σ_0, may be negligible compared to Hall-Petch strengthening and the coefficient k was reported to be 0.3 MN/m$^{3/2}$ for the heavily drawn Cu-Ag filamentary structure [2]. The spacing between deformation band walls were reported to be 0.2 μm in Cu [12–15], which is comparable with the width shown in Fig. 1. The strength component due to the band structure ($k\lambda^{-1/2}$) from Equation 1 was calculated to be 671 MPa, which is close to the observed yield stress (715 MPa). The difference may be associated with the friction stress due to alloying elements in copper matrix between deformation band walls.

Fig. 7 shows the variation in electrical conductivity of Cu-6 wt. Ag alloy as a function of aging temperature. The electrical conductivity did not change appreciable up to the aging temperature of 200°C and increased rapidly at temperatures above 250°C. The temperature

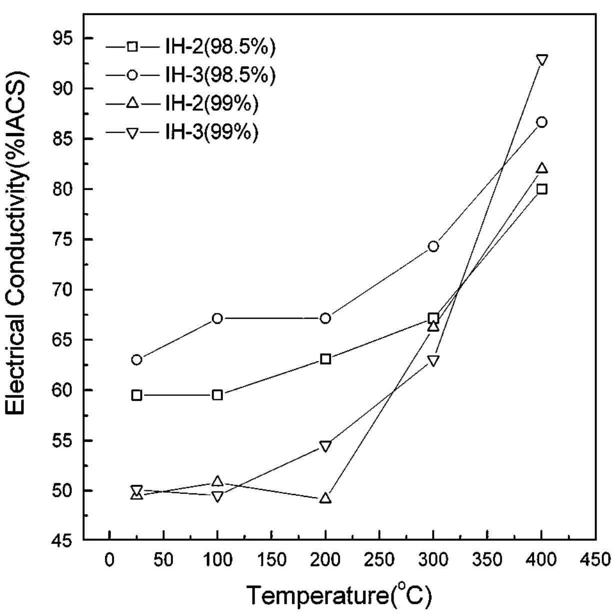

Figure 7 Variation in electrical conductivity of Cu-6 wt. Ag alloy as a function of aging temperature.

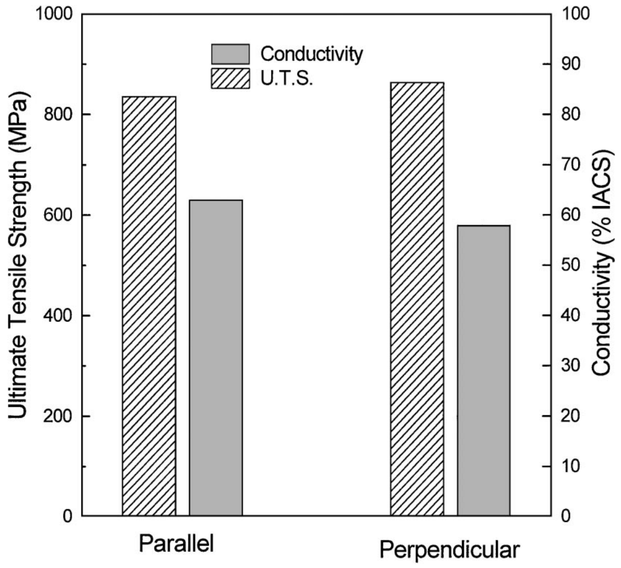

Figure 8 UTS and conductivity parallel and perpendicular to the rolling direction.

range where the conductivity began to increase coincides quite closely with that where the strength began to drop rapidly. The increase of the conductivity and the decrease of the strength can be associated with the microstructural coarsening and break-up of highly deformed linear band structure as shown in Fig. 4. The conductivity of as-rolled Cu-6 wt.% Ag alloy dropped appreciably with increasing rolling ratio as shown in Fig. 8. Again, the conductivity of Cu-6 wt. % Ag alloy with higher rolling ratio (99%) increased more drastically at higher aging temperature. The effects of the orientation on the UTS and the conductivity are shown in Fig. 8. It is interesting to note that the differences of the UTS and the conductivity between the rolling direction and the direction perpendicular to the rolling direction (on the rolling plane) are relatively small. Since the slab-like deformation band structure [17, 18] is approximately parallel to the rolling plane, deformation bands stabilized by Ag atoms can act as effective barriers irrespective of the off-axis angle from the rolling direction (on the rolling plane), supporting the insignificant effect of the orientation on the UTS. In the same way, the effect of the band structure on the electron scattering would not change much with orientation on the rolling plane since the slab-like band structure is approximately parallel to the rolling plane.

