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Precipitated Al₂O₃ phase characterization in internally oxidized Cu–Al alloy sheets



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1. Introduction

Cu–Al₂O₃ composites with more homogeneous microstructure can be prepared by Cu–Al alloy internal oxidation [1,2]. Processing is further divided into Cu–Al alloy powder internal oxidation and Cu-Al alloy thin sheet internal oxidation methods [3,4]. The crystal type, the size and distribution of the precipitated Al₂O₃ particles in the Cu–Al₂O₃ composites prepared by the two internal oxidation methods have been extensively studied. Li et al. [5] and Shen et al. [6] concluded that the crystal types of precipitated Al₂O₃ particles in oxidized Cu–Al alloy powders are γ -Al₂O₃, α -Al₂O₃ and θ -Al₂O₃. The main γ -Al₂O₃ precipitated phase particles are uniformly distributed in copper grains and their size is less than 12 nm. However, Li et al. [4], Yang et al. [7] and Su et al. [8] stated that there are only precipitated γ -Al₂O₃ nanoparticles in the oxidized Cu–Al alloy sheets. Essentially, the mechanism of sheet and powder internal oxidation is the same. Thus, oxidized Cu–Al alloy sheets

ABSTRACT

Cu–Al₂O₃ composite sheets were prepared by Cu–Al alloy sheet internal oxidation. The Al₂O₃ precipitation phase was extracted from the Cu–Al₂O₃ composite sheets. The Cu–Al₂O₃ composite sheets were melted and then solidified to prepare Cu–Al₂O₃ bulk composite ingot. The crystal types and distribution of precipitated Al₂O₃ phase in the Cu–Al₂O₃ composite sheets and the ingot were investigated. In the Cu–Al₂O₃ composite sheet, the crystal types of the Al₂O₃ precipitation phase include γ -Al₂O₃, α -Al₂O₃ and θ -Al₂O₃. The main γ -Al₂O₃ phase has a coherent interface with the Cu matrix, and the amount of α -Al₂O₃ and θ -Al₂O₃ phases decreases from the surface to the bulk. During composite sheets melting, dispersed Al₂O₃ phase into the α -Al₂O₃ phase.

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should contain a certain amount of $\alpha\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$ phases. However, this needs to be verified.

Internal oxidation is commonly used to prepare thin composite sheets, since the solid solution alloy sheet can be fully oxidized. In recent years, oxidized alloy sheets have been used to prepare bulk composites. Bulk Cu–Al₂O₃ composite samples have been successfully prepared by combining Cu–Al alloy sheets internal oxidation with hot extrusion or hot press forming [9,10]. This method requires packaging, encapsulation, vacuum and hot extrusion processes, resulting in high cost. Thus, the use of fully oxidized alloy sheets to prepare bulk dispersion strengthened copper alloy needs to be further investigated. Although the density of Al₂O₃ nanoparticles is less than liquid Cu, Al₂O₃ nanoparticles may be metastably suspended in liquid Cu instead of being floated. If this is true, Cu–Al₂O₃ bulk composites can be prepared by melting and then solidifying Cu–Al₂O₃ composite sheets (oxidized Cu–Al alloy sheets).

This paper aims to identify the Al_2O_3 crystal types in the Cu- Al_2O_3 composite sheets and determine whether the Cu- Al_2O_3 bulk composite preparation is feasible by melting and then solidifying Cu- Al_2O_3 composite sheets. Cu-0.5 wt%Al alloy sheets were fully





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oxidized to prepare Cu–Al₂O₃ composite sheets. The Al₂O₃ precipitation phase was extracted from the Cu–Al₂O₃ composite sheets at different depth from the sample surface. The Cu–Al₂O₃ composite sheets were melted and then solidified. Precipitated Al₂O₃ phase crystal types in the Cu–Al₂O₃ composites sheets and Al₂O₃ particles distribution in the bulk, prepared by melting and then solidifying Cu–Al₂O₃ composite sheets (oxidized Cu–Al alloy sheets), were investigated.

