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Deformation processing and strength/conductivity properties of Cu–Fe–Ag microcomposites

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Abstract

Thermo–mechanical treatment was employed in this study to optimize the strength and conductivity of Cu–Fe–Ag microcomposites. The strength/conductivity properties of Cu–Fe–Ag microcomposites drawn to $\eta = 4.8$ without intermediate heat treatments (NH) were observed to be 1006 MPa/39% IACS and those drawn to $\eta = 6.3$ with three intermediate heat treatments (IH-3) were 939 MPa/56.2% IACS. A substantial increase of conductivity was obtained at the expense of a modest loss of the strength by the employment of intermediate heat treatments. The precipitation of impurities and alloying elements during intermediate heat treatment is thought to increase the conductivity due to the reduced impurity scattering. The activation volume was measured to be $170b^3$ for the as-drawn Cu–Fe–Ag (IH-2). Numerous particles were observed in Cu matrix and the spacing between these particles (∼30 nm) were found to be comparable to the activation length ($170b = 43$ nm). The most probable rate controlling mechanism of Cu–Fe–Ag microcomposites is suggested to be the interaction between dislocations and precipitates in Cu matrix.

Keywords: Cu–Fe; Deformation processing; Microstructure; Strength; Electrical conductivity

1. Introduction

The microstructural development and strengthening mechanism of deformation processed Cu based microcomposites incorporating a body centered cubic (bcc) phase have been the subjects of extensive studies [1–22]. Deformation during cold working leads a fine two-phase microstructure with strong crystallographic textures [1–9,13–15,19,22]. The strength of heavily deformed Cu base microcomposites exceeds that predicted by the rule of mixtures (ROM), and a fundamental understanding of the strengthening mechanisms has been the subject of much discussion [1–3,10,12,14,16]. The particularly attractive feature of these microcomposites is the combination of high strength plus high electrical and thermal conductivity. The conductivity of the copper is not greatly reduced by the addition of alloying elements such as Nb, Mo, W and Cr [2–4,20]. The Cu–Fe system has attracted the interest of some investigators because of the relatively low cost of iron compared to the other possible insoluble bcc phase. However, the slow precipitation of iron dissolved during processing is known to reduce the electrical conductivity [21,22].

Recently, thermal/mechanical treatments [17,18,21,22] have been employed to find a way to improve the strength/conductivity properties. Intermediate heat treatment during deformation processing was found to be useful for the optimization of the strength and conductivity of Cu base microcomposites. The precipitation of impurities and alloying elements during intermediate heat treatment was suggested to increase the conductivity due to the reduced impurity scattering [18,19,21,22]. It was also suggested that the size and distribution of filaments can be affected by thermo–mechanical processing incorporating intermediate heat treatment

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[18,21–23]. Hong and coworkers [17,18,21,22] investigated the effect of the third alloying element on the microstructure and the physical properties of Cu–Fe microcomposites. They found that the conductivity can be improved by the introduction of intermediate heat treatments in Cu–Fe microcomposites [17–19,21,22]. Since the addition of silver was found to refine the microstructure and increase the strength of Cu–Fe microcomposites effectively [22], attractive combination of strength/conductivity properties can be obtained in Cu–Fe–Ag microcomposites. In this study, the effect of thermo–mechanical processing on the physical properties of Cu-9 wt.% Fe-1.2 wt.%Ag microcomposites was examined.

