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Morphology evolution of two-phase Cu-Ag alloys under different conditions*

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Abstract: Cu-Ag filamentary microcomposites with different Ag contents were prepared by cold drawing and intermediate heat treatments. The microstructure characterization and filamentary distribution were observed for two-phase alloys under different conditions. The effect of heavy drawing strain on the microstructure evolution of Cu-Ag alloys was investigated. The results show that the microstructure components consist of Cu dendrites, eutectic colonies and secondary Ag precipitates in the alloys containing 6%~24% (mass fraction) Ag. With the increase in Ag content, the eutectic colonies in the microstructure increase and gradually change into a continuous net-like distribution. The Cu dendrites, eutectic colonies and secondary Ag precipitates are elongated in an axial direction and developed into the composite filamentary structure during cold drawing deformation. The eutectic colonies tend to evolve into filamentary bundles. The filamentary diameters decrease with the increase in drawing strain degree for the two-phase alloys, in particular for the alloys with low Ag content. The reduction in filamentary diameters becomes slow once the drawing strain has exceeded a certain level.

Key words: Cu-Ag alloy, Microstructure, Strain, Filamentary composite
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INTRODUCTION

As advanced conductor materials, the nano-structured microcomposites of copper alloys have high strength and conductivity. Therefore, they have been expected to receive preferential development for their practical applications in technological fields, such as modern nuclear physics, high field magnet designs, large-scale integrated circuits, high-speed electric locomotives, and modern medical apparatus (Grünberger *et al*., 2001; Herlach, 2001; Rosseel *et al*., 2001; Hong *et al*., 2004; Gaganov *et al*., 2004; Li and Meng, 2005; Zhang and Meng, 2005; Liu and Meng, 2006). In general, strong drawing or rolling strain is an effective approach for producing nano-scale microcomposites in copper alloys containing two phases with high ductility. In the two-phase alloys, if the additional phase produced from metallic elements belongs to the face-centered cubic (FCC) system, both phases in the alloys must exhibit excellent strain compatibility and a coordinative structure during strong deformation, because the slip system of the added phase is the same as that for the Cu matrix. Therefore, a reasonable structure and distribution of two-phase filaments should be obtained more easily in the nano-structured microcomposites with an FCC-FCC matching of the phase components, which can be expected to result in an excellent combination of strength and conductivity (Benghalem and Morris, 1997; Song *et al*., 2005; Liu *et al*., 2007).

As a typical alloy with FCC-FCC matched phases, Cu-Ag has strongly attracted attention (Sakai *et al*., 1991; Benghalem and Morris, 1997; Grünberger *et al*., 2002; Zhang *et al*., 2005; He *et al*., 2008). The evolutionary course of the microstructure

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morphology in the Cu-Ag is mainly dependent on the chemical composition, strain level, heat treatment, and lattice distortion (Lee and Hong, 2003; Zhang and Meng, 2003; Ohsaki *et al*., 2003; Gaganov *et al*., 2006; Lin and Meng, 2008). In particular, the Ag content plays an important role in its effect on practical strength and conductivity, because the aspect, distribution, proportion and precipitation of the added phase can change with the Ag content and control the filamentary formation and evolution. Previous studies indicated that the as-cast alloys containing lower than 6% (mass fraction, unless otherwise stated, the percentage referred to mass fraction in the rest of the paper) Ag had only a single Cu matrix while the alloys containing higher than 6% Ag had an eutectic structure besides a Cu matrix (Sakai *et al*., 1991; Grünberger *et al*., 2002; Liu *et al*., 2006; Liu and Meng, 2008). The Ag filaments in as-drawn microstructure increased with the increase in the Ag content due to the increase in the eutectic proportion. On the basis of the presented investigations, Cu-Ag alloys with isolated, discontinuous and continuous eutectic colonies were prepared by changing the Ag content. The filamentary composite structure was produced by heavy drawing and intermediate heat treatments in order to study the relationship between the microstructure and Ag concentration. The microstructure under different conditions was observed and the evolutionary behavior discussed for the FCC-FCC double phases in Cu-Ag alloys during strong strain.