2. Experimental details

2.1. Materials preparation

The Cu–Al alloy was internally oxidized to prepare the Cu–Al₂O₃ composite. The higher Al content in the Cu–Al alloy naturally resulted in higher Al₂O₃ content in the Cu–Al₂O₃ composite. High Al₂O₃ content causes the Cu–Al₂O₃ composite to become fragile and brittle, making it difficult to clean its surface and prepare the specimens. Lower Al₂O₃ content makes it difficult to directly analyze the Al₂O₃ precipitation phase in the Cu–Al₂O₃ composites by X-ray diffraction. In this work, the Cu–Al alloy with lower Al content of 0.5 wt% was used to prepare the Cu–Al₂O₃ composite, and then the Al₂O₃ precipitation phase was extracted from the composite for crystal type analysis.

Cu-0.5 wt%Al alloy sheets, 0.5 mm thick, were internally oxidized at 900 °C for 8 h to prepare the Cu $-Al_2O_3$ composite sheets. The specific internal oxidation procedure was the same as in Ref. [9]. Some of the Cu $-Al_2O_3$ composite sheets were divided into three equal parts, each about 700 g. These three parts were all used to extract the Al_2O_3 precipitation phase from the Cu $-Al_2O_3$ composite by the enrichment method. The extraction was performed using 20% aqueous nitric acid solution.

Cu in Cu $-Al_2O_3$ composite reacts chemically with diluted nitric acid to generate water-soluble Cu(NO₃)₂. The corresponding reaction is as follows:

$$3Cu + 8HNO_3(dilute) = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$
(1)

Al₂O₃ can not react with dilute nitric acid and precipitates out of the solution.

To analyze the Al₂O₃ precipitation phase at varying oxidized depth of the Cu–Al₂O₃ composite sheets, different processing routes were used prior to extraction. One sample was simply soaked in the 500 ml 20% aqueous nitric acid solution. The solution was gently stirred with a glass rod until the sheets were melted completely. After the sheets were melted, the Al₂O₃ powder settled at the bottom of the container. The extracted Al₂O₃ phase powder was repeatedly washed with distilled water, and then the cleaned powder was dried at about 200 °C. Before extraction, the second and third samples were first etched to different thickness with 30% aqueous nitric acid solution. Their corresponding thickness was 0.4 mm and 0.3 mm. The extraction procedure was the same for the three samples. The powders corresponding to the first, second and third samples were marked as powder 1, powder 2 and powder 3, respectively.

Some of the Cu-Al₂O₃ composite sheets were melted in a medium-frequency induction furnace in open atmosphere. The molten composite was poured in a graphite crucible mold at about 1200 °C to prepare Cu-Al₂O₃ bulk composite ingot. The size of the composite columnar ingot was Φ 30 mm \times 120 mm. The composite ingot was cut into two pieces along the ingot longitudinal axis by wire electrical discharge machine. One piece was cut into five equal sections perpendicular to its longitudinal axis by wire electrical discharge machine. Each section was sequentially numbered as 1–5, from top to bottom. A small 1.5 mm thick piece, named sample

6, was cut from the sample 5. The sample 6 and the industrial copper sample (\geq 99.95 wt% pure) 1.5 mm thick were cold-rolled to the thickness of 0.3 mm (80% thickness reduction). Their hardness before and after rolling was compared to investigate whether the composite ingot sample 6 had an obvious secondary phase strengthening.

2.2. Structure and mechanical properties characterization

Microstructure of the composite sheets and the composite ingot samples 1-5 was characterized using OLYMPUS PMG3 metallographic microscope. Metallographic corrosive agent was FeCl₃ hydrochloric acid alcohol solution (FeCl₃:hydrochloric acid:alcohol = 1:1:19, weight proportion). Phase analysis of the extracted Al₂O₃ powder was carried out using D8-ADVANCE X-ray diffractometer (Bruker Corp.). Cu target was used with corresponding X-ray wave length of 0.154056 nm and XRF1800 X-ray fluorescence spectrometer (Shimadzu Co.). High resolution images of the composite sheet surface layer and extracted powder was obtained by JEM-2100 transmission electron microscope (Japan Electronics Co., Ltd).