2. Experimental

Billets of Cu-9 wt.% Fe-1.2 wt.% Ag (Cu-10 vol.% Fe-1 vol.% Ag) were prepared by induction melting in air. Cylindrical billets were about 60 mm in diameter and about 112 mm in length. Extrusion of cylindrical billets was carried out at 500 °C, reducing the billets from 60 to 24 mm in diameter. The extruded rods were then rod rolled to 6 mm in a series of steps and subsequently drawn into wires, using successively smaller dies, to a minimum diameter of 2 mm. While drawn to 2 mm diameter wires, some part of wires were annealed twice at 450 °C (IH-2) and some of them were drawn without intermediate heat treatments (NH). Some 2 mm diameter wires with two intermediate heat treatments (IH-2) were annealed at 450 °C and further drawn to a diameter of 1 mm (IH-3). The cold drawing strain η after high temperature extrusion is 4.8 and 6.2 for 2 and 1 mm diameter wires, respectively, where $\eta = \ln (A_0/A)$ and A_0 and A are the original and final cross-sectional areas, respectively.

The evaluation of mechanical strength of wires was carried out on a tensile testing machine equipped with an extensometer using specially designed wire grips for 1 mm diameter wires. At least 30 mm long wires were needed to wind the wires along the round-shaped grips for mechanical testing was possible to evaluate the strength of 1 mm diameter wires. For 2-mm wires, the tensile samples with a gage length of 20 mm were machined and the regular grips were used. All tensile test at constant strain rates were performed at room temperature using a strain rate of $5.5 \times 10^{-4}\,\mathrm{s}^{-1}$. For the measurement of activation volumes, the strain rate jump tests were performed from the strain rate of 1×10^{-4} to $1 \times 10^{-2}\,\mathrm{s}^{-1}$. Hardness was also measured with a load of 300 g using a Vickers microhardness tester. TEM specimens were prepared by mechanical thinning and ion milling on a liquid nitrogen stage at 5 kV using an incidence angle of 11–12°. TEM observations were carried out using a Jeol JEM 2010 electron microscope operating at 300 kV. The width of Cu matrix between filaments was determined using an image analyzer (Leica Q5001W with Leica Qwin software). Electrical resistivity measurements were made at room temperature using a standard four-probe technique.

3. Result and discussion

The microstructural observation of Cu–Fe–Ag microcomposite exhibited the ribbon-like morphology of the filaments on the transverse section and the alignment of the filaments with wire axis on the longitudinal section [18,21,22]. As reported by Hong and Song [21], Fe filaments are finer in Cu–Fe–Ag microcomposites than in Cu–Fe–Cr microcomposites. It was shown by Hong and Song [21] that Ag atoms were mostly distributed in the Cu matrix and the filaments were almost free of Ag atoms. Hong and Song suggested that Cu matrix was strengthened by the addition of silver and Fe filaments were strengthened by the addition of chromium. Fig. 1(a) and (b) shows the TEM micrographs showing the longitudinal and transverse sections of Cu–Fe–Ag microcomposites, respectively. Elongated subgrains and thin filaments parallel to the drawing axis were observed in the longitudinal section and equi-axed subgrains and thin filaments were observed in the transverse section. The filaments are indicated by arrows in 1(a) and (b). The spacing between Fe filaments and the thickness of Fe filaments in the longitudinal section were measured to be 134 and 18 nm, respectively, which are smaller than the inter-filamentary spacing (166 nm) and the filament thickness (24 nm) of Cu–Fe–Cr microcomposite [18]. The finer microstructural scale in the Cu–Fe–Ag microcomposite was attributed to initial finer dendrites in Cu–Fe–Ag and easier refinement of filaments due to stronger Cu matrix strengthened by silver precipitates [21,22]. It should also be noted that there are small precipitates in Cu matrix as indicated by white arrows.

The strength, hardness and conductivity of variously processed Cu–Fe–Ag microcomposite wires are summarized in Table 1. The strength/conductivity properties of Cu–Fe–Ag microcomposites drawn to η = 4.8 without intermediate heat treatments (NH) were observed to be 1006 MPa/39% IACS and those drawn to η = 6.3 with three

Table 1
Strength, hardness and conductivity of Cu–Fe–Ag microcomposites

Specimen (diameter; mm)	Strength (MPa)	Hardness (Hv)	Conductivity (%IACS)	Thermo–mechanical processing
NH (2)	1006	218	39	η = 4.8, no intermediate heat treatment
IH-2 (2)	916	208	43	η = 4.8, two intermediate heat treatment
IH-3 (1)	939	213	56.2	η = 6.3, three intermediate heat treatment

