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Synthesis of smooth copper deposits by simultaneous electroforming and polishing process

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Abstract

Copper deposits with smooth surface were prepared on a cylindrical cathode by a simultaneous electroforming and polishing process. In a specifically developed equipment, the cathode was embedded in insulating ceramic beads, and the beads were forced to polish the deposit surface during electrodepositing. The prepared deposits were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). It was found that simultaneous polishing in electrodeposition could evidently affect the microstructure of the deposits and smooth their surfaces. In contrast with the deposits electrodeposited by traditional method, the ones produced by the new process present higher microhardness and better corrosion resistance in neutral aqueous NaCl solution. Their structure and properties depend on the strength of the polishing effect, which can be enhanced by increasing the cathode rotational speed.

Keywords: Copper electrodeposition; Electroforming; Microstructure; Hardness; Corrosion

1. Introduction

Electroforming is the manufacturing process using electrodeposition, and has attracted much attention in recent years. Copper is one of the main metals that can be used in electroforming. Now copper electroforming has been employed in fabricating microwave device, EDM electrodes, shaped charge liner, and other precise micro-components [1–4]. However, there are some drawbacks in the traditional electroforming process [2,3,5]. One is hydrogen evolution, which is always possible in electrodeposition from water solution. If bubbles of hydrogen gas adhere to the cathode surface, deposition is prevented and a pit or pinhole in the coating results. Another is nodules or trees, which are generally caused due to the embedding of impurities and marginal discharge of electric field. As deposits grow progressively thicker, the irregularities on the surface will become worse.

To improve the quality and properties of the deposits, many additives are commonly used in the acid copper sulfate bath for copper electroforming. But most of them tend to be consumed during the longer electroforming process and some even become unstable in the bath after a period of time. Further more, many additives tend to be absorbed on the cathode and lead to co-deposition of sulfur, which may affect the structure and reduce some properties of deposits. [6–9]

In this paper, simultaneous polishing of dynamical hard particles was employed to the copper electroforming process to overcome the drawbacks above-mentioned. The copper deposits were electroformed in the alkaline pyrophosphate bath without any additives and their microstructure and properties were examined.

2. Experiments

Fig. 1 shows the schematic diagram of the experimental arrangement. A cylinder mandrel rotated inside a cylinder through-carved basket as cathode. Isolating and insoluble little hard particles filled the space between the cathode and the basket wall. Anodes were placed around outside the basket. While the cathode rotates, the particles will be forced to move around and slightly polish the surface of deposition layer continuously.

The experiments were performed in the bath with and without hard particles. The electrolyte contained $Cu_2P_2O_7$ 65 g/l, $K_4P_2O_7 \cdot 3H_2O$ 300 g/l, $(NH_4)_2HC_6H_5O_7$ 22 g/l, pH = 8.2–8.8,

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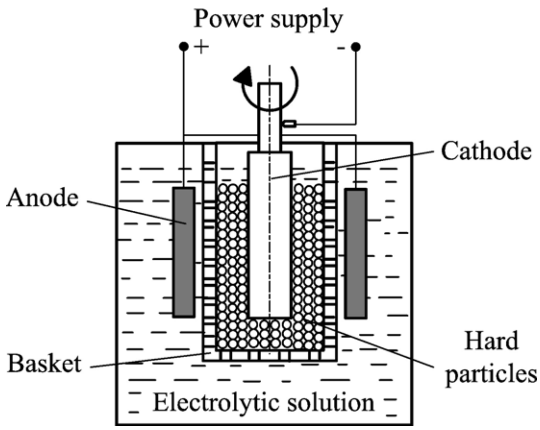

Fig. 1. Schematic diagram of the experimental setup.

$T=45\pm1$ °C. Current density was held constant at 3A dm^{-2}. A stainless cylinder mandrel was used as the cathode, and the deposit area was Ø 25 mm×40 mm. Ceramic beads with diameter of Ø 1–2 mm were chosen as the hard particles. Before deposition, the mandrel was mechanically polished, degreased and rinsed. The depositing process lasted 2 h. At the end of the process, the cathode was immediately withdrawn, washed, and dried.

The surface morphology of the deposits was examined by a LEO-1530VP FEG-SEM. A JEM-2000EX transmission electron microscope (TEM) was used to characterize the microstructure of the deposits at an operating voltage of 160 kV. Microhardness measurements were performed at room temperature using a HXS-1000A Vickers microhardness tester. The corrosion studies were carried out at room temperature in neutral aqueous solution of 0.1M NaCl using weight-loss measurements.