EXPERIMENTS

The tested Cu-Ag alloys containing 6%, 12% and 24% Ag were melted in a vacuum induction furnace and cast into cylindrical ingots of 23.0 mm in diameter. The ingots were step-annealed at 700 °C for 2 h and then at 720 °C for 2 h. The surface layer of about 0.8 mm in thickness was removed from the ingots after step-annealing. Cold drawing was performed at ambient temperature. Drawing reduction was expressed as the draw ratio by $\eta=\ln(A_0/A)$, where A_0 and A are the original and final cross-section areas of the drawn specimens. The drawn samples were intermediate-annealed for 1 h at 400, 380 and 360 °C at η=1.3, 2.0 and 2.8, respectively.

Optical microscopy (LEICA DMLM, Germany), scanning electron microscopy (SEM) (HITACHI S-570, Japan), field emission scanning electron microscopy (FESEM) (FEI SIRION200, the Netherlands) and transmission electron microscopy (TEM) (JEOL JEM-2010, Japan) were employed to observe the microstructure. The metallographic samples for the observation of optical microscopy and SEM were taken respectively on the transverse section and longitudinal section of the cylindrical ingots and drawn wires. The metallographic samples from the cylindrical ingots were the cubic blocks of 15 mm×15 mm×15 mm and from the drawn wires the wire segments of 15 mm in length. The solution for etching the polished samples was composed of 100 ml C_2H_5OH, 5.0 ml HCl and 2.0 g $FeCl_3$. Some apparent 3D microstructures were clearly shown by engaging the observed images from the transverse and longitudinal sections. The scale of the filamentary structure was determined according to the observation results from SEM.

RESULTS AND DISCUSSIONS

The microstructure of the as-cast alloys with different Ag content is shown in Fig.1. All alloys consist of pro-eutectic Cu dendrites and eutectic colonies. There is obvious dendritic segregation, in particular in the alloys with a lower Ag content. Cu-6%Ag is primarily composed of Cu dendrites besides some small eutectic colonies dispersed between Cu dendritic arms due to low Ag content in the alloy. The small eutectic colonies in Cu-6%Ag should belong to the products of non-equilibrium freezing because the solubility limit of Ag solute in Cu matrix is about 7.9% and the eutectic colonies are unable to form in equilibrium freezing. The eutectic colonies display extended island-like branches in Cu-12%Ag and a continuous net-like structure surrounding Cu dendrites in Cu-24%Ag due to increased Ag concentration. The dendritic morphology is exhibited more apparently in alloys with middle and high Ag content because the primary Cu grains are separated by more eutectic colonies.

The microstructure from SEM observation is shown in Fig.2 for the drawn alloys with a high draw ratio. The eutectic colonies and Cu dendrites evolved into filamentary bundles during heavy drawing. Similar plastic flowing and strain hardening behavior from an identical slip system in Cu and Ag lattices resulted in symmetrical elongation in the axial direction and uniform shrinkage in the radial direction for both phases. Island- or net-like morphology on the transverse section was still kept after heavy drawing for the alloys with different Ag content, in particular with 12% and 24% Ag. The eutectic filamentary bundles in Cu-12%Ag and Cu-24%Ag tended to develop into ribbons. These observed results imply that there is high strain compatibility between eutectic colonies and Cu dendrite.

The Ag filamentary morphology of the two-phase structure (Fig.3) can be distinguished more clearly by FESEM observation on the transverse section of the test alloys with heavy drawing strain, because the Cu phase has been removed by strong metallographic etching. The eutectic structure developed into filamentary bundles during drawing strain. Cu-24%Ag displays the most distinct morphology of fascicular Ag filaments in these alloys. Moreover, in the intermediate annealing treatments some secondary Ag particles were precipitated in the supersaturated

