**Microstructure and Properties of Nanostructured Cu28wt.%Ag Microcomposite
Deformed after Solidifying under a High Magnetic Field**

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Abstract

We have studied the effect of an external high magnetic field (HMF) on the solidified microstructure of Cu28wt%Ag alloys, and we have modeled the impact of microstructural parameters on both the mechanical strength and the electrical resistivity of CuAg microcomposites. Subjecting CuAg alloys to an external HMF during solidification resulted in microstructural changes. In microscale, suppression of convection by HMF increased **respectively** the solubility of Ag in proeutectic Cu by 41% and the dendrite arm spacing throughout the alloy by 18%. In nanoscale, however, HMF decreased the spacing of nano-sized Ag precipitations in proeutectic Cu and increased rod-like Ag precipitates. HMF resulted in an increase in the growth

velocity of Ag precipitates. This caused changes in Ag morphology and concentration, thus enhancing local microhardness in proeutectic Cu regions. After introduction of heavy deformation in solidified Cu28%Ag alloys, we observed that the microstructure of these microcomposites remained coarser in the presence of HMF than in its absence. The application of HMF increased electrical resistivity at 293K and 77K, but reduced hardness and ultimate tensile strength. Our model demonstrated that Ag precipitate in proeutectic Cu impacts significantly to both mechanical strength and electrical conductivity.

Keywords: Cu-Ag; High magnetic field; solidification; precipitation; strength; resistivity modeling

1. Introduction

Cu-Ag material with an excellent combination of high strength and high conductivity is an important conductor for both DC resistive and pulsed high-field magnets [1-4]. Previous literatures reported that the high strength of the CuAg microcomposites was closely related to the microstructural parameters of proeutectic Cu. These parameters were the dendrite spacing, volume fraction[5], and dispersion of nano-sized Ag precipitates [3, 6]. The strength of CuAg composite can be increased by refining the Cu dendrites and precipitating as much fine Ag in proeutectic Cu as possible [6]. Understanding the precipitation behaviors of CuAg system is necessary in order to alter precipitate kinetics and to optimize the Ag distribution in proeutectic Cu. Numerous investigators have reported their work on

Ag precipitate kinetics [7-12]. The Cu-rich solid solutions transformed by discontinuous precipitation into a structure with rod-like Ag-rich precipitates embedded in Cu-rich matrix [7]. The nano-sized rod-like precipitation began mainly from the grain boundary in the polycrystals [7]. An external stress field was reported to have enhanced the growth of discontinuous precipitates [13]. A mechanism for precipitation kinetics of this type was proposed on the basis of the ageing process of CuAg solid solutions with lower compositions [7, 10, 14, 15]. However, descriptions of the relevant effects of the solidification process on the resultant precipitate behaviors were rarely reported even though nano-scaled Ag precipitate was verified to have a great strengthening on overall mechanical properties [16, 17]. High conductivity as another valuable aspect of CuAg material has been attributed to low solubility of Ag in Cu and vice versa, and high electrical conductivity of Cu and Ag. The electrical conductivity of CuAg can be improved by reducing the resistivity that results from impurity scattering. However, the other influence factors to electrical conductivity need to be addressed, and some efforts have been made to understand the relationship between the conductivity and the microstructure parameters. For instance, individual contributions of various defects to the resistivity of CuAg material may possibly be predicted by relevant models, where the contributions from electron scattering at the surface and phase boundary is dependent on the Cu channel diameter and the mean free electron path in Cu [18-21]. These models were presented [19, 20] to estimate the resistive behavior of Ag-Cu two-phase composites and to compare the estimated values to values resulting from extensive experimental

quantitative microstructure analysis. This model demonstrated that resistivity was dependent on microstructure. In other words, improving the performances of CuAg materials requires optimization of microstructure. The microstructure can be optimized by altering the thermomechanical process [3]. Numerous researchers also studied the effects of additions of third elements on properties of CuAg [22-24]. Because the strength and conductivity are dependence on the initial microstructure before the thermomechanical processing, other researchers have proposed that solidified microstructure might be refined beforehand [5, 6]. An external high magnetic field (HMF) had a strong effect on solidification microstructure because it suppressed the natural convection of the melt by introducing a Lorentz force in a direction opposite to the direction of melt flow [25, 26]. Other investigators [27, 28] have suggested that a new thermoelectromagnetic convection (TEMC), by contrast, was produced by the interaction between the magnetic field and the thermoelectric effect. This new type of convection could promote rather than suppress the overall convection of the melt. Thus, both the Lorentz force and TEMC should be taken into account even though they have opposite effect. With respect to Cu-Ag systems, the imposition of an magnetic field of about 1 T would drastically increase the primary dendrite arm spacing and it was analyzed from the effect of TEMC on convection [29]. The effect of a 12 T HMF on the hardness and the electrical conductivity of CuAg alloys, and on precipitations of Ag in Cu-rich dendrites have been investigated and their studies revealed that the properties of the alloys vary according to differences in Ag precipitate size and morphologies induced by the HMF [30]. Our previous work

[31] stated that convection suppression by electromagnetic forces during solidification of Cu-Ag alloys was attributable to solute redistribution and temperature gradients near the liquid-solid interface. ~~both of which cause marked changes the microstructure~~ However, the impact of HMF on such parameters as the microstructural evolution, chemical concentration and properties has not been studied systematically in a quantitative manner.

This paper presents our systematic and quantitative studies of the HMF influence on the microstructural evolution, concentration contributions, and relevant properties. The effects of an external HMF on the size and distribution of proeutectic Cu/eutectic colonies and the morphology of discontinuous Ag precipitates in proeutectic Cu were investigated quantitatively by field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), and Energy Dispersive X-ray Spectrometer (EDS) analysis. The microstructural analysis in individual phases initially induced by HMF was introduced to model the hardness, as-drawn strength and resistivity. These theoretical prediction values were in good agreement with experimental values.

