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MICROSTRUCTURE DEVELOPMENT AND CORROSION BEHAVIOR OF COPPER-SILVER NANO-FILAMENTARY COMPOSITES

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ABSTRACT

Corrosion properties of Cu–24 wt% Ag nano-composites in both the as-drawn and heat-treated condition were investigated and correlated with the microstructural changed caused by thermal treatments. One of the most important features in two-phase Cu–Ag filamentary nano-composites is the abundance of interfaces compared with conventional copper-based alloys. The Cu–Ag filamentary composites have extremely fine microstructure and the inter-phase area is too large to maintain a stable internal dislocation structure because of closely spaced filaments. The thin Ag filaments tend to be spheroidized by annealing. The corrosion potential and rate of as-received condition a aqueous 1M-NH_3OH with 35g/L of $(NH_4)_2SO_4$ solution at 25 ^oC were -374.4 mV_{SHE} and $9.998x10^{-6}$ A/cm^2 for cross sectional direction and -386.1 mV_{SHE} and $2.005x10^{-5}$ A/cm^2 for longitudinal direction, respectively. The corrosion potential and rate after annealing at 600 ^oC for 24 hours were -385.2 mV_{SHE} and $2.058x10^{-5}$ A/cm^2 for cross sectional direction and -398.4 mV_{SHE} and $3.7804x10^{-5}$ A/cm^2 for longitudinal direction, respectively.

Keywords: Cu-Ag nano-filamentary composites, Corrosion.

1. INTRODUCTION

Nano-filamentary composites based on copper and copper alloys have been attractive attentions in materials research and applications because of their superior electrical and thermal conductivity associated with magnetic fields [1]. The nano-filamentary copper-silver composites were generally prepared by heavy drawing [2]. The nano-filamentary structure contributes to the ultrahigh strength of the copper-silver micro-composites to have an excess properties predicted by the rule-of-mixtures [2, 3]. Problems of filamentary composites are introduced by their microstructure. For examples, the metallic filaments are polycrystalline so that they are thermally unstable. The matrix has texture so that they show an-isotropic properties about corrosion behavior. In case of cooper–silver thin film couples, vacancies play an important role during anodic dissolution, in which vacancies are formed when subsurface atoms jump into surface kinks or ledges on a dissolving crystal surface [4]. Corrosion-generated vacancies are attracted to dislocation and modify dislocation configuration [5] Copper ion and electron must migrate through the cuprous oxide film for the corrosion to proceed.[6] Although many researches were carried out about mechanical properties of the nano-filamentary composites, little information is available about corrosion and microstructure change of the composites. Hence, the objective of this study is to study performance of the filamentary copper-silver composites, especially on the corrosion behavior and microstructure change with heat treatment.

2. EXPERIMENTAL METHOD

Copper powder and silver filaments were pre-sintered at 900 ^oC. The sintered material was canned in a copper can prior to extrusion at 750^oC and cold drawn to 1.5 mm. After drawn, the specimen was hot isostatically pressed at 750^oC at a pressure of 100 MPa, followed by heavy extrusion. The extruded bundled wire was then swaged and drawn to achieve its final size of a 2 mm x 3 mm rectangular cross section. Longitudinal section, parallel to the drawing direction, and transverse section, perpendicular to the drawing direction, were cut for tests. Microstructure were observed by field emission scanning electron microscopy (Jeol JSM 6700F) and transmission electron microscopy (Jeol 2010), respectively. The foils for TEM were ion milled on a liquid nitrogen stage at 5 kV using an incidence angle of 11^o-12^o. [7]. Typical milling times were 7-10 hrs. Tensile tests were performed at a strain rate of 1.67 x 10^{-3} sec^{-1} at room temperature with a universal tensile test machine (MTS 880). Corrosion behavior was also determined with a potentiostat (Gammy CMS300) in a aqueous 1M-(NH_3OH) with 35g/L of ($(NH_4)_2SO_4$) solution at 25 ^oC.

