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Ti-added alumina dispersion-strengthened Cu alloy fabricated by oxidation

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ABSTRACT

Two types of alumina dispersion-strengthened Cu alloy were fabricated by surface oxidation reaction by the aging of Cu–0.31 wt%Al and Cu–0.28 wt%Al–0.07 wt%Ti alloys in air. After heat treatment at 980 °C for 1 h in air, a 0.2 mm-thick alumina-dispersed plate could be prepared. The alumina-dispersed alloy with Ti addition showed higher values of conductivity, hardness, and tensile strength than the alloy without Ti.

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1. Introduction

Alumina dispersion-strengthened alloys have been widely used as electrode materials in welding process because of their high thermal and electric conductivity, and reasonable mechanical strength and thermal stability [1–6].

The commercial alumina dispersion alloys are generally fabricated by consolidation methods including internal oxidation [7,8]. However, it has been reported that the alumina dispersions in the Cu matrix are less homogeneously distributed during the fabrication process [9,10], and attaining both high strength and conductivity is limited.

The internal oxidation process in powders of Cu alloys could produce nano-sized alumina in a powder matrix. However, the Cu oxides, which have low hardness, inevitably remain on the surface of particles, and to fabricate alumina-dispersed Cu alloys, a reduction process is necessary to remove undesired oxides. The fabrication of the alumina dispersion-strengthened Cu alloys by powder metallurgy includes complex and multi-step processes, such as raw powder preparation [10,11], calcination [4], reduction [6], compaction [1,12], and sintering [8]. Besides the complicated process, the oxidization of metal in a high-oxygen atmosphere may cause an explosive reaction by active oxidization.

The hard and stable alumina in the Cu matrix is produced by the strong bonding between Al and the O atom, where oxygen is supplied from the outer surface. When more oxygen diffuses into the Cu–Al matrix, it reacts with Al to produce more alumina, deeper in matrix. It could be suggested that if bulk type of alumina dispersion-strengthened Cu alloy could be fabricated by diffusion of oxygen into the bulk alloy in ambient atmosphere, it would be a potent method for making highly conductive and high strength Cu alloys without the aforementioned complicated powder process. For this diffusion process, we also have to consider the strict stoichiometry required for alumina to form as Al_2O_3 internally in the Cu matrix. The Al and O atoms should meet in an exact integer ration of 2:3. Therefore, when one element is deficient, alumina cannot form in the Cu matrix appropriately. Another strong oxide former is also required to form the oxide from the atmosphere without remaining oxygen and oxide former atoms in the matrix.

In this study, the oxidation of Al in a Cu–Al alloy was carried out by a simple heat treatment in air, and an alumina-dispersed layer on the surface of the Cu alloy was prepared. We also examined how addition of a small amount of Ti, as another strong oxide former, affected the mechanical and electrical properties of an alumina-dispersion Cu alloy.

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2. Experimental procedure

The 99.99% pure Cu, Al and Ti were used to prepare ingots of Cu–Al and Cu–Al–Ti alloys by vacuum induction melting. The chemical compositions are shown in Table 1. The ingots were cold-rolled at room temperature with 75% reduction in thickness, and subsequently heat-treated at 440 °C for 5 h, 900 °C for 1 h and 980 °C for 1 h in air for oxidation.

The specimens were mechanically polished and etched in an etchant solution of 5 g $FeCl_36H_2O$, 12.5 ml HCl and 100 ml H_2O. The microstructure was observed by an optical microscope (OM, Olympus model: GX51) and a scanning electron microscope (SEM, JEOL, model: JSM-6610LV). Characterization of alumina was carried out using a 200 kV field-emission transmission electron microscopy (TEM, JEOL, model: JEOL-2100F) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector along with a scanning TEM.

3. Results and discussion

When Cu–Al and Cu–Al–Ti alloys were heat-treated in ambient atmosphere, the thickness of the oxide scale, which was composed of oxidized Cu, increased with increasing temperature. However, the oxidized Cu could be easily removed by mechanical brushing and acid treatment because of a low-density oxide layer on the surface.

After removing the oxide scale from the plate, the vertically sectioned bulk alloys revealed regions distinguished by brightness, as shown in Fig. 1. The thickness of the brighter region increased with increasing temperature, similar to the scale thickness.

The comparatively bright region was characterized by higher oxygen content in the Cu alloy matrix (Fig. 1d). The bright region had an oxygen concentration of more than 1.2 wt%. It was though that the oxygen near the surface mainly reacted with the Cu atoms, forming the Cu oxide scale, and the oxygen that diffused deeper inside the matrix met Al atoms, which resulted in the formation of the Al_2O_3 compound. The thickness of oxidation layer in the Cu–Al–Ti alloy exceeded 0.2 mm after aging at 980 °C for 1 h in air (see Fig. 1c and d). The thickness of the oxidized layer in the Cu–Al alloy also showed almost the same value when the Cu–Al alloy was heat-treated under the same conditions. These observations could therefore provide the key factor: when the alloy plate was aged on both sides under the same conditions (in here 980 °C for 1 h), the oxidized layer reached a thickness of more than 0.4 mm, which might be considered as the bulky material.