2. Experimental procedure

Cu-28wt.%Ag (~~weight percent, expressed as Cu28%Ag in the context~~) master ingot was prepared by intermediate-frequency vacuum induction melting under the high-purity Ar atmosphere. A specimen (9 mm in diameter and 65 mm in length) machined from the ingot by an electro-sparking device was placed in a graphite crucible (10 mm in inner diameter, 15 mm in outer diameter). They were together

sealed in a quartz tube with the vacuum of about 10^{-3} Pa. The quartz tube was loaded to the center of a resistance furnace under a superconducting high-field magnet. The magnet generates a longitudinal magnetic field with a maximum magnetic flux density (denoted by B) of 12 T at the center of a cool bore with 100 mm in diameter. At about 25 mm from the center of the field, the magnetic field strength is about 98.66% of the center field. The central point of the sample was coincided with the center of both the HMF and the vacuum furnace. The specimen was reheated at a heating rate of 5 °C /min to 1050 °C held for 40 minutes, cooling down at a cooling rate of 20 °C /min, to 790 °C, holding for 30 minutes, and then cooled to room temperature at an average cooling rate of 10 °C /min. The solidification process was carried out with or without an external HMF of 12 T and the specimens are referred as 12T and 0T samples. More detailed experimental procedure could be found in a previous publication [31]. The as-cast samples with 50 mm in length were cold drawn at ambient temperature without intermediate annealing. The drawing strain is calculated by $\eta = \ln(A_0/A)$, where A_0 and A are initial and final cross-sectional areas, respectively. The total drawing strain η was 3.5. The experiments were repeated three times.

Both the as-cast and as-drawn samples were sectioned, polished and etched in a solution of 2g FeCl_3 , 5ml HCl and 100ml $\text{C}_2\text{H}_5\text{OH}$. SSX-550 scanning electron microscope (SEM) was used to examine the microstructures. To probe the Ag fine precipitates, some samples were electropolished in a solution of 25% nitric acid in 75% deionized water at a voltage of 12V. The morphology of Ag precipitates was

examined by a field emission Zeiss SEM equipped with an energy dispersive x-ray spectrometer system (EDS). The Ag concentration in proeutectic Cu region was detected on $20 \times 20 \mu\text{m}^2$ areas by EDS with a $120 \mu\text{m}$ aperture at 20 kV accelerating voltage. The sizes and spacing of both proeutectic Cu and Ag precipitates were quantitatively measured on more than 10 SEM images. Thin foils for transmission electron microscopy (TEM) were prepared by grinding to thickness between 100 and $200 \mu\text{m}$ and punching into 3mm-diameter-discs. The discs were twin-jet polished using a solution of 33% nitric acid in 67% methanol at a temperature of -30°C and a voltage of 6 V. The residual contamination at the surfaces of the TEM foils were finally cleaned by argon ion-milling with a voltage of 4 kV at an incidence angle of 6° with a cryogenic stage cooled by liquid nitrogen. The foils were observed in a JEOL-2011 TEM operating at 200 kV and equipping with an EDS system.

Microhardness tests were performed on a Tukon 2100 microhardness tester with a diamond square-based pyramid under a load of 50 g for proeutectic region and 100 g for the overall samples, respectively. The loading duration time was 10s. The average value was calculated on at least 15 measurement points. Tensile tests were performed on a ~~100 kN~~ MTS machine at a rate of 10^{-3} sec^{-1} at room temperature. The resistivity was measured by four- probe DC method at room temperature (RT, 293K) and in a liquid nitrogen bath at 77 K.

3. Results

3.1 As-cast microstructure and Ag content of CuAg alloy

Figure 1 shows typical microstructures of hypoeutectic Cu28%Ag alloys

(solidified with and without HMF) consisting two components: 1) Cu-rich proeutectic dendrites (dark contrast in Figs. 1a & b) embedded with Ag precipitates (light contrast in Figs. 1c & d) and 2) eutectic components (light contrast in Figs. 1a & b) which surround Cu-rich dendrites forming networks. The shape of the network, which shows light contrast in Figs 1a&b, was not significantly changed by the introduction of external HMF, but the eutectic Cu lamellas within the network did become slightly coarser. In the proeutectic Cu region, as shown in Figs 1 c&d, Ag precipitated out of the supersaturated Cu solid solution. This precipitation occurred largely because our solidification process was a non-equilibrium process with a rapid cooling rate of (10°C /min). The Ag precipitates, as reported in previous publications [7], were discontinuous and appeared in cross-section in two shapes: rod-like and sphere-like. Figs. 1 c & d show that these Ag precipitates nucleate and grow along at least two arrays. Without HMF, as shown in Fig.1 c, the arrays appear to be dominated by discontinuous sphere-like morphology with rod-like Ag precipitate accounting for a volume fraction of only $1\pm0.2\text{vol}\%$. With a 12T HMF (Fig.1 d), however, rod-like Ag precipitates (areas d1 to d4 in Fig. 1d) increased to about $3\pm0.9\text{vol}\%$. In 12-T-HMF treated samples, the angle between the projected arrays of rod-like Ag and sphere-like Ag, verified in several FESEM images, was about 45 degree. Previous researchers had suggested that these arrays had predictable orientation [7, 8]. We quantified the orientation using accepted measures of quantitative metallography [32] and the spacing was evaluated by the linear intercept method on more than 5 images. Table 1 summarizes the size and spacing of

both the proeutectic Cu and precipitated Ag. It shows that an external 12T HMF increases both the average arm spacing of proeutectic Cu dendrites by 18% and the spacing of eutectic lamella by 20%, but the spacing of nano-sized Ag precipitates decreases by 24%. Table 1 shows no significant changes, however, under an external magnetic field, with regards to length of proeutectic Cu and the size of Ag precipitates themselves. Because our solidification was a non-equilibrium process, the volume fraction of proeutectic Cu in this case (>80 vol%) was higher than the 73 vol% normally expected for an equilibrium solidification [32]. Table 1 indicates that the volume fraction of proeutectic Cu increases by 4% with external HMF. We concluded that the application of external HMF to Cu28%Ag alloys during cooling affected the morphology and distribution of both the eutectic colonies and the rod-like Ag precipitations.