3. RESULTS AND DISCUSSION

Fig. 1 is the three dimensional view of copper-silver filamentary composites observed by transmission electron microscopy. As show in Fig. 1, silver nano-filaments were well aligned along drawing direction. 2% yield strength, ultimate tensile strength and elongation of bundled Cu-25% Ag filamentary micro-composite wires were 866, 924 MPa, 0.07, respectively. The microstructure is similar to the previous report, in which increasing draw ratio results in decreasing averages spacing between silver filaments.[8]

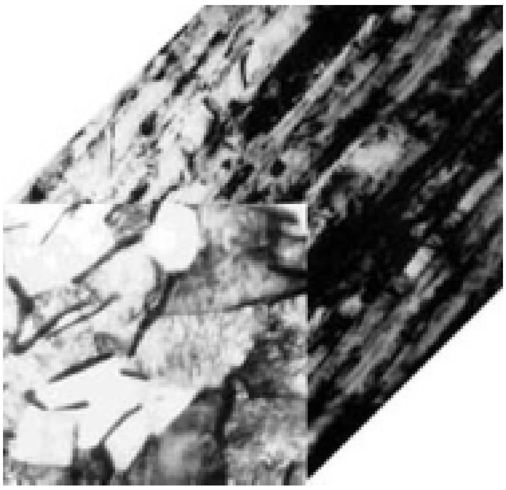
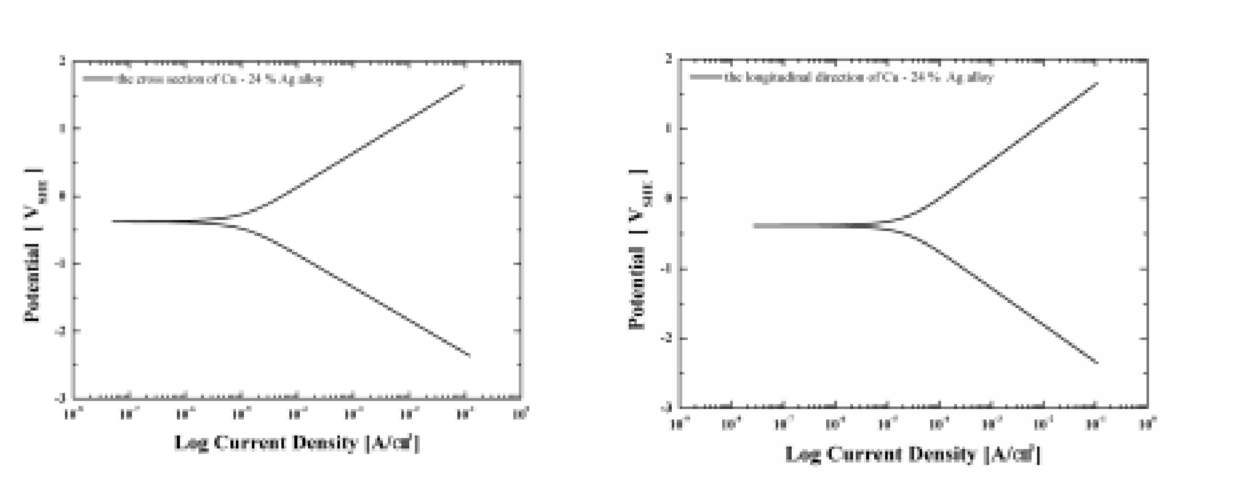


Fig. 1 Three dimensional TEM image of Cu-Ag nano-composites

Fig. 2 is typical polarization curves of copper-24% silver composites in aqueous 1M-NH_3OH with 35g/L of ($(NH_4)_2SO_4$) solution at 25 ^oC. The corrosion potential and rate for the drawing direction show different values. Table 1 is the corrosion potential and corrosion rate of the copper-silver nano-filamentary composites with dwawing direction. As shown in Table 1, the corrosion potential and rate of as-received condition were -374.4 mV_{SHE} and 9.998x10^{-6} A/cm^2 for cross sectional direction and -386.1 mV_{SHE} and 2.005x10^{-5} A/cm^2 for longitudinal direction, respectively. The corrosion potential and rate after annealing at 600 ^oC were -385.2 mV_{SHE} and 2.058x10^{-5} A/cm^2 for cross sectional direction and -398.4 mV_{SHE} and 3.7804x10^{-5} A/cm^2 for longitudinal direction, respectively.

Fig. 3 is typical corroded surface, in which selective dissolution of the boundary between copper and silver was observed. This is well agreement with previous observation.[9] Fig. 4 is the microstructure of the composites after annealing at 600 and 700^oC. As shown in figure 4, it is clear that poly-crystalline filaments become broken after annealing and tend to be faceted and spherical shape. This means that the boundary area between copper matrix and silver filaments becomes larger after annealing. Accordingly, the decrease of corrosion resistance after



annealing is related to microstructure change.