3. Results and discussions

3.1. Microstructure

Fig. 2 shows the surface morphology of two typical copper deposits electroformed. As shown in Fig. 2a, the surface of the deposit electroformed from the bath without hard particles is grey with nodules and pits allover the surface. By comparison, when the hard particles are added to the bath, the deposit prepared becomes bright and smooth without any nodules and pits on the surface (Fig. 2b). The SEM photos of the two deposits appear with different morphology, as shown in Fig. 2c and b. It can be seen that the morphology of the deposit electroformed from the bath with hard particles represents distinct abrasion marks. It has been found that the marks become more notable with the increase of rotation speed. It appears that hard particles can polish the surface of the deposits and sweep off the nodules during electroforming. When speeding up the rotation of mandrel, the polishing effect of hard particles can be strengthened and more distinct abrasion marks result.

Fig. 3a and b show the TEM micrograph of two typical copper deposits electroformed. Although both micrographs feature long columnar ultrafine grains, the dominant growth directions of the two kinds of the grains are evidently different. In the bath without hard particles, the grains of the deposit grow mainly along the normal line of cathode surface. Contrastively, the grain growth direction of the deposit from the bath with hard

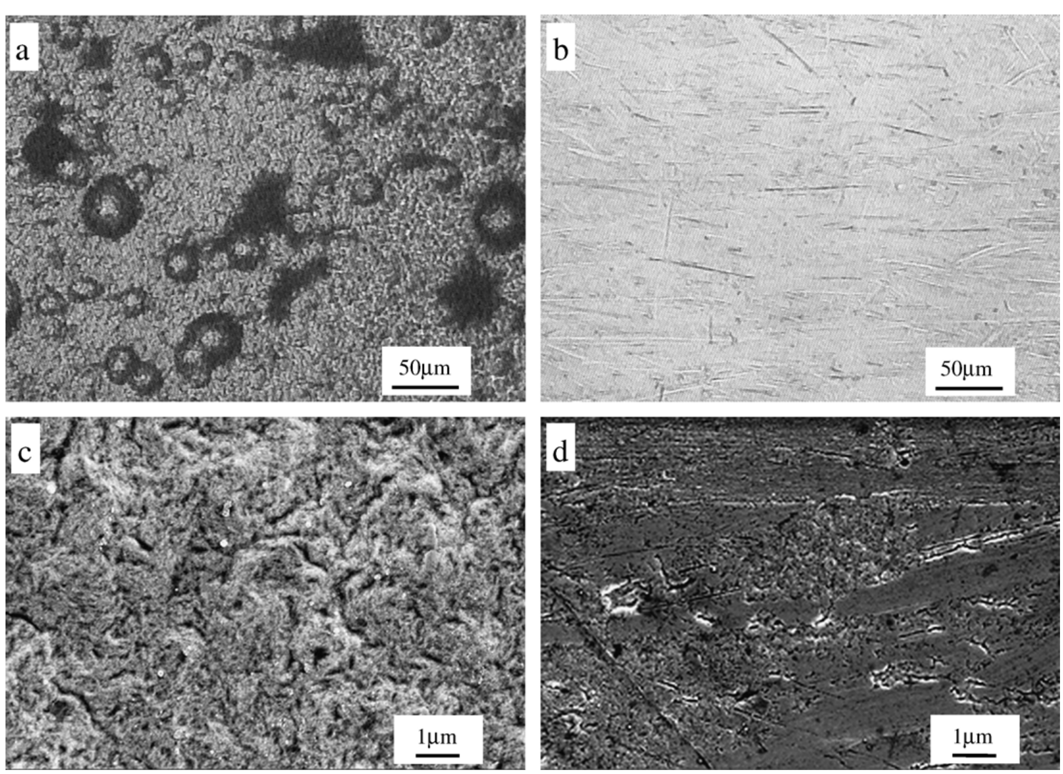

Fig. 2. Surface morphologies of two typical copper deposits electroformed at 200 r/min: (a) modified photo of the copper deposit electroformed from the bath without hard particles, (b) modified photo of the copper deposit electroformed from the bath with hard particles, (c) SEM photo of the copper deposit electroformed from the bath without hard particles, (d) SEM photo of the copper deposit electroformed from the bath with hard particles.