Fig.1**Table 1**

Selected area diffraction patterns (SADPs) show that the Ag precipitates have a cube-on-cube orientation relationship (OR) with Cu matrix, as depicted in Fig. 2, which is consistent with previous work [6, 12]. The external HMF did not change this OR, however, the volume fractions of rod-like and sphere-like Ag morphology precipitates were changed. In Fig.2b, the rod-like morphology Ag precipitates, as typically shown in the inset, grow with projection of the long axis about 10 degree of $\langle 331 \rangle$ crystallographic direction. Examinations of several regions revealed that the rod-like morphology of Ag precipitates had relatively high volume fraction in CuAg

alloy heat treated in the presence of HMF, which was consistent with the results of FESEM examinations, as shown in Fig.1d.

Fig. 2

We used two methods to estimate Ag solubility in the proeutectic Cu regions –FESEM/EDS and TEM/EDS. The whole Ag concentration, which is the sum of both the solubility and the precipitate of Ag in proeutectic Cu, was detected by EDS (the probe size is about 1 μm that is significantly larger than the size of the proeutectic Cu (5 μm)) in the FESEM. The volume fraction of Ag precipitates was quantified from their FESEM images, thus making it possible for Ag solubility in Cu matrix to be deduced. In TEM/EDS analysis, the Ag solubility in the Cu matrix was measured directly by a 3~5nm incident beam. The results, shown in Table 2, indicate that a similar comparable consensus that when the samples have been solidified under 12T HMF, Ag concentration in proeutectic Cu region is higher than it would be without HMF. This might be a result of more Ag trapped at the liquid-solid interface by decreased convection. Both methods of estimating solubility, FESEM/EDS and TEM/EDS, show comparable trends under a 12 T HMF. We chose to use TEM/EDS data in subsequent sessions because TEM/EDS method depends on direct measurement rather than deduction, so that possibility of error is reduced. TEM/EDS results demonstrated that, in the presence of HMF, the volume fraction of Ag precipitates decreased by 3%, but the solubility of Ag in proeutectic Cu matrix increased by 41%.

Table 2

3.2 As-drawn microstructure of CuAg microcomposites

The longitudinal images in Fig.3 show reductions in both spacing and thickness of Cu dendrites under increased drawing strains. Dendrite spacing and thickness in 12T samples (Fig. 3 d-f) are coarser than those in OT (Fig. 3 a-c). This is inherited from the coarser solidified microstructure induced by the external HMF, as depicted in Fig. 1. Fig. 3 also shows that network microstructure (the eutectic component) gradually aligns along the drawing direction, forming fiber-like microstructure. Fig. 4 shows eutectic fiber spacing decreases as strain increases. At lower strain levels, each unit of drawing strain causes greater decrease in spacing. At higher strain levels, less change is induced by each unit strain. At the same magnitude of strain, eutectic fiber spacing of samples with a 12T HMF is greater than without HMF, reflecting the inherent size differences of the original as-cast microstructure. The eutectic fiber spacing shown in Fig. 4 could be fitted as a function of drawing strain by the equation

$$\lambda_1 = \lambda_0 \exp^{-0.5\eta} \quad (1)$$

where, λ_1 and λ_0 are the eutectic fiber spacing of as-drawn and as-cast samples, respectively.

This fitting equation is similar to that of previous works on Cu-12%wtAg [33] and Cu25wt%Ag [6] . This indicates that initial scale of the microstructure and chemistry make no significant change to strain-hardening behavior of Cu-Ag composite.

Fig.3

Fig. 4

The SADPs in Fig. 5 show that the Cu and Ag phases still have a cube-on-cube OR,

but there is an about 1° slight deviation between the diffraction spots of Cu and Ag. This deviation may be a result of reducing misfit between nanosized Cu and Ag in the proeutectic region during heavy deformation. The DF images in Fig. 5 show that both Ag precipitates and proeutectic Cu grains are aligned along the drawing direction after a heavy deformation. In other words, heavy deformation made the Cu matrix, and sphere-like and rod-like Ag precipitates shown in Figs.1 c & d into elongated proeutectic Cu grains and Ag filaments. The size and spacing of Ag precipitates in proeutectic regions of samples in the presence of HMF, as shown in Fig. 5a, are slightly greater than that of non-HMF samples, as shown in Fig.5b. The results shown in Table 3 demonstrate that HMF increases the spacing and thickness of Ag fibers in proeutectic regions by 50% and 25%, respectively, but decreases the volume fraction of Ag fibers by 4%.

Fig.5

Table 3

3.3 Properties of Cu28%Ag materials cold-drawn after solidifying under HMF

3.3.1 Microhardness in the proeutectic region of as-cast CuAg alloys

The microhardness values of proeutectic Cu regions in 0T and 12T samples were 99.8 ± 2.8 and 112.3 ± 3 HV, respectively. Application of 12T HMF increased microhardness in proeutectic Cu regions by 13%. This increase in hardness might result from decreased spacing of Ag precipitates and increased solubility of Ag, as shown in Tables 1 & 2. This will be addressed in section 4.1.

3.3.2 Microhardness and ultimate tensile strength of as-drawn CuAg

microcomposites

Figure 6 shows that, because of refinement of microstructure by heavy deformation, both microhardness and ultimate tensile strength (UTS) of as-drawn samples are increased as a function of drawing strain. Figure 6 also shows that, because of their coarser solidification microstructure, 12 T samples have lower hardness and UTS than 0T samples at the same drawing strain, as shown in Figs. 4 & 5. Fig. 6a shows that the indentations in or near the eutectic area have slightly longer diagonal length than the indentation in the proeutectic [areas](#), demonstrating that eutectic component is softer than the rest.

Fig.6

3.3.3 Electrical resistivity of as-drawn CuAg microcomposites

Measurements of electrical resistivities at 293K and at 77K are shown in Table 4. In the presence of HMF, resistivity at both temperatures was higher, probably because of changes solubility of Ag in Cu and in the microstructures of the composite. These changes could affect the scattering of electrons [34].

4. Discussion

4.1 Effect of HMF on as-cast microstructure

Application of an external HMF during the solidification process of Cu28%Ag alloys resulted in changes to the local chemical composition and to the microstructure at both microscale and nanoscale.

