



Precipitation and dissolution of Ag in ageing hypoeutectic alloys



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ABSTRACT

Understanding the precipitate kinetics of Ag in proeutectic Cu is valuable to optimize the precipitation and morphology of Ag for high strength high conductivity hypoeutectic Cu–Ag alloys. The precipitation behaviors of as-solution treated Cu28 wt.%Ag alloys were analyzed by differential scanning calorimetric (DSC). The results indicated that the activation energies of Ag-rich phase formation and dissolution were 55.3 ± 22.4 kJ/mol and 129.1 ± 20.7 kJ/mol, respectively. The as-solution alloy was further aged at different temperatures for 2 h. Their microhardness and electrical resistivity were measured. The results demonstrated that at the ageing temperature of 405 °C, less scattering effects reflected more Ag precipitations from Cu matrix than the rest of temperatures. At 475 °C, however, Ag precipitates produced more strengthening effects. Above results were related to the competition between precipitation and dissolution of Ag in proeutectic Cu. This interpretation is supported by TEM observations on Ag precipitation.

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1. Introduction

Cu–Ag hypoeutectic materials with high strength and high conductivity are vital winding conductors for both DC resistive and AC pulsed high-field magnet coils [1–4]. Previous reports [4–7] have shown that microstructures of hypoeutectic CuAg alloys have two components: (a) eutectic networks that surround (b) Cu-rich proeutectic dendrites with nano sized Ag precipitates. Cu-rich proeutectic dendrites with a large proportion of volume fraction play crucial roles in properties of the Cu–Ag alloys. The morphology of nano sized Ag precipitations and Ag dissolution in proeutectic Cu dendrites are the most important influencing factors [5,8]. Therefore, understanding the precipitate kinetics is necessary to optimize the precipitate and distribution of Ag in proeutectic Cu. Moreover, the investigation of precipitation and dissolution could be also applied to clarify the Ag diffusion theories along migrating or stationary grain boundaries [9,10]. Two (discontinuous and continuous) precipitation reactions are strongly dependent on the silver content [11]. As the Ag composition was less than 8 wt.%, the Cu-rich solid solutions were transformed into structures with rod-like Ag-rich precipitations embedded in Cu-rich

matrix by discontinuous precipitation. Coarse precipitates from the high-angle grain boundaries were generated [9,10,12,13]. The estimated activation energy of Ag precipitation [10,12,14], growth direction, morphology and habit planes [15] were reported. Whereas the silver content was more than 8 wt%, a sufficient volume fraction of eutectics suppressed discontinuous precipitation by the absence of grain boundaries and fine precipitates were observed by continuous precipitation mode. By comparison, fine Ag precipitations by continuous reaction had greater strengthening contributions than coarsening precipitations by discontinuous one [11]. Consequently, in order to improve the strengthening effect, continuous mode should be promoted and discontinuous mode should be suppressed [11]. However, up to date, most of the precipitate kinetics of Cu–Ag alloy was paid attention to the low Ag content. Rare investigations were focused on the precipitation and dissolution of Ag in Cu–Ag alloys with higher silver content. Their activation energies and the properties have not been carried out so far. The investigation of precipitation and dissolution could be used to design heat treatment procedure that could provide Ag solid solution strengthening effects and precipitation effects. Additionally, the dissolution of Ag could increase the electrical resistivity of CuAg microcomposites if inappropriate thermomechanical process was employed [16]. In this paper, the activation energy, the precipitation behaviors, the properties and microstructure of Cu–28 wt.% Ag alloys were analyzed by differential scanning calorimetric (DSC) analysis, microhardness, resistivity tests and transmission electron microscopy (TEM).

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2. Experimental methodologies

A Cu–28 wt.% Ag (weight percent, expressed as Cu28%Ag in the context) alloy was melt in a vacuum induction furnace and cast in a Cu mould under high-purity Ar atmosphere. The alloy was solution treated at 760 °C for 2 h followed by quenching into water. The solid-solution specimen was machined into several sheets with about 0.4 mm in thickness and aged at temperatures between 300 °C and 580 °C for 2 h. Microhardness tests were conducted on an Instron Wilson-Wolpert Tukon 2100 microhardness tester with a diamond square-based pyramid under a load of 50 g and the dwelling time of 10 s. The resistivity was measured by four-probe DC method in the deionized water. The differential scanning calorimetric (DSC) analysis was carried out under argon atmosphere with a Shimadzu DSC-60. The calibration procedures of DSC tests could be found in a separate paper [17]. As there is a eutectic reaction at about 540 °C between Al pans and Cu matrix in Cu28%Ag alloys, Al₂O₃ powders with 100 µm were used to separate the interfaces between Al and Cu. Thin foils for TEM were prepared by argon ion-milling with a voltage of 5 kV at an incidence angle of 3°. The foils were observed in a FEI-Tecna G2 TEM operating at 200 kV.