(a) **(b)**

Fig. 2 Typical Polarization Curves of Cu-24% Ag Nano-filamentary Composites with Drawing Direction. : (a) cross-section (b) longitudinal directions

Table 1. Corrosion potential and corrosion rate of Cu-Ag micro-composites

	As received		Annealing at 600 ^{o}C	
	E_{corr} [mV]	I_{corr} [x10^{-5}A/□]	E_{corr} [mV]	I_{corr} [x10^{-5}A/□]
cross section	-374.4	0.999	-385.2	2.058
longitudinal	-386.1	2.005	-398.4	3.7804

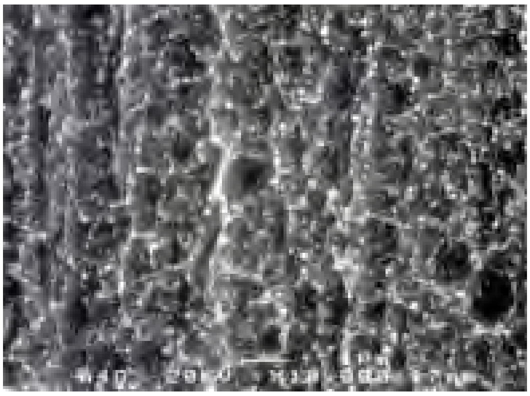
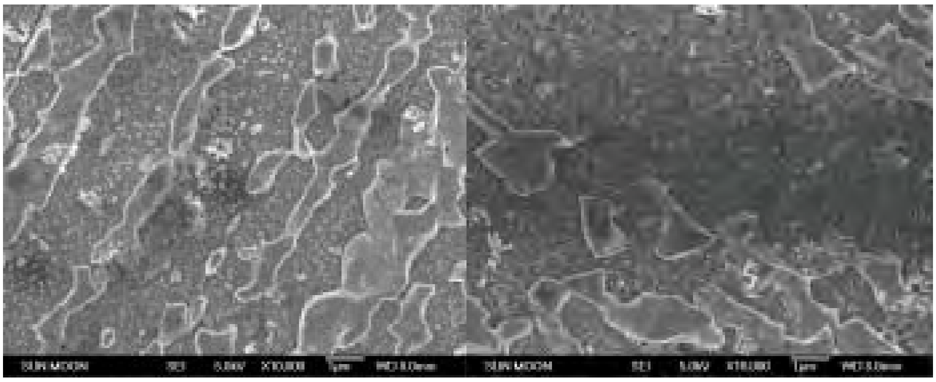


Fig. 3 Typical corroded surface of Cu- 24% Ag nano-filamentary composites

Many parameters such as vacancy concentration, dislocation density and grain boundary will be changed during annealing. At this moment, it is difficult to evaluate each parameter related to microstructure separately. However, one of most effective parameter on the corrosion behavior is the change of the area ratio of anode and cathode due to grain size change. Considering Pourbaix diagram of copper-water, the copper reacts with water to form copper oxide.[10] Although the copper forms a very stable passive film on the surface, if copper is anodically polarized by silver, the copper can be well attacked in corrosive environment. It is difficult to classify the effect of corrosion-generated vacancies on the corrosion of copper-silver nano-filamentary composites, however, it is clear that the corrosion potential and rate significantly depend on the spheriodizing of poly-crystalline silver filaments, which means that the boundary area between copper and silver becomes larger after annealing. Hence, the corrosion potential was decreased and corrosion rate was increased because the copper micro-coupled with silver in the nano-filamentary composites is more active than copper, the copper at the boundary between copper and silver can be selectively dissolved.



(a) **(b)**

Fig. 4 Microstructure of Cu-Ag nano-filamentary composites after annealing : (a) 600 oC (b) 700 oC.

4. SUMMARY

Cu-24 % Ag nano-filamentary composites prepared by heavy show that 0.2% yield strength, ultimate tensile strength and elongation 866, 924 MPa, 0.07, respectively. The thin Ag filaments in the composites tend to be spheriodized by annealing. The corrosion potential and rate of as-received condition in aqueous 1M-NH_3OH with 35g/L of $(NH_4)_2SO_4$ solution at 25 ^oC were -374.4 mV_{SHE} and 9.998x10^{-6} A/cm^2 for cross sectional direction and -386.1 mV_{SHE} and 2.005x10^{-5} A/cm^2 for longitudinal direction, respectively. The corrosion potential and rate after annealing at 600 ^oC for 24 hours were -385.2 mV_{SHE} and 2.058x10^{-5} A/cm^2 for cross sectional direction and -398.4 mV_{SHE} and 3.7804x10^{-5} A/cm^2 for longitudinal direction, respectively. Selective dissolution of the boundary between copper and silver was observed which was related to the increase of boundary area between the copper and silver after annealing.

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