In microscale, HMF increased both the dendrite arm spacing (by about 18%) and the volume fraction (by 4%) of proeutectic Cu. We assumed that these changes

occurred during rather than after the solidification process. The increase in dendrite arm spacing was likely caused by the reduced nucleation or branching rates of the dendrites. These rates are partially controlled by the effect of HMF on convection. Previous work [31] indicates that increased dendrite arm spacing of proeutectic Cu dendrites results from the elimination of interfacial instability because of electromagnetically damped convection (EDC). We assumed that EDC increased the solubility of Ag in Cu dendrites by reducing the diffusion of Ag. In other words, the slowed diffusion of Ag caused an increased Ag rejected from solid to liquid phase that was steadily replaced by proeutectic Cu.

Dendrite arm spacing $\lambda_{\text{Dendrite}}$ follows a relationship with the diffusion coefficient in liquid (D_L), undercooling (ΔT), and other parameters[35].

$$\lambda_{\text{Dendrite}} = \frac{4.3(\Delta T D_L \Gamma)^{0.25}}{k^{0.25} V^{0.25} G^{0.25}} \quad (2)$$

where, Γ is Gibbs-Thomson coefficient, k is equilibrium distribution coefficient, V is the rate of interface movement, G is the interface temperature gradient.

Previous works indicate that under an applied high magnetic field B , the diffusion coefficient in liquid (D_L) displays a function of B^n . Here B is the external magnetic field, and n is 4 or 2 when thermal convection or solutal convection is predominant, respectively [36, 37]. Lehmann et al [29] found that primary arm spacing of CuAg alloy depended on the convection near the diffusive solute transport regime. It could be deduced that solutal convection might be predominant during cooling of CuAg alloy under HMF and the exponential value of n was 2. The diffusion coefficient in liquid of Cu60%Ag alloy is $3.3 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ [29]. Our alloy was likely to have

an approximate value because of its close composition. If we assume that only D is changed with the applied HMF and B is greater than 1 T, dendrite arm spacing could be rewritten as

$$\lambda_{\text{Dendrite}} = 4.3 \left(\frac{\Delta T F}{k V G} \right)^{0.25} [D_0 / (1 + C B^2)]^{0.25} \quad (3)$$

where C is a constant relating to Ha number, magnetic field and composition.

Equation (3) indicates that dendrite arm spacing increases with increasing HMF.

In our work, the melt subjected to HMF was held at the approximate eutectic temperature for 30 minutes, which further damped the convection. Reduced convection might make the temperature gradient increase further at the interface between proeutectic Cu and liquid melt, thus decreasing the nucleation and growth of branches between dendrites. In other words, isothermal heat treatment at near-eutectic temperature in our studies resulted in greater increased spacing than occurred in previous studies without isothermal heat treatment [31]. Moreover, the suppressed convection in our studies decreased diffusion between the inter-branches of Cu dendrites, and more Ag solutes were thus preserved. This increased the thickness of dendrites as well as the volume fraction and spacing of proeutectic Cu.

It has been established that the growth and solute distribution of the eutectic component depend on the diffusion that occurs in front of the liquid-solid interface [38, 39].

$$C_{\alpha 0} = C_{\beta m} - \frac{\pi^2 A k D_L}{-m_L V \lambda^2} \quad (4)$$

where k is the equilibrium partition coefficient, $A = \frac{\sigma_{\alpha L} T_E}{\Delta H_m \rho_S}$ is a constant, $C_{\alpha m}$ and

$C_{\beta m}$ are the equilibrium concentration of the α -Cu phase and β -Ag phase, respectively; and m_L is the liquidus slope.

According to Eq. (4), an applied high magnetic field will increase the $C_{\alpha m}$, owing to the decrease of the diffusion coefficient (D_L) if eutectic lamellar spacing is increased, as shown in Table 1. An increase in $C_{\alpha m}$ means a shift of the Ag solubility line, which will increase Ag solubility. Experimental results of our studies and in that of Li et al [40] were consistent with equation (4).

In nanoscale, Ag precipitation in proeutectic Cu occurred as a result of solid state reactions [41]. In our study and in that of Hamana et al [41] of these reactions, even though nucleation rates were high, slow diffusion rates made growth slow [6]. Because of the weaker diamagnetic properties of Cu and Ag, external HMF may have a negligible direct influence on these solid state reactions that occur during Ag precipitation. During the liquid to solid reaction, a strongly influence, however, was detected by the application of HMF on the size of Cu dendrites and the solubility of Ag in proeutectic Cu. This led us to believe that rod-like and sphere-like Ag precipitates formed at either certain solidification temperatures or at certain precipitate temperatures [6]. Nucleation and growth of Ag precipitates are related to the solubility of Ag in proeutectic Cu. An external 12T HMF changed the solubility of Ag and the volume fraction of proeutectic Cu, as discussed in the previous section, in other words, HMF increased the trapping of Ag in proeutectic Cu, which in turn increased the driving force of nucleation for Ag precipitates. We conclude that the higher driving force brought about indirectly by HMF is one of the reasons for the

increase of the volume fraction of rod-like Ag precipitates.

The growth velocity of discontinuous precipitate, v , governed by volume diffusion satisfies the following equation [7, 42]

$$v = 2 \frac{C_0 - C_e}{C_0} \frac{D_S}{\lambda_{Ag}} \quad (5)$$

where C_0 is the concentration of the supersaturated matrix; C_e is the equilibrium solute concentration in the matrix; D is the volume diffusivity of solute, and λ_{Ag} is the spacing of Ag precipitates.

The ratio v_{12T}/v_{0T} can be written by

$$\frac{v_{12T}}{v_{0T}} = \frac{C_{0,0T}(C_{0,12T} - C_e)}{C_{0,12T}(C_{0,0T} - C_e)} \frac{\lambda_{Ag,0T}}{\lambda_{Ag,12T}} \quad (6)$$

v_{12T}/v_{0T} was estimated to be 1.17 using the data in Tables 1&2, which indicated that the growth velocity of discontinuous precipitate after HMF treatment was possibly larger than that without HMF treatment.

