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Inner surface alloying on pores of lotus-type porous copper through electroless plating with supersonic vibration and annealing treatment

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ABSTRACT

A new method was explored for inner surface alloying on pores of lotus-type porous copper. Zinc was deposited on the inner surface of pores by electroless plating with thorough supersonic vibration. Then, the Cu substrate together with Zn coatings was transformed into a brass layer by annealing treatment. From images filmed by a digital single lens reflex camera and a field emission scanning electron microscopy, it can be observed that the appearance and microstructure of lotus-type porous copper surface and pore walls were changed after the sequential treatments. The statistical thickness of the alloy layer at the distance of 0.5 mm from pore openings increased with the electroless plating time increase, attaining a maximum of about 1.7 μm when the time exceeded 1.5 h. The alloy layer thickness at the sample height of 2.5 mm along the pore axial direction was determined as about 1.5 μm by the nano-indentation technique. Uniform coating and alloy layer can be achieved on the inner surface of 5 mm-long pores. The influence of annealing temperatures on phase compositions was studied by X-ray diffraction.

1. Introduction

Lotus-type porous or Gasar metals with elongated directional pores have attracted many attentions because of their peculiar physical and mechanical properties, such as impacting energy absorption capacity, air and water permeability, and the anisotropy of thermal and mechanical properties [1–3]. These make them suitable for applications in heat sinks [4], filters [5], biomedical materials [6], and so on. Copper (Cu) is one of the most popular pure metals for fabricating the lotus-type porous structure, but whose undesirable strength and hardness have hindered its widespread use in many applications. Many researchers have tried lots of methods to overcome these drawbacks [7–9]. Thereinto, depositing a metal or alloy coating on the inner surface of pores has been justified as an efficient way. Brass is made up of Cu and Zn elements and is superior in mechanical properties (such as strength, hardness, and wear resistance) compared with Cu. Therefore, if a brass coating is formed on the inner surface of lotus-type porous Cu pores, the strength of substrate is expected to be improved. Given this, Aoki T et al. [8] attempted the combined the technology of electroplating or vapor deposition Zn and annealing treatment to transform pure Cu into brass, and results proved that the method was feasible. Furthermore, Hao Du et al. [9] successfully deposited nickel (Ni) coatings on the inner surface of pores by electroplating, and finally concluded that Ni coatings could improve significantly the yield strength and the energy absorption in compression of lotus-type porous Cu samples. In addition, according to references [10–13], depositing a metal or alloy coating on the surface of metallic substrates had other uses as well, such as protecting the surface and conducting as an intermediate step for dealloying. For the substrate of lotus-type porous Cu, the criterion to evaluate the feasibility of a depositing method is to see whether or not it succeeds in depositing a uniform coating on the inner surface of pores. However, even if there are lots of methods for surface modification, only two methods, electroplating and vapor deposition, have been reported to deposit coatings on the inner surface of pores so far. The main reason is that the barrier of elongated pores makes some classical methods, such as mechanical plating, hot dipping and laser cladding, difficult for depositing metals on the inner surface of pores but easy on the outer surface of samples [9,10]. Therefore, it is challenging to explore a new method to achieve the aim of depositing uniform coatings on the inner surface of pores.

Electroless plating has become popular in recent years due to its inherent virtues by contrast of conventional electroplating, such as no requirement of electrical current and all contours of the substrate [14–16]. For depositing a Zn coating on the inner surface of lotus-type porous Cu pores, electroless plating also has its own unique advantages comparing with the reported method of electroplating. Especially, it can effectively avoid the current shielding effect resulted from the pore walls, and therefore improve the coating distribution uniformity along the pore axial direction. Although electroless plating is potentially feasible for deposition on the inner surface of lotus-type porous Cu pores theoretically,

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several problems still need to be solved. One key point is what the composition of material system is suitable for depositing a Zn coating on the surface of Cu. In this work, the classical material system whose composition was Zn powders, Cu and high concentration of sodium hydroxide (NaOH) solution was employed. They could react with each other to form a Zn coating on the surface of Cu at the temperature of approximately 70 °C. The possible reaction equations are expressed as follows:

$$Zn + 2OH^- = ZnO_2{}^{2-} + H_2 \quad (1)$$

$$ZnO_2{}^{2-} + Cu = CuO_2{}^{2-} + Zn. \quad (2)$$

As shown in Eq. (1), Zn powders reacted with NaOH to form Na_2ZnO_2 which together with the excess Zn powders and Cu constituted a kind of a copper–zinc cell. And then Eq. (2) occurred. Thus, Zn was deposited on the surface of Cu. Another key point is how the depositing process proceeds on the inner surface of pores. Difficulties mainly lie in two parts. First, the H_2 produced from the reaction of Eq. (1) in pores must be discharged immediately to assure that Eq. (2) occurred on the inner surface of pores. Second, adequate solution must be driven into pores in time to assure the sufficient supply of reactants for Eq. (2) proceeding. Considering these aspects, the technique of supersonic vibration was applied throughout the whole process to assist bubbles in discharging out of pores and solution in flowing into pores. Thus, via the electroless plating with supersonic vibration, the inner surface of lotus-type porous Cu pores would be deposited with a uniform Zn coating hopefully, and then, the as-deposited lotus-type porous Cu would be alloyed via the traditional method of thermal treatment which was proceeded in Ar atmosphere at different temperatures. Finally, the Cu–Zn alloy layer was formed on the inner surface of Gasar Cu pores.

