Applied Surface Science 257 (2011) 10294–10299

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Study of deposition patterns of plating layers in SiC/Cu composites by electro-brush plating

Xiangliang Li[a,b], Xibao Wang[a,b,*], Rui Gao[a,b], Li Sun[a,b]

[a] School of Material Science and Engineering, Tianjin University, Tianjin 300072, China
[b] Tianjin Key Laboratory of Advanced Joining Technology, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 30 April 2011
Received in revised form 9 July 2011
Accepted 10 July 2011
Available online 20 July 2011

Keywords:
Electro-brush plating
SiC
Plating layers
Growth mode
Deposition patterns

ABSTRACT

SiC reinforced copper composite coatings were prepared by electro-brush plating with micron-size silicon carbide (SiC) ranging from 1 to 5 μm on pure copper sheet in this paper. The micro-structural characterizations of SiC/Cu composite coatings were performed by optical microscope and Scanning Electron Microscope (SEM) coupled with spectrometer, to study co-deposition mechanism of SiC/Cu. It was found that there were three different patterns of SiC deposition in plating layers during electro-brush plating process, i.e. the particles could deposit inside copper grains, in grain boundaries, or in holes of the surface. To investigate deposition mechanism of each pattern, size of SiC and copper grains was compared. By comparison of size of copper grains and hard particles, SiC were either wrapped in copper grains or deposited in grain boundaries. Moreover, electro-brush plating layers at different brush velocities and current densities were obtained respectively, to analyze the microstructure evolution of the composite coatings. The hardness of plating layers was measured. The results indicated at the current density of 3 A/dm^2, the SiC/Cu coating was compact with SiC content at a high level and the hardness reached a maximum.

1. Introduction

Copper is used extensively in the application of industry, attributed to its superior electrical and thermal conductivity, corrosion resistance, plasticity, and ease of machining [1]. However, with a rather low strength and poor wear resistance, copper is prone to adhesive and abrasive wear for some special applications where an excellent strength or good wear resistance is required [2]. An interest in particle reinforced copper composites by electro-deposit hard particles has gradually increased. Many studies on co-deposition composites of metal surfaces are reported at present [2–6]. But as to mechanism of co-deposition, incorporation of hard particles in layers is not yet fully understood due to the complex factors influencing co-deposition process. Earlier Guglielmi proposed a successive two-step adsorption mechanism, explaining the results related to the volume fraction of co-deposited particles to the volume of particles suspended in the plating bath with the Langmuir adsorption isotherm [3]. This adsorption theory indicates that hard particles carrying solution ion and molecular film are firstly adsorbed on the electrode surface, and then deposited on the cathode forming irreversible electro-chemical adsorption. However, an influence of particle size and shape on adsorption is not very clear. Some relative bigger particles, for instance, may be divorced out of the surface even they have formed strong adsorption at liquid flow [4]. More recently, Hamid et al. [5] reported that at higher current density (up to 2 A/dm^2), fine-grained deposit (81 nm) can be obtained. Whereas, applying of such higher current density leads to the formation of coarser deposit. Li et al. [6] indicated crystalline grains of layers are refined by nano-SiO_2 in the acidic sulfate copper plating bath and the ceramic particles cause an increase in hardness of layers. Nevertheless, no details about how the particles deposited on the layers were provided. To the best of our knowledge, few studies have been reported on the microstructure and morphology to explain co-deposition mechanism except our previous work.

In this paper, SiC/Cu composite coatings were prepared using electro-brush plating method. Microstructure and morphology of layers were analyzed to investigate deposition patterns of plating layers in the SiC-reinforced copper composites. Electro-brush plating at different brush velocity and current density were adopted, to analyze the microstructure evolution of the composite coatings.

2. Experimental

SiC particle reinforced copper composite coatings were produced by a set of brush plating devices containing electric power with direct current, ZDB-1 plating pen, cold graphite anode and

* Corresponding author at: School of Material Science and Engineering, Tianjin University, Tianjin 300072, China. Tel.: +86 22 81520211; fax: +86 22 27407022.
E-mail address: w.xibao@126.com (X. Wang).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.07.045

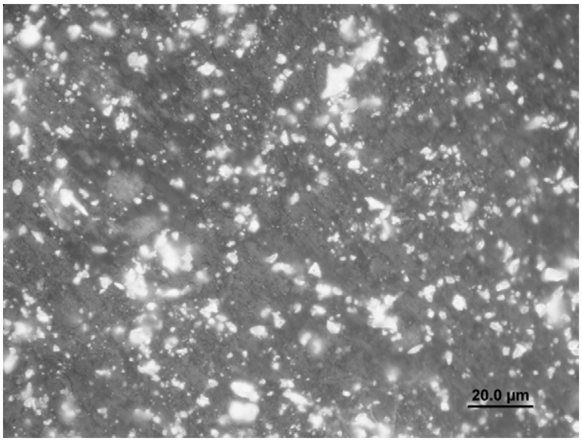

Fig. 1. Microscope image of silicon carbide (SiC).