4.2 Strength and hardness related to microstructural changes caused by HMF

Local strength and microhardness in the proeutectic Cu region can be enhanced by both solid solution and precipitation of Ag. Solid solution hardening can be expressed by following equation [43]

$$HV_{SS} = k_1 \sqrt{\frac{x_a}{3}} \quad (7)$$

where k_1 is a function of alloying element and lattice parameter change due to added elements, and x_a is the Ag content in Cu. Using the experimental data of precious research [44], our calculation indicates that 0.59at% Ag dissolved in Cu increased the hardness by 112MPa.

The Hall-Petch equation can be used to describe the effect of size on hardness

[45, 46].

$$HV = HV_0 + k_H d^{-1/2} \quad (8)$$

where HV_0 is a constant d is the spacing between Ag precipitates (λ_{0AP} in our case).

In our calculations, we followed other researchers in using $k_H = 0.11 \text{ MPa}\sqrt{\text{m}}$ as the value for pure Cu [43].

Combining equations 6 and 7, the total microhardness of proeutectic Cu can be written as

$$HV_{\text{Curegion}} = HV_{0\text{Cu}} V_{\text{Cu}} + k_1 \sqrt{\frac{x_a}{3}} + HV_{0\text{Ag}} V_{\text{Ag}} + k_H d^{-1/2} \quad (9)$$

We believe that HMF has no impact on the microhardness of the Cu matrix expressed as a constant $HV_{\text{Cu}0}$, and on the microhardness of Ag, expressed as $HV_{0\text{Ag}}$. Therefore, the difference in microhardness between samples solidified with and without HMF in microhardness is rewritten as

$$\Delta HV_{\text{Curegion}} = \Delta [k_1 \sqrt{\frac{x_a}{3}} + k_H \lambda_{0AP}^{-\frac{1}{2}}] \quad (10)$$

Using Eq.(10), we found that when 12 T HMF was applied during the solidification, microhardness was increased by 11.5 HV, because of increased Ag solubility and decreased spacing between Ag precipitates. This value corresponds closely to our experimental data (12.5 HV). Therefore, we conclude that applying HMF during the solidification of [Cu28%Ag](#) alloy increases the local microhardness of proeutectic Cu.

In hypoeutectic Cu-Ag systems, previous models [6] [47] took the imposed strain and the initial scale of microstructure formed during solidification into account, but these models did not give separate consideration to the strengthening impact of Ag

solubility. In the present study, components of both the eutectic and the Cu matrix with Ag solid solution are calculated by the rule of mixture

$$\sigma = V_M \sigma_M + V_E \sigma_E \quad (11)$$

where V_M and V_E are the volume fraction of proeutectic Cu and the eutectic, respectively. σ_M and σ_E are the flow stress of proeutectic Cu and the eutectic, respectively.

The $V_M \sigma_M$ term is the strengthening result from the proeutectic Cu. It consists of the solid solution hardening ($\sigma_{\text{Solid Solution}}$, as Eq. 7), and the strengthening role of nanoscale Ag fibers ($\sigma_{\text{Precip.}}$, as in Eq. 8). The right second term, $V_E \sigma_E$, is the strengths of the eutectic, where the strengths are mainly from the working hardening, closely satisfying the Hall-Petch relationships as well [48]. Therefore, Eq. (11) rewritten as

$$\sigma = V_M \left[\sigma_{0\text{Cu}} + k_{\text{Cu/Ag}} \lambda_{\text{Ag precip.}}^{-0.5} + k \sqrt{\frac{x_a}{3}} \right] + V_E \left[\sigma_{0\text{Ag}} + k_E \lambda_{0\text{E}}^{-0.5} \exp(0.25\eta) \right] \quad (12)$$

where, $\sigma_{0\text{Cu}}$ and $\sigma_{0\text{Ag}}$ are the intrinsic friction stress of the pure Cu and pure Ag, respectively; k is k_1 in Eq(6). $k_{\text{Cu/Ag}}$ and k_E are the strengthening coefficients for proeutectic Cu/Ag and eutectic, respectively. $\lambda_{\text{Ag precip.}}$ and $\lambda_{0\text{E}}$ are the initial spacing of eutectic and Ag precipitate in proeutectic, respectively.

All the measured data shown in Table 3 from as-cast and as-drawn samples with a drawing strain of 3.5 are applied to Eq. (12), The term of $\sigma_{\text{Solid Solution}}$ could be deduced by the solubility of Ag as as-cast solid solution hardening in session 4.1 [44]. The strengthening coefficients and the intrinsic friction stress could be simplified as a Hall-Petch constant and intrinsic friction stress of Cu, the values of which are 0.11 MPa $\sqrt{\text{m}}$ and 25 MPa, respectively [43]. The individual contributions to the total

strength are summarized in Table 5. The contribution of Ag precipitate hardening exceeded over 70%, which showed that the overall strength was resulted from the strengthening of Ag precipitate, consistent with previous analysis[6]. In the presence of HMF, the overall strength was decreased, although the Ag solid solution hardening was increased by 20%. However, the Ag concentration in proeutectic Cu and the volume of proeutectic Cu were increased by the imposition of HMF, as shown in Table 1. Therefore, if the reasonable heat treatment is applied, the higher strength is supposed to be attained by applying the HMF to enhance the Ag precipitates [3].

Table 5

4.3 Modeling of resistivity of CuAg microcomposite

Electrical resistivity of CuAg composite can be calculated by combining the electrical resistivities of its constitutional components: proeutectic Cu matrix, Ag precipitates within proeutectic Cu and the eutectic component. The resistivity of Cu matrix, $\rho_{\text{Cu matrix}}$, is primarily dependent on interface scattering and on impurity scattering from Ag dissolved in the Cu matrix. Impurity scattering resistivity, $\rho_{\text{Ag solubility}}$, can be estimated by the solubility of Ag in Cu. The resistivity increase per 1wt% Ag addition is 3.55 nΩm [49]. The resistivities of eutectic component and Ag precipitate result from the respective scattering interface. Therefore, overall resistivity could be written as

$$\rho = \left(\frac{f_{\text{Cu matrix}}}{\rho_{\text{Ag solubility}} + \rho_{\text{Cu interface}}} + \frac{f_{\text{Eutectic}}}{\rho_{\text{Eutectic interface}}} + \frac{f_{\text{Ag precipitate}}}{\rho_{\text{Ag precipitate interface}}} \right)^{-1} \quad (13)$$

where f is the volume fraction and ρ is the electrical resistivity. Each suffix depicts the relevant phase.