3. Results and discussion

In our Cu28%Ag alloy, [18] the volume fraction of proeutectic Cu was larger than 80% [18]. Consequently, the heat flow of proeutectic Cu would be obviously over that of the eutectic component in DSC data obtained from Cu28%Ag alloys. The heat flow of proeutectic Cu is expected to dominate the total heat flow. At elevated temperature (>250 °C), both exothermic Ag precipitation and endothermic Ag dissolution in proeutectic Cu will occur [14]. Those two reactions are shown in the DSC curves of as-solution treated Cu28%Ag alloys in Fig. 1. At the exothermic peak temperature between 250 °C and 400 °C, the solid arrow indicates the precipitation of Ag. The solid arrow marking lowest point between 400 °C and 500 °C indicates Ag dissolution. We observed another abnormal peak between 350 °C and 450 °C when the Al₂O₃ powders in Al pans were used in the DSC measurements. When Al₂O₃ crucibles were used instead, no abnormal peak was detected. We verified that this peak was the result of the Al₂O₃ powders. In our DSC measurements, we detected reactions of exothermic Ag precipitation and endothermic Ag dissolution.

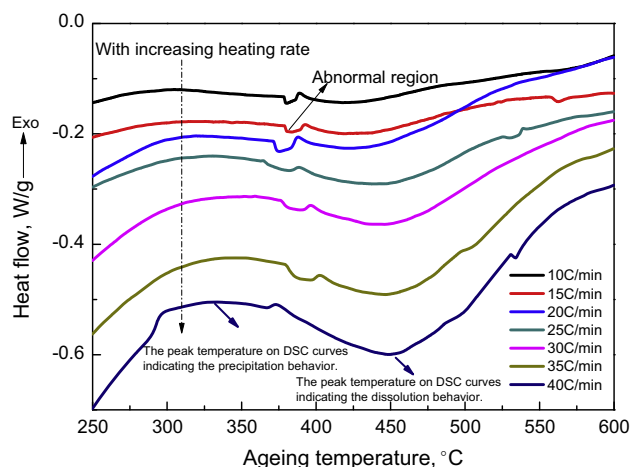


Fig. 1. Differential scanning calorimetric curves of Cu28%Ag alloys after solution treated at 760 °C for 2 h with different heating rates from 10 °C/min to 40 °C/min (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

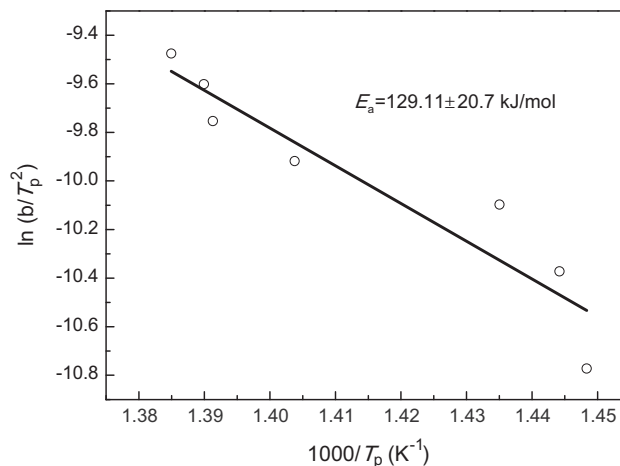


Fig. 2. The experimental data and fitting curve of Kissinger equation plotted between $\ln(b/T_p^2)$ and $1000/T_p$.

The activation energy (E_a) could be calculated by the shift of the reaction temperatures in DSC measurements with different heating rates. E_a could be determined by the Kissinger equation:

$$\ln \left(\frac{b}{T_p^2} \right) = -\frac{E_a}{RT_p} + C \quad (1)$$

where b is the heating rate, E_a the activation energy (kJ/mol), T_p the reaction (or peak) temperature in the DSC curves, R the universal gas constant and C is a constant.