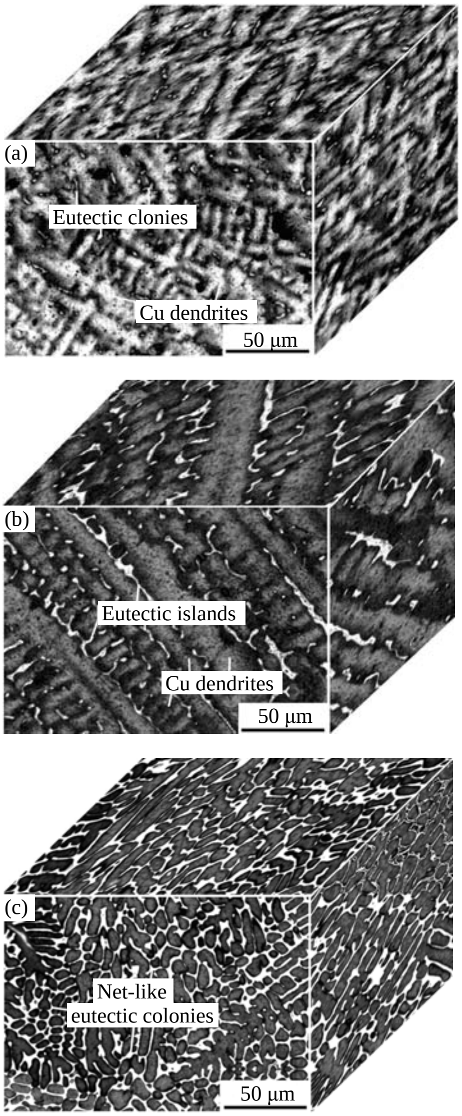

Fig.1 Combined metallographic morphology on transverse and longitudinal sections of the tested alloys after solidifying. (a) Cu-6%Ag; (b) Cu-12%Ag; (c) Cu-24%Ag

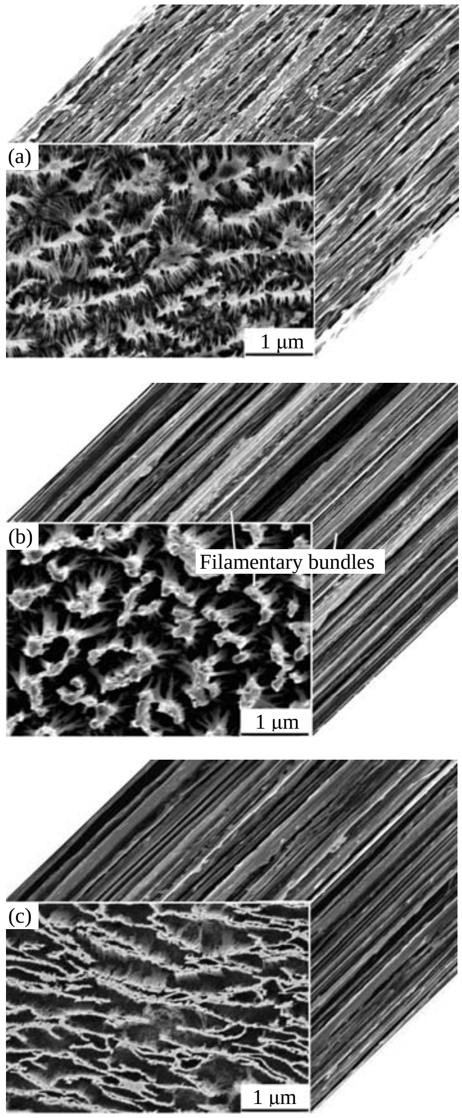

Fig.2 SEM microstructure of the alloys drawn to η=6.0. (a) Cu-6%Ag; (b) Cu-12%Ag; (c) Cu-24%Ag