The interface scattering resistivity of each phase can be simulated by the model developed by Dingle et al [18]

Wire models that are applicable for proeutectic Cu components:

$$\rho = \rho_0[1 + (1 - p) l_0/\lambda] \text{ for } \lambda \ll l_0 \quad (14)$$

$$\rho = \rho_0[1 + 0.75(1 - p) l_0/\lambda] \text{ for } \lambda \gg l_0 \quad (15)$$

Thin film models that are applicable for eutectic components:

$$\rho = \rho_0 \frac{4}{3} [(1 - p)/(1 + p)] l_0/[T \log(l_0/t)] \text{ for } t \ll l_0 \quad (16)$$

$$\rho = \rho_0 \left[1 + \frac{3}{8} (1 - p) l_0/t \right] \text{ for } t \gg l_0 \quad (17)$$

where, ρ_0 is bulk electrical resistivity, p is interface scattering or specularity factor; l_0 is the mean free path of conduction electrons in the bulk phase, λ is the characteristic length, t is the thickness of the film, and T is the temperature.

Comparing the mean electron free path of proeutectic Cu, eutectic and Ag precipitate to the dimensions of respective phases, as illustrated in Table 1, equation (15) was available for the resistivity of proeutectic Cu and eutectic and equation (17) was for the resistivity of Ag precipitates. Interface scattering, p , and mean electron free path, l_0 , was used by following other researchers [20]. The modeling parameters and modeling results are summarized in Table 6. It shows that the modeling values of total resistivities of as-drawn CuAg composites at 293K and at 77K are approaching to our experimental results. The total resistivity of CuAg composite was close to the resistivity of proeutectic Cu, which indicated that the overall resistivity was dependent on the resistivity of the Cu matrix. The Ag precipitates, with minor volume fraction, did reduce the resistivity of the Cu matrix because of their excellent

electrical transport. The dissolved Ag, however, significantly increased the resistivity of Cu matrix, and increased the overall resistivity. Table 6 shows that the resistivities of the samples with HMF are higher than that without HMF. The increasing of resistivity in the presence of HMF was verified by both experiments and modeling, though there were some deviations between the measured and predicted data. In our study, external HMF trapped more Ag in the proeutectic Cu matrix during the cooling process, and Ag did not precipitate more enough in the further solid reaction. As predicted by the model, dissolved Ag increased resistivity, but Ag precipitates did just the opposite, thus increasing the overall resistivity of the composite.

Table 6

5. Conclusion

We studied the effects of external HMF on microstructure and microhardness in solidified Cu28%Ag alloy. HMF resulted in an increase in dendrite arm spacing of proeutectic Cu by about 18% because of the convection suppression effect caused by the interaction between the HMF and the conductive melt. Moreover, HMF increased the solubility of Ag in proeutectic Cu, and decreased the spacing of Ag precipitates in proeutectic Cu. The Ag precipitates in the proeutectic component had a cube-on-cube orientation relationship (OR) with the Cu matrix. HMF didn't change the OR, but increased the volume fraction of rod-like Ag precipitates and decreased the spacing of all Ag precipitates. The decreased spacing was attributed to the increased growth velocity of Ag precipitates during the subsequent solid reaction after solidification. Changes in the solubility and the morphology of Ag precipitates increased local microhardness in proeutectic Cu regions. We developed a

strengthening model ([Equ 12](#)) relating hardness to the microstructural parameters.

The microstructural changes caused by HMF during solidification affected the microstructure, and therefore mechanical and electrical properties of as-drawn CuAg microcomposites. The microstructure of as-drawn CuAg composites solidified under HMF is coarser in both microscale and nanoscale. This microstructure feature is inherited from the coarser microstructure under HMF. The Cu and Ag phases in proeutectic region of as-drawn samples still had a cube-on-cube OR, but there was slight deviation of about 1 degree. In the presence of HMF, both hardness and strength of the composites were decreased, and resistivity at room temperature and of 77K was increased. The results were discussed with respect to microstructural parameters, strength and resistivity. Our model demonstrates that Ag precipitates play an important role in strengthening and resistivity. This provides a quantitative evaluation of the effect of HMF on microstructural evolution, concentration contributions, and relevant properties of CuAg alloys.

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References

- [1] C.A. Davy, H. Ke, P.N. Kalu, S.T. Bole, [IEEE Trans. Appl. Super.](#) 18 (2008) 560-563.
- [2] K. Han, V. Toplosky, R. Goddard, J. Lu, R. Niu, J. Chen, [IEEE Trans. Appl. Super.](#) 22 (2011) 6900204.
- [3] Y. Sakai, H.J. SchneiderMuntau, [Acta Mater.](#) 45 (1997) 1017-1023.
- [4] Y. Sakai, K. Inoue, T. Asano, H. Wada, H. Maeda, [Appl. Phys. Lett.](#) 59 (1991) 2965-2967.
- [5] A. Benghalem, D.G. Morris, [Acta Mater.](#) 45 (1997) 397-406.
- [6] K. Han, A.A. Vasquez, Y. Xin, P.N. Kalu, [Acta Mater.](#) 51 (2003) 767-780.
- [7] R. Monzen, K. Murase, H. Nagayoshi, C. Watanabe, [Phil. Mag. Lett.](#) 84 (2004) 349-358.
- [8] C. Watanabe, R. Monzen, H. Nagayoshi, S. Onaka, [Phil. Mag. Lett.](#) 86 (2006) 65-73.
- [9] I. Manna, S.K. Pabi, [J. Mater. Sci. Lett.](#) 9 (1990) 1226-1228.
- [10] S.P. Gupta, *Can. Metall. Q.* 37 (1998) 141-159.
- [11] R. Raty, H.M. Miekkoja, [Phil. Mag.](#) 18 (1968) 1105-&.
- [12] T. Miyazawa, T. Fujii, S. Onaka, M. Kato, [J. Mater. Sci.](#) 46 (2011) 4228-4235.
- [13] R. Monzen, T. Terazawa, C. Watanabe, [Metall. Mater. Trans. A](#) 41 (2010) 1936-1941.
- [14] W. Gust, J. Beuers, J. Steffen, S. Stiltz, B. Predel, [Acta Metall. Mater.](#) 34 (1986) 1671-1680.
- [15] D. Hamana, L. Boumaza, [J. Alloy. Compd.](#) 477 (2009) 217-223.