polyester cotton sheathing. Pure copper was used as the substrate material with deposition area of 7 × 25 mm. The reinforced particles in this experiment were 1–5 μm SiC of diamond shape (Fig. 1). Before the experiment, the substrates were polished by 800 grade papers to surface smooth and electro-cleaned in dilute sulphuric acid for 5 min. SiC powders were cleaned by hydrofluoric acid for 24 h to remove impurities, washed in distilled water for 5–8 times, then dried. The electro-brush plating bath was fabricated by adding clean SiC powders into copper plating bath. Then SiC powders in the bath were dispersed though KQ-100DE ultrasonic cleaner for 20 min. A noncyanide alkaline copper plating bath was used in this study. The composition was $CuSO_4 \cdot 5H_2O$ 200 g/L, ethylenediamine 120 g/L and pH is 9–10. The current densities were 1, 3, 5, 7 and 10 A/dm^2. Each plating process lasted 20 min maintained at 15–30 °C. Based on the prophase experiment, SiC content in composite coatings presented a parabolic curve trend with raise of SiC concentration in the plating bath from 0 g/L to 40 g/L. At 25 g/L, SiC content reached a peak in composite coatings. Therefore, 25 g/L SiC in the plating bath was chosen as the optimum plating bath. The size distribution of copper grain has been verified by means of Lineal Intercept Procedure. The achieved estimated average grain size was compliant to tensile test standard ASTM-E112-96.

Morphology and microstructure of the coatings were carried out on the OLYMPUS GX51 optical microscope and Hatchi S-4800 Field Emission Scanning Electron Microscope (SEM). SiC volume content on SiC/Cu composite coatings was determined by EDAX Genesis XM2 Spectrometer attached to the Scanning Electron Microscope. The Vickers hardness of SiC reinforced copper composite coatings by electro-brush plating was measured through a MHV2000 digital microscopical sclerometer with 100 g load for 10 s.

3. Results and discussion

3.1. Grow mode of copper plating layers

In the process of electrocrystallization, both single-crystal and polycrystalline growth tends to establish a preferred orientation due to the tendency to minimize the volume strain energy developed in the films [7,9]. Schlesinger et al. [8] pointed out two basic orientations of crystallization in the formation of plating layers, i.e. layer orientation and out-of-plane orientation. According to the mechanism of plating growth, Diebold et al. [9] established two models, the flat island model and the hemispherical cap model, to feature crystal growth. From the mechanism of plating growth mentioned above, the polycrystalline growth modes of plating layers can be illustrated by both orientations of crystallization (Fig. 2). In this study, two typical morphologies of copper deposition are obtained by electro-brush plating of pure copper at 10 A/dm^2 and 1 A/dm^2. From Fig. 3a, agglomerate copper grains of layers are spherical, which can be attributed to growth of vertical direction (Fig. 2a). While from Fig. 3b, as a result of horizontal growth (Fig. 2b), the surface of Cu layer is smooth and flat in spite of some cracks. The differences in morphologies of the two layers can be interpreted exactly by theory of polycrystalline growth. It is obviously that in most cases, copper grows in both horizontal and vertical directions, and the deposit morphology is rather in between (Fig. 3a and b).

3.2. Effect of particle size on patterns of SiC deposition in plating layers

Fig. 4 shows the surface morphology of Cu layers deposited with SiC particles at a current density of 3 A/dm^2. It can be seen that SiC particles are dispersedly distributed on the surface and combined well in the copper layers (Fig. 4b). An interesting phenomenon noticed from micrographs is that SiC particles are either deposited on the boundary of copper grains or wrapped in them. Since 1–5 μm SiC particles are used in the present work, the micrographs may indicate that smaller particles are prone to be wrapped in copper grains, while bigger particles could deposit on the grain boundaries or be brushed off from the surface. This indicates there might be different patterns of deposition during electro-brush plating process. Moreover, some microscopic cracks (Fig. 4a) could be observed on the plating surface, which may be due to accumulative internal stress with increased thickness of the layers.

Typical micro-structural characterizations of SiC deposition are presented in Fig. 5. From the micrographs, three different patterns of co-deposition mentioned above can be clearly observed. Fig. 5a shows SiC particles are wrapped inside copper grains. Fig. 5b depicts the particles deposit in grain boundaries. And deposition of particles on refined copper grains is shown in Fig. 5c. It is obviously that comparison of size of copper grains and SiC particles

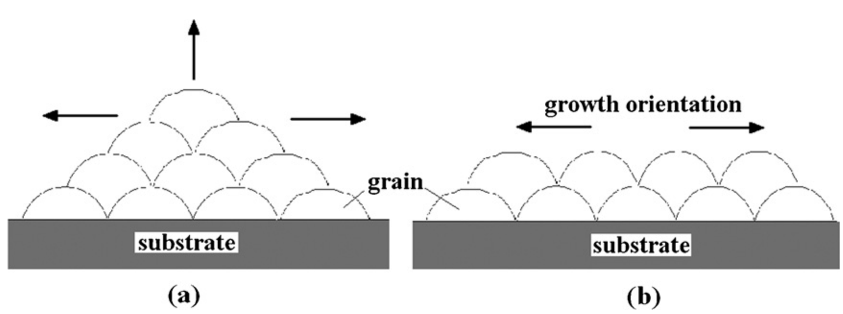

Fig. 2. Schematic illustration of polycrystalline growth: (a) out-of-plane orientation; (b) layer orientation.