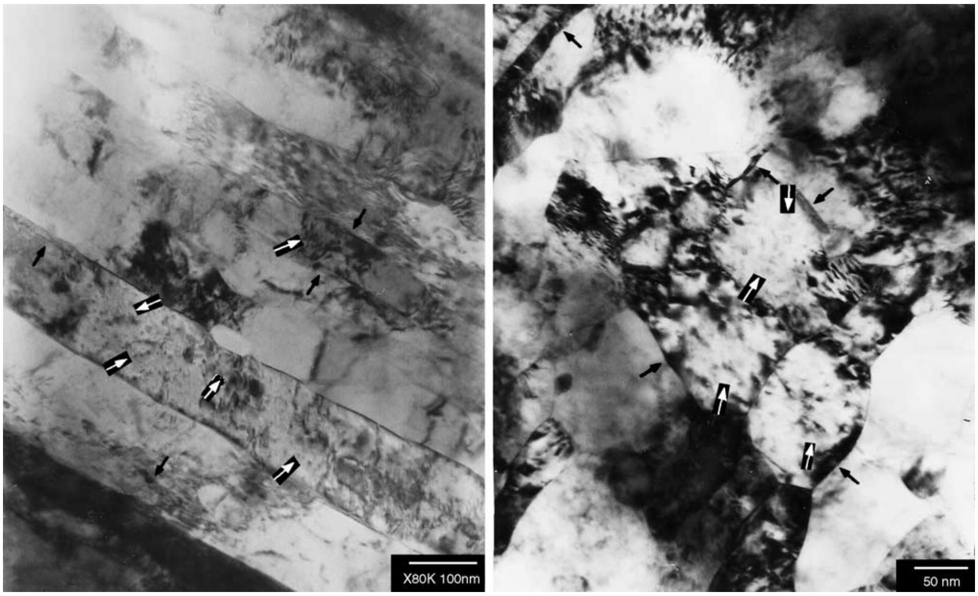

Fig. 1. TEM micrographs showing the longitudinal (a) and transverse (b) sections of Cu–Fe–Ag microcomposites.

intermediate heat treatments (IH-3) were 939 MPa/56.2% IACS. A substantial increase of conductivity was obtained at the expense of a modest loss of the strength by the employment of intermediate heat treatments. The optimum strength/conductivity properties of Cu–Fe–Ag obtained in the present study (939 MPa/56.2% IACS) was found to be better than 891 MPa/45.5% IACS obtained for Cu–Fe–Cr microcomposite [18]. The increase of the conductivity with minimal loss of strength for microcomposites is mainly due to the reduced impurity scattering [7–9], caused by the precipitation of impurities and alloying elements. The effect of recovery of the Cu matrix during intermediate heat treatment is thought to be contributory to the increase of the conductivity. The better strength/conductivity properties in Cu–Fe–Ag can be attributed to the effective precipitation and the finer microstructural scale in Cu–Fe–Ag compared in Cu–Fe–Cr. It was suggested by Hong [22] that the nucleation and precipitation of Fe was facilitated in the presence of Ag.

Hong and coworkers [18–23] suggested that the microstructural scale of filaments can be refined by thermo–mechanical processing involving intermediate heat treatments in Cu base microcomposites. Deformed filaments are known to be broken-up or spheroidized during intermediate heat treatments [20,23]. These broken-up particles and spheroids develop into finer and thinner filaments upon further drawing after intermediate heat treatments [20,23]. Indeed some investigators [6,17,21–24] observed very rapid recovery of the strength upon redrawing after an intermediate heat treatment, which may have resulted from refining of filaments. The increase of conductivity in Cu–Fe–Ag after intermediate heat treatments at 450 °C is attributed to the precipitation of Fe and Ag atoms that were dissolved during heavy drawing.