The linear fitting of data $\ln(b/T_p^2)$ against $1000/T_p$ is plotted in Fig. 2. The fitting gave 55.3 ± 22.4 kJ/mol as [20] the activation energy of Ag-rich precipitation (the first reaction of the DSC curves in Fig. 1), which is lower than that in Cu–7 wt.%Ag alloy (95 ± 4 kJ/mol) [14], Cu–3.8 at.%Ag bicrystals (144.1 kJ/mol) [10] and Cu–5.7 wt.%Ag single crystal (185 kJ/mol). The activation energy of Ag-rich dissolution (the high temperature reaction in the DSC curves in Fig. 1) was 129.1 ± 20.7 kJ/mol. This value is lower than that measured by others (195 kJ/mol) [19]. These discrepancies could be related to the fact that the activation energies and diffusion rates were influenced by both Ag contents and heating rate. Since both precipitation and dissolution were diffusion-controlling reactions that require finite times and driving forces to complete. Different supersaturated Ag contents induced different driving forces. Variation in heating rates alters solvus concentrations. These caused in the changes of the activation energies. Therefore, higher Ag composition reduced the activation energy of the precipitation and dissolution of Ag in Cu matrix, which might be beneficial for the precipitation and dissolution of Ag in Cu matrix.

With increasing ageing temperatures, the Ag precipitation competes with the Ag dissolution in proeutectic Cu if the Ag content remains constant. In Fig. 3, samples experienced ageing at various temperatures at constant time before DSC measurements. In those samples, similar nucleation and growth process of Ag precipitates should occur. The similarities and differences could be identified from the measured reaction temperatures. At lower ageing temperatures, Ag precipitations required longer than 2 h of precipitation times to complete. Therefore, the samples treated at higher temperatures have less supersaturated Ag in proeutectic Cu, and the driving force for further precipitation is reduced. This pushed the measured precipitation temperature higher in subsequent DSC measurements. The precipitation temperatures of DSC samples shown in Fig. 3(a) indicated that as the ageing temperature increased, the peak temperature increased until 405 °C. The ageing temperature higher than 405 °C was likely to promote the

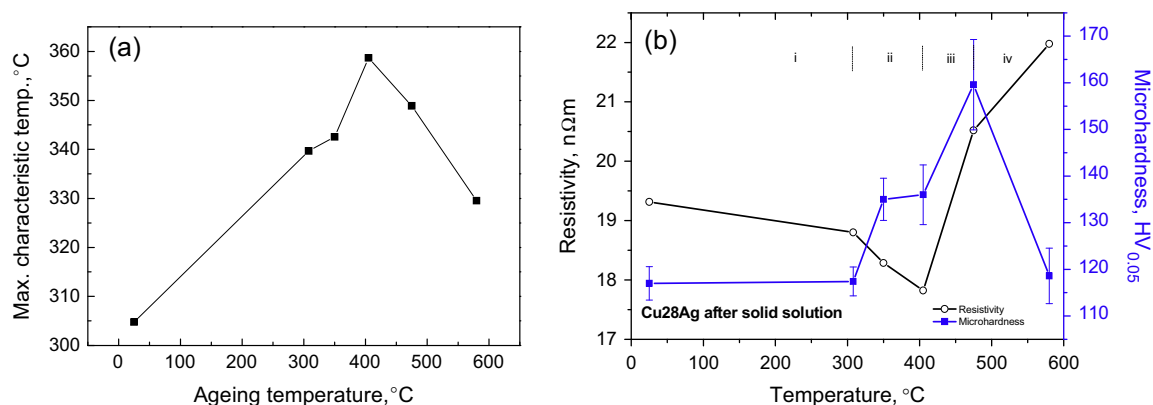


Fig. 3. (a) The DSC peak temperatures relative to precipitation reactions of Cu28%Ag alloys after aged with different ageing temperatures as a function of the ageing temperature. (b) Both the resistivity and the microhardness of Cu28%Ag alloys with different ageing temperature after solid-solution treatment at 760 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