Hardness of the composite ingot samples 1-5 and the industrial copper sample was measured using the MH-3 microhardness tester. Load and hold time were 0.98 N (100 g) and 10 s, respectively. The mean value of the hardness was taken as an average of 5 measurements.

3. Experimental results and analysis

3.1. Microstructure of the Cu–Al alloy sheets after internal oxidation

Microstructure of the Cu–0.5 wt%Al alloy sheet with 0.5 mm thickness after internal oxidation at 900 °C for 25 h is shown in Fig. 1. The brighter zone in the middle of the oxidized sheet is the border of the internal oxidation layers on both sides. The internal oxidation depth of a single side is 210 μ m at 900 °C for 15 h (a thicker sample was tested). Measured thickness of the alloy sheet was about 410 μ m, which indicated that 15 h were enough for complete internal oxidation of the alloy sheet. In this paper, the sheet was oxidized for 25 h to ensure full internal oxidation of the alloy sheet. The reason why there is always a brighter zone in the middle of the oxidized sheet after complete internal oxidation is unclear.

Microstructure of the superficial layers of the composite sheet is shown in Fig. 2. Fig. 2(a) is the high resolution transmission

Sample 100 µ m

Fig. 1. Metallographic structure of the Cu-Al alloy sheet after internal oxidation.





Fig. 2. Microstructure of the superficial layers of the composite sheet (a) HRTEM image (particles regions and IFFT images); (b) FFT pattern image of the D region in Fig. 2(a).

electron microscopy (HRTEM) image of the Cu–Al₂O₃ composite sheet. In Fig. 2(a), C, D and E regions contain precipitation phase particles distributed in the matrix. Images c-e are the inverse fast Fourier transforms (IFFT) of the C, D and E regions, respectively. In Fig. 2(a) the interface between the precipitation phase particle and the matrix is coherent. Fig. 2(b) is the fast Fourier transform (FFT) pattern of the D region in Fig. 2(a), showing indexed results of the pattern (card number PDF 10-0425, Al₂O₃, face centered cubic, lattice constant a = 0.79 nm; card number PDF 70-3039, Cu, face centered cubic, lattice constant a = 0.3613 nm).

3.2. Composition analysis of the extraction powders

Fluorescence spectrum quantitative analysis results of powders 2 and 3 are shown in Table 1. The main phase in powders 2 and 3 is Al₂O₃, but the exact types of the Al₂O₃ phase could not be analyzed by the fluorescence spectrometer.

The origin of CuO, SO₃, PbO, SiO₂ and Fe₂O₃ is speculated as described below, and S, Pb, Si and Fe are impurity elements. The reactions between them with dilute nitric acid are as follows:

$$3Pb + 8HNO_3(dilute) = 3Pb(NO_3)_2 + 2NO\uparrow + 4H_2O$$
 (2)

 $Fe + 4HNO_3(dilute) = Fe(NO_3)_3 + NO\uparrow + 2H_2O$ (3)

 $3Si + 4HNO_3(dilute) + H_2O = 3H_2SiO_3 + 4NO\uparrow$ (4)

$$3S + 4HNO_3(dilute) = 3SO_2 + 4NO\uparrow + 2H_2O$$
(5)

When the extracted powders were repeatedly washed, $Pb(NO_3)_2$, $Fe(NO_3)_3$, H_2SiO_3 , SO_2 and $Cu(NO_3)_2$ could have still remained. Their residuals were decomposed or oxidated ($2SO_2+O_2=2SO_3$) to produce CuO, SO_3, PbO, SiO_2 and Fe₂O₃ during powder drying.

X-ray diffraction (XRD) pattern of the power 3 after background substraction and CuK α_2 stripping is shown in Fig. 3. The Al₂O₃ phase crystal types of the power 3 were γ -Al₂O₃, α -Al₂O₃ and θ -Al₂O₃ (PDF standard cards 10-0425, 46-1212 and 23-1009). Three

 Table 1

 Quantitative analysis of the fluorescence spectra of powder samples 2 and 3.