Fig. 2 shows the mechanical responses of as-drawn Cu–Fe–Ag wires (IH-2) with intermediate heat treatments and Cu–Fe–Ag wires (IH-2) annealed at various temperatures after the final drawing process. As shown in Fig. 2, the strength decreased appreciably with increase of temperature. For Cu–Fe–Ag wires (IH-2), inappreciable work hardening and subsequent work softening were observed. Fig. 3(a)

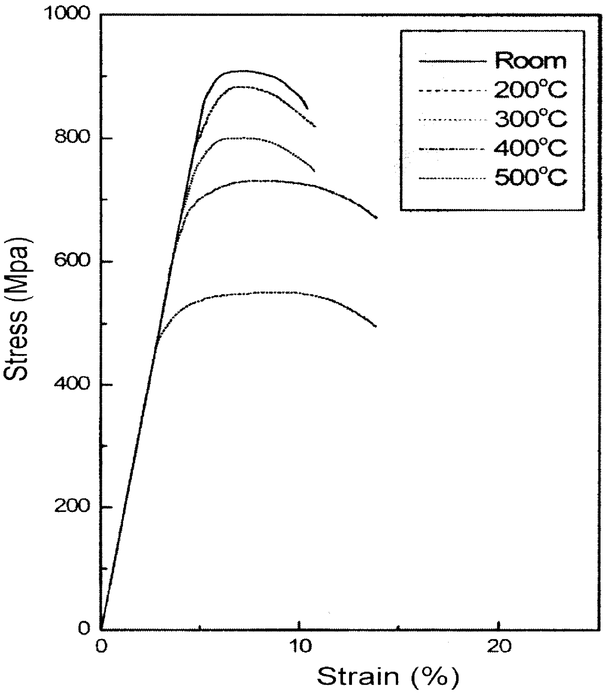

Fig. 2. Stress–strain responses of as-drawn Cu–Fe–Ag wires (IH-2) with intermediate heat treatments and Cu–Fe–Ag wires (IH-2) annealed at various temperatures.

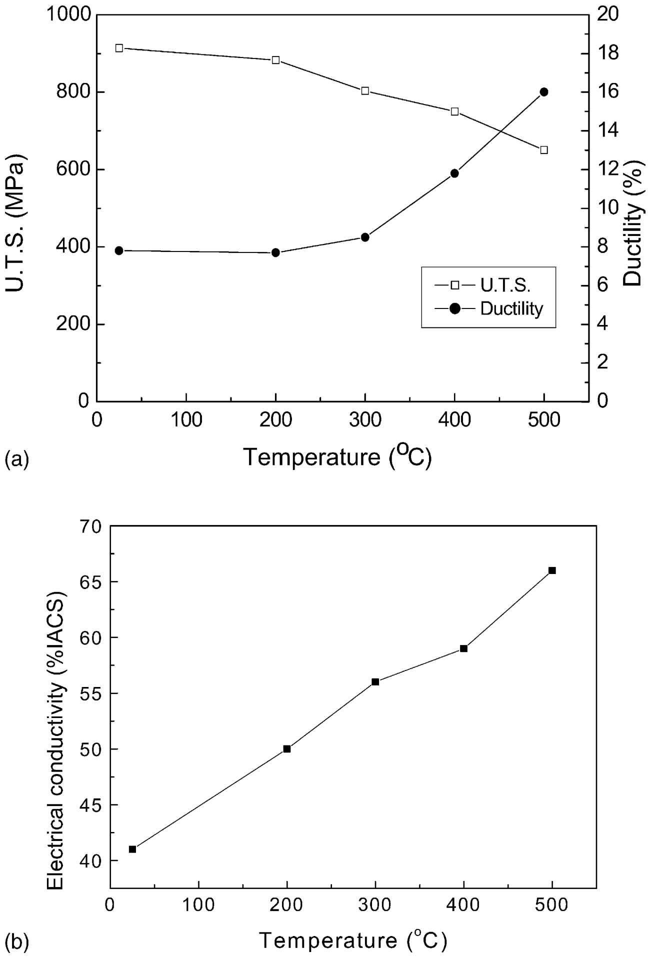

Fig. 3. Variations of the strength and the ductility (a) and conductivity (b) as a function of treatment temperature.