- [16] D.W. Yao, L.N. Song, A.P. Dong, L.T. Wang, L. Zhang, L. Meng, [Mater. Sci. Eng. A](#) 558 (2012) 607-610.
- [17] J.B. Liu, L. Zhang, D.W. Yao, L. Meng, [Acta Mater.](#) 59 (2011) 1191-1197.
- [18] R.B. Dingle, [Proc. R. Soc. London Ser. A](#) 201 (1950) 545-560.
- [19] F. Heringhaus, H.J. Schneider-Muntau, G. Gottstein, [Mater. Sci. Eng. A](#) 347 (2003) 9-20.
- [20] F. Heringhaus, [Quantitative analysis of the influence of the microstructure of strength, resistivity, and magnetoresistance of eutectic silver copper](#), Verlag Shaker, Aachen, 1998.
- [21] D. Mattissen, D. Raabe, F. Heringhaus, [Acta Mater.](#) 47 (1999) 1627-1634.
- [22] D. Raabe, D. Mattissen, [Acta Mater.](#) 46 (1998) 5973-5984.
- [23] A. Gaganov, J. Freudenberger, E. Botcharova, L. Schultz, [Mater. Sci. Eng. A](#) 437 (2006) 313-322.
- [24] L. Zhang, L. Meng, J.B. Liu, [Scripta Mater.](#) 52 (2005) 587-592.
- [25] M.W. Yao, A. Chait, A.L. Fripp, W.J. Debnam, [J. Cryst. Growth](#) 173 (1997) 467-480.
- [26] R. Moreau, [Prog. Cryst. Growth Charact. Mater.](#) 38 (1999) 161-194.
- [27] X. Li, A. Gagnoud, Z. Ren, Y. Fautrelle, R. Moreau, [Acta Mater.](#) 57 (2009) 2180-2197.
- [28] R. Moreau, O. Laskar, M. Tanaka, D. Camel, [Mater. Sci. Eng. A](#) 173 (1993) 93-100.
- [29] P. Lehmann, R. Moreau, D. Camel, R. Bolcato, [J. Cryst. Growth](#) 183 (1998) 690-704.
- [30] G.M. Li, E.G. Wang, L. Zhang, X.W. Zuo, J.C. He, [Acta Metall. Sin.](#) 46 (2010)

1128-1132.

[31] X.W. Zuo, C.C. Zhao, E.G. Wang, L. Zhang, K. Han, J.C. He, [J. Low Temp. Phys.](#) 170 (2013) 409-417.

[32] ASM International. Handbook Committee, ASM handbook, 10th ed., ASM International, Materials Park, OH, 1990.

[33] L. Zhang, L. Meng, [Scripta Mater.](#) 52 (2005) 1187-1191.

[34] S.I. Hong, M.A. Hill, [Mat. Sci. Eng. A](#) 264 (1999) 151-158.

[35] W. Kurz, D.J. Fisher, Fundamentals of solidification, 4th rev. ed., Trans Tech Publications, Switzerland, 1998.

[36] V.Botton, P.Lehmann, R.Bolcato, R.Moreau, R.Haettel, [Int. J. Heat Mass Tran.](#) 44 (2001) 3345-3357.

[37] D.J. Maclean, T. Alboussière, [Int. J. Heat Mass Tran.](#) 44 (2001) 1639-1648.

[38] X. Li, Z.M. Ren, Y. Fautrelle, [Acta Mater.](#) 54 (2006) 5349-5360.

[39] H.Q. Hu, Metal solidification theory, Chinese Mechanical Publisher, Beijing, 2000.

[40] X. Li, Z. Ren, Y. Fautrelle, [Acta Mater.](#) 54 (2006) 5349-5360.

[41] D. Hamana, M. Hachouf, L. Boumaza, e. al., [J. Alloy Compd.](#) 2 (2011) 899-910.

[42] C. Zener, [Trans. Inst. Min. Metall., Sect. A](#) 167 (1946) 550-595.

[43] W.F. Smith, J. Hashemi, Foundations of materials science and engineering, 4th ed., McGraw-Hill, Boston, 2005.

[44] J. Freudenberger, J. Lyubimova, A. Gaganov, H. Witte, A.L. Hickman, H. Jones, M. Nganbe, [Mat. Sci. Eng. A](#) 527 (2010) 2004-2013.

[45] N.J. Petch, [J. Iron Steel Inst.](#) 174 (1953) 25-28.

[46] E.O. Hall, [Proc. R. Soc. London, Ser. B](#) 64 (1951) 747-753.

[47] S.I. Hong, M.A. Hill, [Acta Mater.](#) 46 (1998) 4111-4122.

[48] Y.Z. Tian, S.D. Wu, Z.F. Zhang, R.B. Figueiredo, N. Gao, T.G. Langdon, [Mat. Sci. Eng. A](#) 528 (2011) 4331-4336.

[49] J.R. Davis, ASM International. Handbook Committee, Copper and copper alloys, ASM International, Materials Park, OH, 2001.

Fig.1 SEM images of Cu₂₈%Ag alloys solidified with and without a 12T HMF. (a) & (b) indicate micro-scale morphologies without a HMF and with a 12 T HMF, respectively. The arrows indicate the direction of the external high magnetic field, **B**. (c) & (d) show the morphologies of nano-scale Ag precipitates in proeutectic Cu without a HMF and with a 12T HMF, respectively. The ellipses (from d1 to d4) indicate some areas with rod-like Ag precipitates and the rectangular inset shows high magnified image of d1 area.