Composition	Powder 2	Powder 3	Line
Al ₂ O ₃	91.71%	95.07%	Al Ka
CuO	5.53%	2.8%	Cu Ka
SO ₃	1.26%	1.15%	S Ka
PbO	0.54%	0.59%	Pb Lb ₁
SiO ₂	0.5%	0%	Si Ka
Fe ₂ O ₃	0.45%	0.37%	Fe Ka



Fig. 3. X-ray diffraction pattern of the powder 3.

strongest diffraction reflections of the γ -Al₂O₃ phase correspond to the (111), (400) and (440) crystalline planes, while the α -Al₂O₃ phase has (104), (113) and (116), and the θ -Al₂O₃ phase has ($\overline{4}$ 01), (002) and (111) reflections. The amount of the α -Al₂O₃ phase is relatively small. The diffraction reflections of the phases other than the Al₂O₃ phase in powder 3 did not appear due to even lower content.

Microstructure of the powder 3 particle is shown in Fig. 4. The indexed results of the FFT pattern is γ -Al₂O₃ (card number PDF 10-0425, Al₂O₃, face centered cubic, lattice constant *a* = 0.79 nm). The α -Al₂O₃ and θ -Al₂O₃ particles were not found in many HREM obsvervations of the composite sheet and the extracted powders. This maybe due to their low content. X-ray diffraction patterns of the power 3 showed the presence of α -Al₂O₃ and θ -Al₂O₃ besides γ -Al₂O₃, which indicates that the precipitation phase types are the same between the oxidated sheets and the oxidated powders.

XRD spectra comparison of powders 1, 2 and 3 are shown in Fig. 5. These three powders all contained γ -Al₂O₃, α -Al₂O₃ and θ -Al₂O₃ phases. The integral intensity proportion of the γ -Al₂O₃ (440) diffraction peak in powders 1, 2 and 3 was 15.5:20.9:21.8, which showed that the γ -Al₂O₃ content in powder 3 is higher than in powders 1 and 2. This also means that the α -Al₂O₃ and θ -Al₂O₃ content decreases from the surface to the bulk in the Cu-Al₂O₃ composite sheet. The possible reason is as follows. For the long time high temperature exposure, the γ -Al₂O₃ $\rightarrow \theta$ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃. During internal oxidation the diffusion distance of oxygen atoms is relatively short in the surface layer of the Cu-Al sheet, so the γ -Al₂O₃



Fig. 4. Microstructure of a particle from the powder 3 (a) HREM image of a particle; (b) IFFT image of the box region in Fig. 4(a); (c) FFT pattern image of the box region in Fig. 4(a).



Fig. 5. X-ray diffraction spectra of the powders 1, 2 and 3.

precipitation phase is generated early. However, in the Cu-Al sheet bulk, the diffusion distance of oxygen atoms is relatively long, so the generation of the γ -Al₂O₃ phase is delayed. Therefore, there is more time for the γ -Al₂O₃ phase crystallization in the surface layer. Thus, in the Cu–Al₂O₃ composite sheet, the content of the γ -Al₂O₃ phase increases from the surface to the bulk.

3.3. Microstructure and mechanical properties of the composite ingot

The composite ingot prepared by melting and then solidifying $Cu-Al_2O_3$ composite sheets is shown in Fig. 6. A large amount of white educt powders appeared on the surface of the ingot, and the amount of the white educt powders on the upper half surface of the ingot was more than on the lower half surface. The white educt powders were collected. X-ray diffraction spectrum of the collected



Fig. 6. Composite columnar ingot (left is the upper side).



Fig. 7. X-ray diffraction spectrum of the educt powder.

white educt powders is shown in Fig. 7. The diffraction peaks intensity of the α -Al₂O₃ phase are stronger, indicating that the main composition of the educt powder is α -Al₂O₃. Conversely, the α -Al₂O₃ intensity is relatively low in the powder samples (i.e., there is less α -Al₂O₃ in the Cu–Al₂O₃ composite sheets).