shows the variation of the strength and the ductility as a function of heat treatment temperature. As shown in this figure, the strength decreased slowly up to 500 °C and the ductility increased more rapidly with increasing heat treatment temperature above 350 °C. In Fig. 3(b), the electrical conductivity is plotted as a function of heat treatment temperature. The electrical conductivity increased with the increase of heat treatment temperature.

In order to explain the effect of the final annealing on the mechanical strength and electrical conductivity, the effect of volume fraction of filaments on the microstructural evolution and strengthening mechanism of Cu based microcomposites should be discussed. Hong et al. [25] proposed that the strengthening component of Cu–Nb microcomposites consist of interface strengthening, substructural strengthening and precipitation strengthening. It was also suggested that the contribution of the interface strengthening component to the total strength increases with increase of the drawing strain and volume fraction of filaments [16,25]. In Cu–Fe–Ag microcomposite of the present study, the volume fraction of Fe is 10%, which is relatively lower than other Cu based microcomposites studied extensively by many investigators [1–15]. According to Hong et al. [25], the contribution of strengthening components of heavily drawn bundled Cu-20 vol.% Nb can be broken down to approximately 70% interface strengthening, 10% substructure strengthening and 20% precipitation strengthening (see Fig. 5 of [25]). And the strength of Cu-10 vol.% Nb was predicted to be comprised of 42% interface strengthening, 42% substructure strengthening and 16% precipitation strengthening [25].

In the heavily drawn bundled Cu–Nb microcomposites, the precipitation strengthening term is appreciable because of numerous Nb particles which were formed during thermo–mechanical processing at 750 °C [19,25]. In the heavily deformed Cu based microcomposites, the substructural strengthening term was suggested to arise from the presence of elongated sub-grain and/or grain boundaries as in heavily deformed pure metals. As the volume fraction of filaments decreases, the substructural strengthening term becomes more important [16,25]. Cu based microcomposites with low volume fraction of filaments are more likely to soften after heat treatment because heavily deformed Cu matrix with sub-grains and/or grains are more likely to be affected by recovery and recrystallization at high temperatures than the region with filaments. This suggestion is comparable to the increased stability of heavily deformed two-phase alloys than heavily deformed single-phase metals. The strength of Cu–Fe–Ag microcomposite of the present study was observed to decrease more rapidly with increase of temperature than Cu–Nb microcomposites with higher volume fractions of filaments [25,26]. In Cu-15 vol.% Nb and Cu-18 vol.% Nb, the decrease of the strength became appreciable when the heat treatment temperature was higher than 500 °C [4,26] whereas the strength began to decrease above the heat treatment temperature of 300 °C in Cu–Fe–Ag of the present study. The more rapid decrease of the strength in Cu–Fe–Ag of the present study can be mostly due to the significant contribution of the substructural strengthening of Cu matrix to the strength, which is more susceptible to softening at high temperatures.

In addition to the substructural softening due to recovery of heavily deformed Cu matrix, the spheroidization [19] and stress relief of heavily drawn filaments [27,28] are thought to contribute to the softening of Cu–Fe–Ag after heat treatments. It is well established that spheroidization and the residual stress relief occurred at 400 °C in Cu based microcomposites [19,27,28]. The increase of the conductivity after the final annealing can be associated with the reprecipitation of Cu matrix, recovery/recrystallization of Cu matrix and the stress relief of filaments which also induces the stress relief of Cu matrix [28].