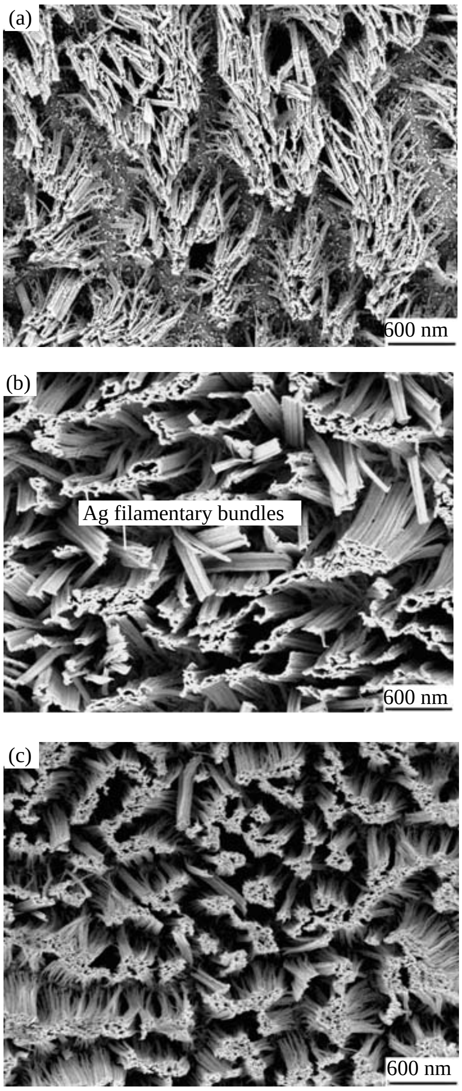

Fig.3 FESEM microstructure of the alloys drawn to η=7.0. (a) Cu-6%Ag; (b) Cu-12%Ag; (c) Cu-24%Ag

Cu dendrites from non-equilibrium freezing, and evolved into fine filaments during drawing strain. The morphology and distribution of these fine secondary filaments are different from those of the eutectic Ag filaments, since the secondary particles and eutectic structure have different original morphologies, formation conditions, and strain experiences. The secondary Ag filaments can be mixed with the eutectic filaments and result in the irregular distribution of the filamentary structure. Therefore, there exists a slightly irregular and incompact distribution of Ag filaments in Cu-6%Ag, since the alloy with a low Ag content has a high volume fraction of supersaturated Cu dendrites or more secondary Ag filaments.

There is a relatively high proportion of the eutectic colonies or a relatively low proportion of the primary Cu dendrites in Cu-12%Ag. The original structure components have approximate formation condition and strain experience in structure evolution because of a relatively small amount of secondary Ag particles in the alloy. Therefore, the filamentary structure can generally maintain a uniform bundle-like morphology, because most filaments in the alloy are evolved from the eutectic colonies, or only a relatively small amount of the secondary Ag filaments are mixed into the filamentary bundles. It can be considered that the highest proportion of the eutectic colonies results in predominant eutectic Ag filaments in Cu-24%Ag, which is responsible for much more uniform and compact morphology of the Ag filamentary bundles in the alloy. The secondary Ag filaments can be ignored in Cu-24%Ag, due to their small proportion in comparison with the eutectic Ag filaments.

The microstructure from TEM observation is shown in Fig.4 for drawn alloys with a high draw ratio. The amount of Ag filaments increases with the increase in Ag content. In the eutectic structure of the alloy with high Ag content, the bundle-like morphology of the filamentary structure can still be observed distinctly. Moreover, fine secondary Ag filaments evolved from the Ag precipitates can also be distinguished by TEM, although they are unable to be observed by SEM.

The microstructure parameters dependent on the draw ratio are given in Fig.5. The average diameters of the filaments evolved from both the Cu dendrites and eutectic colonies decrease with the increase in drawing deformation. The alloys with lower Ag content show higher reduction rates of the filamentary scales. The reduction in the filamentary scales tends to become slow once the draw ratio is higher than a certain degree.