The γ -Al₂O₃ and θ -Al₂O₃ are metastable phases and the α -Al₂O₃ is a stable phase. The metastable θ -Al₂O₃ is a result of the γ -Al₂O₃ to α -Al₂O₃ phase transition. Above room temperature, the Gibbs free energy of the transformation from γ -Al₂O₃ to α -Al₂O₃ is negative, i.e. the free energy is reduced as a result of the γ -Al₂O₃ to α -Al₂O₃ transformation. While the Gibbs free energy decreases with temperature [11], the trend of the phase transformation from γ -Al₂O₃ to α-Al₂O₃ increases with temperature. When temperature exceeded 1200 °C, the transformation from γ -Al₂O₃ to α -Al₂O₃ was accelerated [12,13]. The melting temperature of the Cu-Al₂O₃ composite sheets was above 1200 °C, and most of γ -Al₂O₃ was transformed into α -Al₂O₃ through θ -Al₂O₃ during melting of the Cu–Al₂O₃ composites sheets. At high temperature and long duration, the γ -Al₂O₃ and θ -Al₂O₃ phases can be completely transformed into α -Al₂O₃. Since the melting time is relatively short, there are still residual γ -Al₂O₃ and θ -Al₂O₃ phases present.

The microstructure of the samples 1-5 cut from the composite ingot is shown in Fig. 8. There are many small holes in every sample. Educt Al_2O_3 powder agglomerated in the holes before grinding the samples. The number and size of the holes increased from the ingot bottom to the top, as seen in Fig. 8(a)–(e). This is because the educt

Al₂O₃ powders rosed and were further agglomerated during the melting process. More white powder on the upper half surface of the ingot than on the lower half surface (as in Fig. 6) also happened for the same reason.

From Figs. 6 and 8, a significant amount of Al_2O_3 particles was isolated from the Cu matrix after melting of the composite sheets. In Fig. 8, the microhardness of the no-hole area was measured. The microhardness results of the samples 1–5 are shown in Table 2. The microhardness of the samples has no obvious difference. Namely, the microhardness of the ingot from the top to the bottom is almost the same.

The microhardness of the sample 6 cut from the sample 5 and industrial copper before and after rolling is shown in Table 3. The microhardness of the sample 6 is a little higher than the industrial copper sample after cold rolling (80% thickness reduction). This indicated that the dispersively distributed Al_2O_3 particles were

Table 2

Microhardness of the samples 1-5 cut from the composite ingot (HV).

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Microhardness	74	75	71	72	74



Fig. 8. Microstructure of the samples 1–5 (a)–(e) cut from the composite ingot sequentially; (f) Sketch of the sampling locations.

Table 3

Microhardness of the sample 6 and industrial copper before and after rolling (HV).

	Sample 6	Industrial copper
Before rolling	72 115	68 100
Aiter roning	115	100

almost totally isolated from the Cu matrix after melting of the composite sheets. If there were some Al_2O_3 particles dispersively distributed in the Cu matrix, the composite ingot sample 6 would have exhibited secondary phase strengthening (i.e., the microhardness of the composite ingot should be obviously higher than the industrial copper before and after rolling).

In short, during the composite sheets melting, the dispersively distributed Al_2O_3 particles aggregated and finally became almost totally isolated from the Cu matrix. The Cu $-Al_2O_3$ bulk composites can not be prepared by melting and then solidifying the Cu $-Al_2O_3$ composite sheets.

4. Conclusions

- (1) The crystal type of Al₂O₃ precipitation phase of Cu–Al₂O₃ composite sheet prepared by Cu–Al alloy sheets internal oxidation is mainly γ-Al₂O₃. Meanwhile, a certain amount of the α-Al₂O₃ and θ-Al₂O₃ phases also existed.
- (2) In the Cu–Al₂O₃ composite sheet, the amount of α -Al₂O₃ and θ -Al₂O₃ phases decreased from the surface to the bulk.
- (3) During the composite sheets melting, the dispersively distributed Al₂O₃ particles aggregated, and were almost totally isolated from the Cu matrix.
- (4) During the composite sheets melting, most of the γ -Al₂O₃ phase was transformed into the α -Al₂O₃ phase.

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