In order to investigate the deformation mechanism of Cu–Fe–Ag, the strain rate change tests were performed and the activation volumes for plastic flow were measured. Fig. 4 shows an example of the strain rate change test of Cu–Fe–Ag heat treated at 300 °C. The strain rate was changed well before the UTS was reached (at the plastic strain of 0.008–0.01). It should be noted that a small stress jump occurred when the

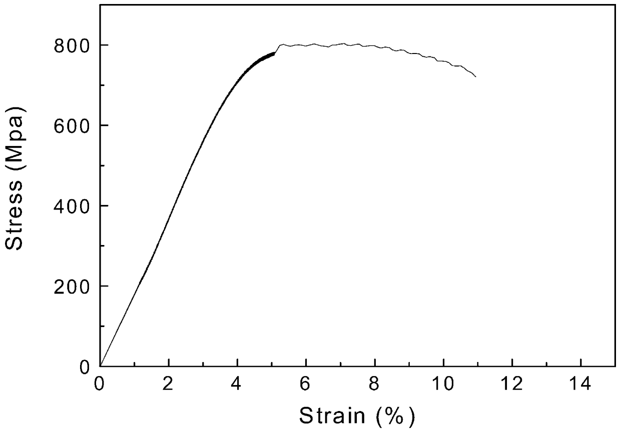

Fig. 4. Stress–strain curve for the strain rate change test of Cu–Fe–Ag heat treated at 300 °C. The strain rate was changed from the strain rate of 1×10^{-4} to $1 \times 10^{-2}\ \mathrm{s}^{-1}$ at the plastic strain of 0.008.

strain rate was changed. The activation volume associated with the deformation process has been obtained from the following classical equation [29]:

$$V_{\mathrm{app}} = kT\partial \ln\frac{\dot{\gamma}}{\partial\tau} \cong mkT\ln\frac{\dot{\varepsilon}_1/\dot{\varepsilon}_2}{\tau_1 - \tau_2} \qquad (1)$$

where k is the Boltzmann's constant, $\dot{\gamma}$ the shear strain rate, τ_1 and τ_2 the applied shear stresses at the normal strain rates $\dot{\varepsilon}_1$ and $\dot{\varepsilon}_2$, respectively and T is the absolute temperature. The shear stress τ was calculated from the yield stress σ_{y} using the relation $\tau = \sigma_{\mathrm{y}}/m$, where m is the Taylor factor. The calculated apparent activation volume was $170b^3$ (where b is the burgers vector for Cu (=0.256 nm)) for as-drawn IH-2 wires at room temperature. And the activation volumes for Cu–Fe–Ag annealed at high temperatures above 300 °C increased to 180–$190b^3$ whereas it decreased to $156b^3$ after being annealed at 200 °C, as summarized in Table 2. The decrease of the activation energy at 200 °C may be associated with the precipitation of silver, which was reported to be precipitated at 100–200 °C after heavy deformation [21–23]. The strain rate sensitivity at the plastic strain of 0.03 was measured to be 6.9×10^{-3} for the as-drawn wires and does not change appreciably with annealing.

The activation volume measured in this study is larger than that ($45b^3$) of Cu-15 vol.% Fe with a drawing strain of 4.4 observed by Biselli and Morris [11]. The smaller activation volume observed by Biselli and Morris is associated with the finer microstructural scale due to powder metallurgy processing and a higher drawing strain. The spacing between obstacles for the thermally activated deformation of Cu–Fe–Ag microcomposites is $170b$ (=43 nm). Hong and coworkers [16,20,22,23] suggested that the filaments in Cu base microcomposites are athermal obstacles and contribute to the athermal strengthening component. In Cu–Fe–Ag, the ratio of yield stresses was found to be 0.92, which is close to that of Young's moduli (0.91) [22]. The sensitivity of the athermal strengthening component to temperature and strain rate, therefore, is negligible. The thickness of Fe filaments and the spacing between Fe filaments of Cu–Fe–Ag microcomposite of the present study is larger than those of powder processed Cu–Fe by Biselli and Morris [11] because of the lower drawing strain and the different processing method (casting versus powder metallurgy) employed in the present study. Fe filaments with the thickness of approximately 18 nm and the spacing of 134 nm in Cu–Fe–Ag of the present study are not likely the rate controlling obstacles during plastic deformation of Cu–Fe–Ag [22,23,26]. They are athermal obstacles [22,23,26,30] which increase the strength by increasing the long-range internal stress and less likely to be strain rate sensitive.