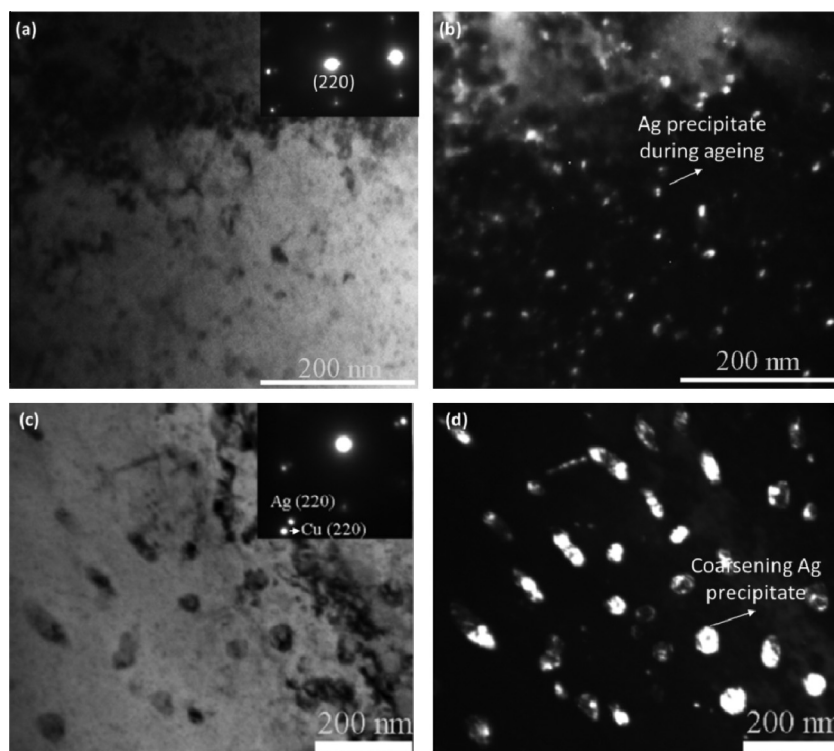


Fig. 4. TEM micrographs of ageing Cu28%Ag alloys, (a) and (b) showing Bright Field (BF) and Dark Field (DF) images at the temperature of 405 °C; (c) and (d) showing BF and DF images at the temperature of 580 °C, respectively; the right-upper insets show the corresponding selected area diffraction patterns.

dissolution of Ag in Cu matrix. This reduced the measured precipitation temperature in DSC measurements. We concluded that the ageing temperature of 405 °C produced more Ag precipitates than that at the rest of ageing temperatures.

Both the electrical resistivity and microhardness of hypoeutectic CuAg alloys are dependent on the precipitation and dissolution of Ag in proeutectic Cu. The Ag dissolution and precipitation of Ag in proeutectic Cu could affect the changes in resistivity and microhardness. Fig. 3(b) shows the effect of ageing temperatures on electrical resistivity and microhardness of Cu28%Ag alloys. The results indicated that as ageing temperatures increased, the electrical resistivity decreased until 405 °C, and the microhardness increased until 475 °C. These findings were thought from the competitive growth between dissolution and precipitation of Ag in proeutectic Cu. We could divide the growth into at least four

different stages to describe the competition. In stage I (ageing temperature lower than 300 °C), Ag precipitates started to nucleate and grow when the energies were larger than the activation energies of Ag phase formation. At this stage, the impact of Ag precipitation on hardness is marginal. The Ag precipitations reduce supersaturated Ag solid solution in Cu matrix, and consequently, decrease the impurity scattering and the resistivity. In stage II (ageing temperature ranging from 300 °C to 405 °C), Ag precipitation became dominant. Because Ag precipitation increased with increased ageing temperatures, as observed in Fig. 4(a) and (b), microhardness rapidly enhanced, and the resistivity decreased obviously. In stage III, obvious Ag dissolutions started with increasing ageing temperature, Ag solute increased, which made the resistivity increase rapidly. The total strengthening contributions from both solid solute hardening and precipitate hardening were likely to increase further

and the peak hardness was reached at the ageing temperature of 475 °C. We thought that it might attribute to the gradual growth of Ag precipitate at the ageing temperature of 475 °C after entire nucleation at 405 °C. In final stage, Ag dissolution was dominant. The large percentage of dissolved Ag further increased resistivity. The dissolution of Ag consumed Ag precipitates. TEM observations, shown in Figs. 4(c) and (d), indicated significant coarsening of Ag precipitations occurred when samples were aged at 580 °C. Consequently, the volume reduction and coarsening of Ag precipitates decreased the hardness. The variations of resistivity with ageing temperature were consistent with the analysis in the peak temperature of Ag precipitations in the DSC measurement, as shown in Fig. 3(a). This indicates that previous optimum ageing temperature for Cu24Ag alloy between 330 °C and 430 °C was attributed to the maximized precipitation and minimized dissolution of Ag [3].

4. Conclusion

The precipitation behaviors of Cu28Ag alloys were analyzed by differential scanning calorimetric, and the activation energies of Ag-rich phase precipitate formation and dissolution were 55.3 ± 22.4 kJ/mol and 129.1 ± 20.7 kJ/mol, respectively. The competition between precipitation and dissolution of Ag could be reflected by both the microhardness and the resistivity. In samples aged at about 405 °C, the volume fraction of refined Ag precipitation in Cu matrix reached maximum, accompanied by minimum electrical resistivity. Samples aged at temperature above 475 °C have the coarsened Ag precipitates, reduced hardness and elevated electrical resistivity.

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