CONCLUSION

The as-cast microstructure of Cu-Ag alloys in a range of Ag content from 6% to 24% mainly consists of Cu dendrites and eutectic colonies. The eutectic colonies increase and tend to present a continuous

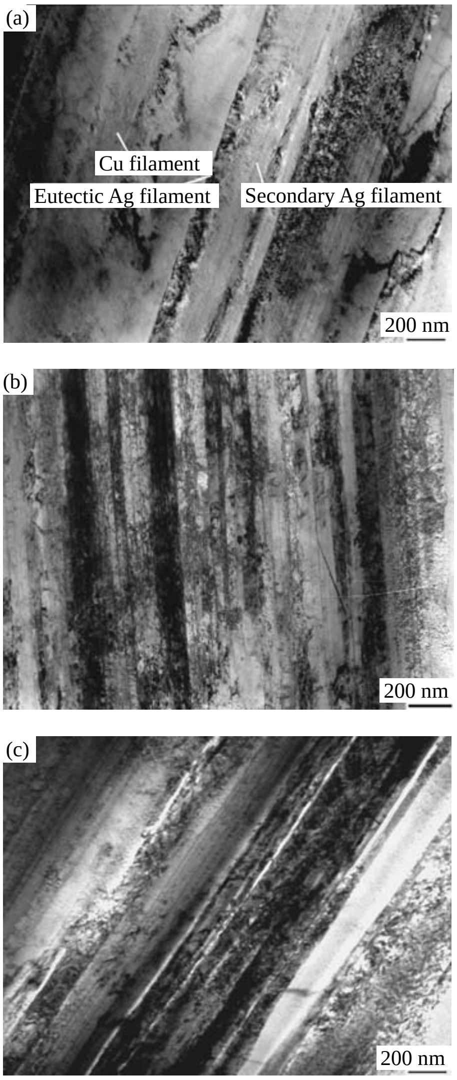

Fig.4 TEM microstructure of the alloys drawn to η=7.0. (a) Cu-6%Ag; (b) Cu-12%Ag; (c) Cu-24%Ag

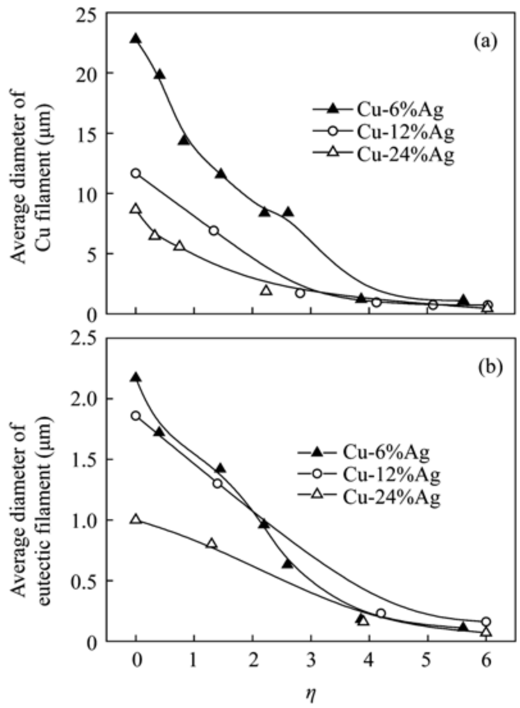

Fig.5 Average diameters of the filaments evolved from (a) Cu dendrites and (b) eutectic colonies dependent on the draw ratio

net-like distribution with the increase in Ag content. The intermediate-annealing processes promote the precipitation of secondary Ag particles in supersaturated Cu dendrites from non-equilibrium freezing.

The morphological character of the original microstructure in the radial direction of the drawn wires can basically be kept during drawing strain due to the excellent strain compatibility between both Cu and Ag phases. The Cu dendrites, eutectic colonies and secondary Ag precipitates are elongated in the axial direction and evolved into filamentary microcomposites of two phases in drawing deformation. The eutectic colonies tend to change into the filamentary bundles. The bundle-like morphology of the eutectic filaments is especially obvious in alloys with high Ag content.

The filamentary scales of the two-phase composites decrease with the increase in drawing strain level. The alloys with lower Ag content have a more significant reduction in the filamentary scales. However, the reduction rate of the filamentary scales becomes slow once the drawing strain is higher than a certain degree.

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