Table 2
Activation volume as a function of annealing temperature

Annealing temperature	Activation volume
As-drawn (IH-2)	$170b^3$
200 °C	$156b^3$
300 °C	$188b^3$
400 °C	$180b^3$
500 °C	$190b^3$

Hong and Hill [20,23] observed numerous second phase particles in Cu–Nb and Cu–Ag nanocomposites. Small second-phase particles in Cu matrix were suggested to result from reprecipitation of the second phase that had dissolved during heavy deformation processing. It was suggested recently that the most probable rate controlling mechanism of Cu–Fe–Cr microcomposites was the interaction between dislocations and precipitates in Cu matrix [18]. As shown in Fig. 1, many particles were also observed in Cu matrix of Cu–Fe–Ag. The spacing between these particles was observed to be 25–35 nm, which is reasonably close to the activation length (43 nm) observed in this study, which supports the interaction between dislocations and precipitates as a rate controlling mechanism. The decrease of the activation volume in Cu–Fe–Ag heat treated at 200 °C further supports that the interaction between dislocations and precipitates plays an important role in thermally activated deformation of Cu–Fe–Ag microcomposites.

Hong and coworkers [21–23] reported that the precipitation of silver phase was particularly pronounced in Cu–Ag nanocomposites and Cu–Fe–Ag microcomposites if they were heat treated at low temperatures (100–200 °C). The decrease of the activation volume of Cu–Fe–Ag heat treated at 200 °C can be associated with more precipitation of silver at 200 °C. The interaction between dislocations and precipitates as the most probable rate controlling mechanism is compatible with the suggestion [25,26] that the precipitation strengthening contribute appreciably to the strength in thermo–mechanically processed Cu–Nb. Although the contribution of the interface strengthening and substructural strengthening to the strength of Cu–Fe–Ag is thought to be greater than that of precipitation strengthening, interface strengthening and substructural strengthening components arose from athermal long-range obstacles such as Fe filaments, elongated sub-grain and grain boundaries.

4. Conclusions

Based upon a study on the optimization of the tensile strength/conductivity combination of Cu–Fe–Ag microcomposites, the following conclusions can be drawn:

(1) The optimum strength/conductivity properties of Cu–Fe–Ag microcomposite drawn to η = 6.3 with three intermediate heat treatments (IH-3) were 939 MPa/56.2% IACS, exhibiting improved properties compared to those of 891 MPa/45.5% IACS for Cu–Fe–Cr microcomposite.
(2) The increase of the conductivity with minimal loss of strength with intermediate heat treatments is mainly due to the reduced impurity scattering, caused by the precipitation of impurities and alloying elements and secondarily to the recovery of the Cu matrix during intermediate heat treatment.
(3) The decrease of the strength for Cu–Fe–Ag after the final annealing is mostly caused by the substructural softening due to recovery of heavily deformed Cu matrix with the spheroidization and stress relief of heavily drawn filaments contributory to the softening of Cu–Fe–Ag after heat treatments.
(4) The activation volumes for deformation increased from $170b^3$ at room temperature in the as-drawn wire. The activation length was in reasonably good agreement with the spacing of the precipitates (25–35 nm). The most probable rate controlling mechanism of Cu–Fe–Ag microcomposites is suggested to be the interaction between dislocations and precipitates in Cu matrix.

Acknowledgements

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