Journal of Alloys and Compounds 676 (2016) 46–53

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Microstructure and properties of Cu-6wt%Ag composite thermomechanical-processed after directionally solidifying with magnetic field

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ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form
15 March 2016
Accepted 17 March 2016
Available online 18 March 2016

Keywords:
Cu-Ag
Thermomechanical processing
Directional solidification
Magnetic field
Hardness
Microstructure

ABSTRACT

High-field magnets require conductors made of Cu–Ag composites that have an exceptional combination of strength and electrical conductivity. Given that increase in strength is generally accompanied by decrease in electrical conductivity, researchers constantly seek the optimum balance between the two. In this paper, we reported the microstructure and properties of Cu-6wt %Ag alloy that had been directionally solidified under a magnetic field (MF) and thermomechanically processed. Thermo-electromagnetic convection by MF changed the mass transportation and diffusion of the melt, thus tilting the growth direction of proeutectic Cu dendrite toward the direction of the heat flow. Applying MF during solidification increased the primary dendrite arm spacing and the presence of supersaturated Ag in proeutectic Cu, but it decreased the volume fraction of the degenerated eutectic component distributed between the proeutectic Cu dendrites. The additional supersaturated Ag increased both the electrical resistivity and the hardness of the alloy. The increase in resistivity occurs because of increased impurity-scattering. The increase in hardness occurs as the result of solid solution strengthening. The precipitation temperature of Ag from Cu was between 275 °C and 325 °C, and the optimized temperature after aging was about 450 °C. After solidifying under MF, rolled Cu-6wt%Ag composite had a lower volume fraction of degenerated eutectic fibers. Thermomechanical processing at 300 °C promoted the precipitation of Ag out of the proeutectic Cu and simultaneously enhanced both the microhardness and the electrical conductivity of the alloy.

1. Introduction

Both DC resistive and AC pulsed high-field magnets depend on conductors made from materials with high strength and high conductivity, most of which are Cu-based alloys. Cu–Ag alloys are known to have an excellent combination of these properties [1–5]. However, increase in strength is generally accompanied by decrease in electrical conductivity. Optimization of the two properties is still an interesting scientific issue. The relationship between the microstructure and the properties of Cu–Ag alloy has been investigated and it was found that the precipitation of Ag from proeutectic Cu played an important role on the properties [4,6]. The precipitation strengthening from supersaturated Ag in proeutectic Cu dominated the overall strength of Cu–Ag composite, and impurity-scattering resistivity from Ag in proeutectic Cu had an evident impact on electrical conductivity [6]. Studies on precipitation kinetics of Ag in Cu indicated that the precipitation of Ag was not only dependent on the chemical composition of Ag [7–10], but also dependent on additional elements and aging temperatures [11–14]. Dis- and continuous precipitation were observed in aged Cu-8wt%Ag alloy. Simultaneously increasing the mechanical properties and electrical resistivity of the alloy was reached by engineering the volume fraction, size, and spacing of continuous precipitates [14]. Thermomechanical [1,5,15,16] and severe plastic deformation (SPD) processing [17,18] have been attempted to adjust the balance between strength and electrical conductivity. Thermomechanical processing superimposed annealing and deformation. Annealing is responsible for the precipitation of Ag, which decreases impurity-scattering to electrons in Cu, thus

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http://dx.doi.org/10.1016/j.jallcom.2016.03.127

increasing electrical conductivity. Deformation is capable of refining Ag precipitation, increasing strength at the expense of electrical conductivity. Although SPD technique has been highly concerned as well [1,5,15–17], it is not widely adopted because of the complexities in fundamental theory, processing design and etc. Solidification/deformation is still one of the best candidates for processing Cu–Ag composite. Optimization of solidification structure has also been proposed to be one of factors affecting the properties of Cu–Ag alloy [15,19]. Our group [6,20] applied an external static magnetic field (MF) to suppress the convection of the melt, which trapped the additional Ag in proeutectic Cu. Although both the electrical conductivity and the strength of Cu-28wt%Ag composite deformed after solidified with MF were reduced compared to that without MF, which was negative for increasing the performance of Cu–Ag composite, these results were not consistent with the inverse relationship between electrical conductivity and strength. We stated that the changes might be owing to the presence of supersaturated Ag in proeutectic Cu [21], however, no heat treatment was applied to precipitate Ag from Cu in our previous work [6]. Appropriate thermomechanical processing [1,5,16] has been sought to enhance combined properties, but less attention was paid to the combined roles of both solidification and thermomechanical processing. Although Morris et al. [15] investigated the influence of solidification conditions, thermomechanical processing, and alloying additions on the structure and properties of Cu–Ag composite, most of their results were discussed in terms of micro-sized dendrites and eutectics instead of nano-sized precipitation of Ag. In this paper, we investigated the influence of solidification conditions and thermomechanical processing, and we took the role of nano-sized precipitation of Ag into account. We applied MF in solidification to trap additional Ag dissolved in proeutectic Cu. Precipitation kinetics of solid-solution Cu-6wt%Ag alloy sought optimized precipitation temperatures by analyzing differential scanning calorimetric (DSC) reactions and the dependence of aging temperature on microhardness and electrical resistivity. We used thermomechanical processing to precipitate Ag from Cu. Simultaneous enhancement of microhardness and conductivity was found in thermomechanical-processed Cu-6wt%Ag alloy at 300 °C after directionally solidified with MF.