Cu-6 wt. % Ag alloy exhibited highly ductile fracture. The fracture morphology did not change noticeably up to the aging temperature of 200°C. Above 300°C, the dimple size, however, increased and coarsened as the aging temperature increases. The increase of the dimple size can be associated with the the microstructural coarsening at higher temperatures.

4. Conclusions

Based on a study of microstructural and mechanical stability in Cu-6 wt. % Ag alloy, the following conclusions can be drawn.

1. The deformation bands were found to be stabilized by silver precipitates. The highly deformed microstructure stabilized by silver precipitates was observed to be unstable at temperatures above 200°C due to increasing solubility and diffusivity of silver atoms.
2. The strength of Cu-6wt.%Ag alloys were found to decrease remarkably if they were heat-treated above 300°C. The drop of the strength can be associated with the morphological instability due to break up of linear band structure.
3. The reduction of the ductility heat treated at or below 200°C can be linked with the precipitation of small shearble precipitates precipitated during heat treating. The strain localization is enhanced by the presence of shearable precipitates, resulting in low ductility.
4. The electrical conductivity did not change appreciable up to the aging temperature of 200°C and increased rapidly at temperatures above 300°C. The increase of the conductivity can be associated with the microstructural coarsening of heavily deformed linear band structure.
5. The difference of the UTS and the conductivity between the rolling direction and the direction perpendicular to the rolling direction (on the rolling plane) were found to be relatively small.

Acknowledgement

The authors acknowledge the support from the Korea Science and Engineering Foundation (971-0803-034-2).

References

1. A. BENGHALEM and D. G. MORRIS, *Acta Mater.* **45** (1997) 397.
2. S. I. HONG and M. A. HILL, *ibid.* **46** (1998) 4111.
3. S. I. HONG, M. A. HILL, Y. SAKAI, J. T. WOOD and J. D. EMBURY, *Acta Metall. Mater.* **43** (1995) 3313.
4. S. I. HONG and M. A. HILL, *Mater. Sci. Eng.* **A264** (1999) 151.
5. S. I. HONG, *Scripta Mater.* **39** (1998) 1685.
6. J. D. VERHOEVEN, L. S. CHUMBLEY, F. C. LAABS and W. A. SPITIZIG, *Acta Metall. Mater.* **39** (1991) 2825.
7. U. HANGEN and D. RAABE, *ibid.* **43** (1995) 4075.
8. P. D. FUNKENBUSCH and T. H. COURTNEY, *Metall. Trans.* **18** (1987) 1249.
9. Y. SAKAI and H. J. SCHNEIDER-MUNTAU, *Acta Mater.* **45** (1997) 1017.
10. Y. SAKAI, K. INOUE and MAEDA, *Acta Metall. Mater.* **43** (1995) 1517.
11. Y. SAKAI, K. INOUE, T. ASANO, H. WADA and H. MAEDA, *Appl. Phys. Lett.* **59** (1991) 2965.
12. D. KUHLMANN-WILSDORF, *Acta Mater.* **47** (1999) 1697.
13. S. S. KULKARNI, E. A. STARKE JR. and D. KUHLMANN-WILSDORF, *ibid.* **46** (1998) 5283.
14. M. HATHERLY and A. S. MALIN, *Metal Technol.* **7** (1979) 308.
15. A. KORBEL, J. D. EMBURY, M. HATHERLY, P. L. MARTIN and H. W. ERBSLOH, *Acta Metall.* **34** (1986) 1999.
16. R. P. SINGH, A. LAWLEY, S. FRIEDMAN and Y. V. MURTY, *Mater. Sci. Eng.* **A145** (1991) 243.
17. C. S. LEE and B. J. DUGGAN, *Acta Metall. Mater.* **41** (1993) 2691.
18. C. S. LEE, B. J. DUGGAN and R. E. SMALLMAN, *ibid.* **41** (1993) 2265.

Received 26 August 1999
and accepted 22 February 2000