Based on this observation, a fully oxidized plate, about 0.2 mm thick, was fabricated by oxidation of both sides in the air at 980 °C for 1 h with the alloy plate where the initial thickness was 0.45 mm considering the oxide scale to be removed on both surface. After oxidation, the removed oxide scales on both sides of the plate were 0.27 and 0.25 mm thick for the Cu–Al and Cu–Al–Ti alloy, respectively (see Fig. 2a). The thickness of the removed scales were similar for alloys 1 and 2, and this could be explained by the fact that the diffusion of oxygen in each alloy should have been almost the same because both alloys were heat-treated at the same temperature and the compositions were almost the same except for the small Ti addition.

Lower values of hardness and conductivity were observed at the inner side of the annealed alloys 1 and 2 (where oxygen could not diffuse) at 980 °C after 1 h (see Fig. 2b and c). The annealed alloys did not present any grain refining, work hardening, or precipitation strengthening, and had low hardness. The annealed alloys without precipitations also showed lower conductivity because the solute interferes with conductive electrons in the Cu matrix.

Table 1
The alloy compositions for oxidation.

Composition (wt%)	Cu	Al	Ti
Alloy 1	Bal.	0.31	–
Alloy 2	Bal.	0.28	0.065

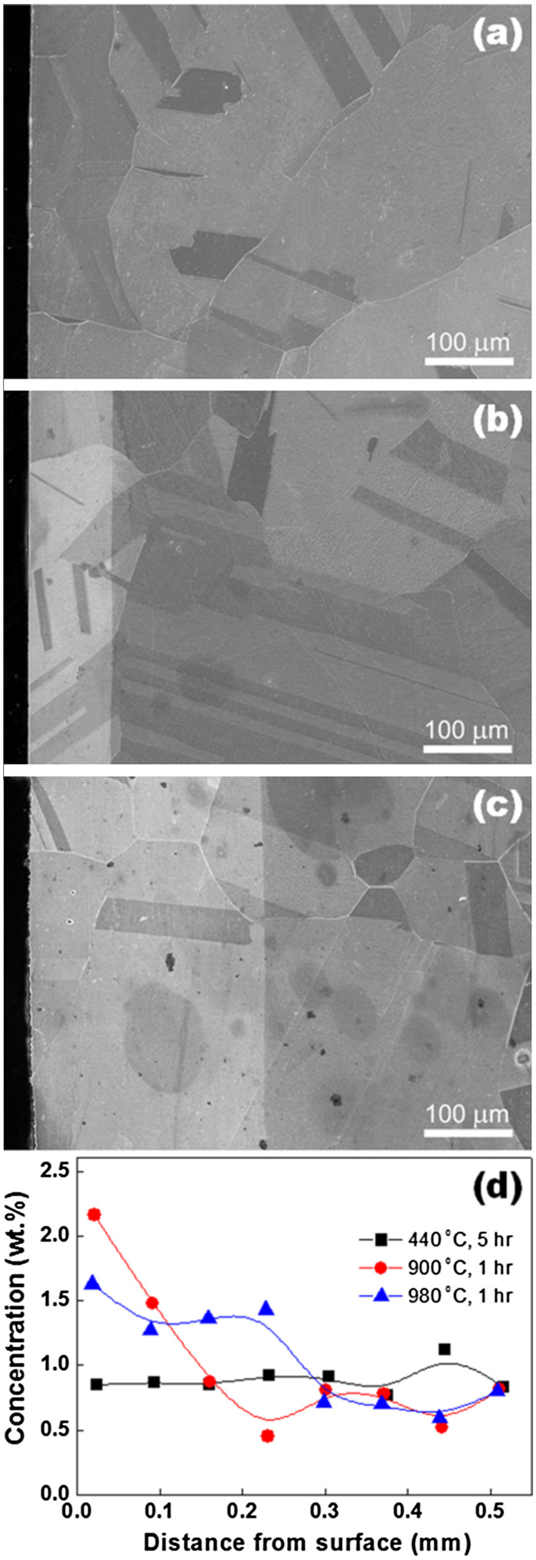

Fig. 1. SEM images of a Cu–Al–Ti alloy aged at (a) 440 °C for 5 h, (b) 900 °C for 1 h, and (c) 980 °C for 1 h, and (d) oxygen concentration profile along the thickness.

The hardness and conductivity on the inner side of annealed alloy 2 were relatively lower than those of alloy 1 under the same conditions of cold rolling and annealing at 980 °C for 1 h, even though alloy 2 has almost the same atomic fraction of alloying elements Al and Ti as alloy 1. This result indicated that the Ti atom had a lower solution hardening effect and might disturb the

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