2. Materials and methods

Cu-6wt%Ag master alloy was prepared by vacuum induction melting under argon atmosphere using oxygen-free Cu and electrolytic Ag rods. The alloy was sectioned into several samples (dimensions: 9.5 mm in diameter and 120 mm in height). Each sample was polished and placed in quartz crucible with 10 mm in diameter. The crucible was loaded in directional solidification apparatus equipped with a transverse static magnetic field (MF) up to 1.12 T (T). At the position of about 60 mm height from the center of MF, magnetic flux density is about 90% of the central MF. The initial central position of the sample was fixed at the center of both MF and heating furnace. The samples were heated to 1200 °C, held for 0.5 h and pulled down at a rate of 100 μm/s into Ga-In-Sn tank. Temperature gradient was remained 4 K/mm. Central MF of 0 T, 0.8 T and 1.12 T were imposed during solidification process of Cu-6wt%Ag alloy.

In order to investigate precipitation temperatures of Ag in Cu, the samples post-solidified without and with MF were solution treated at 760 °C for 2 h and water-quenched. DSC analysis on solution treated samples solidified without MF was carried out under argon atmosphere with a Shimadzu DSC-60. The solution treated samples were machined into several sheets with about 0.4 mm in thickness, and were aged at temperatures between 300 °C and 680 °C for 2 h to clarify the dependence of microhardness and electrical resistivity of Cu-6wt%Ag alloy on aging temperatures. Similar methods on DSC tests and aging treatment of Cu–Ag alloy can be found in our previous paper [21]. Two significant aging temperatures were found and they were applied as annealing temperatures during thermomechanical processing of Cu–Ag alloy.

Directionally solidified (DS) samples with and without a 1.12 T MF were sectioned into rectangular samples, and then cold rolled into Cu–Ag composites in different levels of thickness. The reduction ratio is defined as RA%=$(t_0-t_f)/t_0*100$, where t_0 and t_f are the initial and final thickness of sample, respectively. Thermomechanical process of Cu–Ag alloy was designed as follows. The DS samples with and without a MF were firstly cold rolled to 75% RA, and then two different intermedia annealing temperatures (300 °C and 450 °C selected from the results of precipitation kinetics shown in Section 3.3) were applied. After the annealing, the samples were further cold rolled to 90%RA.

As-DS and as-rolled samples were sectioned, polished and etched in a solution of 120 ml H_2O, 20 ml HCl and 5 g $FeCl_3$. Optical microscope (OM) and scanning electron microscope (SEM) were used to examine the microstructure of the samples. Angle between the temperature gradient and the growth orientation of proeutectic Cu, defined as deviation angle θ (less than 90°), was measured from more than 200 dendrites on the longitudinal sections and the averaged value was adopted as the growth deviation angle. The change of θ was used to describe change in the growth orientation of proeutectic Cu by MF (seen in Section 3.1). The primary and secondary spacings between proeutectic Cu, λ, were measured by linear intercept method [22]. The area fraction of degenerated eutectic components taken from SEM images was measured to qualitatively estimate the volume fraction of eutectic components. Thin foil for transmission electron microscopy (TEM) was prepared by ion-milling with a voltage of 5 kV at an incidence angle of 3°. The foil was observed on a FEI-Tecnai $G^2$20 TEM with energy-dispersive X-ray spectroscopy (EDS) detector operating at 200 kV. Our previous paper [6] compared the data among SEM-EDS, TEM-EDS, and simulated results of electrical resistivity. The results indicated that the data by TEM-EDS was approximately capable of describing the supersaturation of Ag in Cu. Therefore, in this paper, we used TEM-EDS data as the Ag concentration in proeutectic Cu region. Microhardness measurements were carried out on polished surfaces of samples using 100 g load and a dwelling time of 10 s. The electrical resistivity was measured on the samples with gage length of 40 mm and cross-section of about 4 mm × 2 mm by standard four-point probe method.

3. Results

3.1. Macro-morphology of DS Cu-6wt%Ag alloy

Macrostructure of DS Cu-6wt%Ag alloys with and without MF (Fig. 1) show that the application of MF during solidification tends to tilt the growth orientation of proeutectic Cu dendrite parallel to the direction of heat flow. The result of the deviation angles (Fig. 1d) indicates that the application of MF decreases the deviation angle of proeutectic Cu dendrite. Previous study [23] thought that the change of dendrite growth by MF was as a result of the change in crystalline anisotropy induced by MF. Thermoelectromagnetic convection by MF was believed to be one of factors affecting the convection of the melt and the diffusional transportation of the solute, resulting in the changes in solidification structure [24]. With respect to feeble magnetic Cu–Ag alloy, we believed that thermoelectromagnetic convection by MF was capable of changing the mass transportation and the diffusion of Cu, thus tilting the growth direction of proeutectic Cu dendrites parallel to the direction of the heat flow.