Fig. 2 TEM dark images showing crystallographic morphology of Ag precipitates in proeutectic Cu of Cu₂₈%Ag alloys solidified with and without a HMF, (a) 0T, (b) 12T. The left-upper insets show the corresponding SADPs, and the arrows indicate the axis direction of the samples, which is parallel to the HMF direction. The zone axis is close to $[\bar{2}33]$, and some diffraction spots are indexed. The rectangular inset shows a magnified image of rod-like Ag precipitates inside the ellipse.

Fig.3 Longitudinal SEM images with different drawing strains. Fig. 3 (a)(b)(c) indicates the morphologies of non-HMF solidification sample with drawing strain of 1.4, 2.4, and 3.5, respectively; (d)(e)(f) show the morphologies of 12T-HMF solidification sample with drawing strain of 1.4, 2.4 and 3.5, respectively. The lighter regions are eutectic colonies with bundles of Ag and Cu. The darker ones are proeutectic Cu (embedded with Ag precipitates).

Fig. 4 Experimental data and fitting curves of eutectic fiber spacing of as-drawn Cu28%Ag microcomposites plotted against drawing strain, where the scattering points are experimental data, and the solid curves are the fitting results, as expressed by Eq.(1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig.5 Dark field TEM micrographs of their corresponding SADPs of as-drawn samples at the drawing strain of 3.5. (a) non-HMF sample and (b) the 12T-HMF sample. The zone axis is close to $[011]$, and g vector is $\{200\}$. The drawing direction is parallel to the direction of the external HMF during solidification, as depicted by the arrows.

Fig.6 Comparison of microhardness and ultimate tensile strength of Cu28%Ag composites on longitudinal sections plotted as the drawing strains with and without a HMF. The inset image in Fig. 6(a) shows the indentations on eutectic and proeutectic region of as-cast sample and the diagonal lengths of the diamond indentation are labelled. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1 Quantitative results from the morphologies of proeutectic Cu and Ag precipitates indicated in Fig.1

Region	Characterization	0T	12T
Proeutectic Cu	Length(μm)	115 $\pm$ 3.0	114 $\pm$ 3.9
	Dendrite arm spacing(μm)	51.2 $\pm$ 3.6	60.3 $\pm$ 2.7
	Volume fraction	82.2 $\pm$ 1.7	85.5 $\pm$ 2.1
Eutectic colony	Lamellar spacing (μm)	1.33 $\pm$ 0.1	1.59 $\pm$ 0.1
Ag precipitate in proeutectic Cu	Spacing (nm)	177 $\pm$ 21	134 $\pm$ 15
	Size (nm)	29 $\pm$ 8	25 $\pm$ 10

Table 2 The Ag concentrations in proeutectic Cu regions of Cu28%Ag alloys solidified with and without a 12T HMF

Description	Case	Weight fraction	Volume fraction	Atom fraction
Sum of both Ag solubility and Ag precipitate in proeutectic Cu detected by FESEM/EDS	0 T	11.5±0.3	/	/
	12T	12.8±0.6	/	/
Statistical Ag precipitate in proeutectic Cu by FESEM	0 T	10.7±0.3	9.2±0.2	/
	12T	10.3±0.4	8.9±0.3	/
Predictable value of Ag solubility in proeutectic Cu by FESEM/EDS and morphology analysis	0 T	0.8	/	/
	12T	2.5	/	/
Ag solubility in proeutectic Cu by TEM/EDS	0 T	1.7±0.02	/	1.0
	12T	2.4±0.1	/	1.4

Table 3 Quantitative results from the morphology characterization of Ag precipitates

indicated in Fig.5

Case	Spacing, nm	Thickness, nm	Volume fraction, %
0T	24.1±5.3	9.2±2.8	9.4±0.5
12T	36.2±8.0	11.5±4.5	9.0±0.3

Table 4 The resistivity and electrical conductivity of as-drawn Cu28%Ag microcomposites with a drawing strain of 3.5, where IACS= International Annealing Copper Standard.

	Conductivity (%IACS)	Resistivity ρ (n Ω m)	
		293 K	77 K
0T	77.5	22.24	7.08
12T	73.1	23.58	7.16

Table 5 The individual contributions to the total strength of as-drawn with a drawing strain of 3.5 for Cu28%Ag microcomposites (MPa)

	0 T	12 T
Ag Solid solution hardening	121.6	148.3
Ag precipitate hardening	603.0	515.7
Eutectic work hardening	43.5	33.1
Total strength	768.1	697.1
Difference in strength between 0T		
and 12T samples	-71.0	

Table 6 Modeling parameters and individual contributions to the total resistivity of as-drawn with a drawing strain of 3.5 for Cu28%Ag micorocomposite (Resistivity unit: nΩm)

The relative parameters applied in Eqs(14-17)						
	Ag precipitate		Cu matrix		Eutectic	
	293 K	77 K	293 K	77 K	293 K	77 K
$\rho_{0,(n\Omega m)} [20]$	16.86	3.28	17.87	2.43	17.18	3.01
$\rho [20]$	0.5	0.5	0	0	0.81	0.84
Mean electron free path, l_0 , nm [20]	41	119	34	150	38	131
As-drawn CuAg composite with a drawing strain of 3.5						
Contents			293 K		77 K	
			0T	12T	0T	12T
Volume fraction of Cu matrix			0.74	0.78	0.74	0.78
Resistivity of Cu matrix	Interface scattering		17.90	17.88	2.52	6.21
	Solubility scattering		5.36	7.85	5.36	7.85
Volume fraction of Eutectic			0.18	0.15	0.18	0.15
Resistivity of Eutectic	Interface scattering		17.58	17.52	3.01	3.10
Volume fraction of Ag precipitate			0.08	0.07	0.08	0.07
Resistivity of Ag precipitate	Interface scattering		16.90	16.89	3.28	3.29
Total resistivity			21.37	23.24	5.61	7.98
Measured data			22.24	23.58	7.08	7.16