In this work, we reported a new method for inner surface alloying on pores of lotus-type porous Cu whose average pore diameter was 380 μm and smaller than the adoptive value of 603.5 μm in Ref. [9]. The thickness distribution, microstructure and phase composition of alloy layers at different experimental conditions were studied by means of images filmed using a digital single lens reflex camera (DSLRC) and a field emission scanning electron microscopy (FESEM) and the analysis of X-ray diffraction (XRD), respectively. The alloy layer thickness at the sample height of 2.5 mm was detected by the nano-indentation technique. Element compositions of inner surface were characterized by the energy dispersive X-ray detector (EDX) analysis.

2. Experimental procedure

A lotus-type porous copper with an average pore diameter of 380 μm and porosity of 36% was employed as the substrate. For the deposition of Zn coatings, cubic specimens of 10 (length) × 10 (width) × 5 (height along the pore axial direction) mm^3 were cut from the lotus-type porous Cu ingot. Prior to electroless plating, substrates were first activated in 8 mol/L nitric acid for 3 s and then were degreased in 1 mol/L hydrochloric acid for 5 min with ultrasonic washing to remove grease and surface oxide and finally were rinsed by deionized water for 5 min to remove residual ions. In order to avoid the oxidation of Zn coating furthest and to hasten the drying process, the pretreated specimens were immersed in absolute ethanol for 10 s and then dried with Ar flow for the next operation. Electroless plating was performed for 0.5–2.5 h at the temperature of 70 °C in electroless bath containing: 100 mL NaOH solution (5 mol/L) and 3 g Zn powders. The supersonic vibration technique was employed throughout the electroless plating process. The as-prepared specimens were annealed in a tube furnace at different temperatures (150 °C, 300 °C and 410 °C) in Ar atmosphere and then cooled to room temperature under Ar flow. In addition, all annealing times were set at 0.5 h. Specimens of S1–S8 used in this work at different experimental conditions were shown in Table 1.

Table 1
All specimens used in this work.

Specimens	Electroless plating time (h)	Annealing temperature (°C)	Annealing time (h)
S1	–	–	–
S2	2.5	–	–
S3	2.5	410	0.5
S4	0.5	410	0.5
S5	1	410	0.5
S6	1.5	410	0.5
S7	2.5	150	0.5
S8	2.5	300	0.5

In order to know whether the inner surface of the pore walls was alloyed or not and to preserve the original morphology of alloy layers without destroying it, the longitudinal section of specimens were grinded mechanically to expose the first layer pores beneath the surface. Specimens after electroless plating and annealing treatment were mounted, grinded and polished to observe the alloy layer thickness by means of FESEM images of the cross section of lotus-type porous Cu. The measured alloy layer thickness was the average value of 20 points chosen from 10 different pores randomly. The inner surface and cross section of lotus-type porous Cu were observed by the FESEM (Zeiss MERLIN-VP-COMPACT) analysis. Element compositions of alloy layers were determined using EDX (Oxford INCA). The hardness and thickness of alloy layers at the sample height of 2.5 mm were detected by the nano-indentation technique (MTS-XP). The crystalline phases of specimens were identified by the XRD analysis on a D8-Advance diffraction meter (Cu Kα radiation, $\lambda = 0.154$ nm) at a scanning rate of 4 min^{-1}. In addition, to test the reproducibility of experimental results, the experiments have been always repeated several times for each sample.

3. Results and discussion

Fig. 1 shows photos of the substrate of lotus-type porous Cu, S1 (a), after electroless plating, S2 (b) and after thermal treatment, S3 (c–d). As can be seen from Fig. 1(a–c), the appearance of lotus-type porous Cu has gone through Cu's, Zn's and Cu–Zn's sequentially. The heat-treated specimen was grinded on the longitudinal section to expose the first layer pores beneath the surface, and the morphology is shown in Fig. 1(d). It can be seen that the inner surface of pores was also covered by alloy layers after sequential steps of electroless plating and annealing treatment. Owing to the thin thickness of the Zn coating and the weak bonding strength between substrates and coatings, Zn coatings could be easily destroyed in processes of grinding and polishing. Therefore, in order to avoid the damage and to increase the statistical accuracy, the varying law of the alloy layer (after annealing treatment) thickness was employed to represent that of the Zn coating (before annealing treatment) as a function of electroplating time under the same thermal conditions.

The thickness distribution of alloy layers on the inner surface of pores was investigated, which is shown in Fig. 2. Fig. 2(a) shows the alloy layer thickness of S3–S6 at the distance of 0.5 mm from pore openings as a function of electroless plating time. The thickness increases firstly and then tends to be in constant with electroplating time increase. The maximum value of alloy layer thickness is kept at approximately 1.7 μm when electroplating time reaches up to 1.5 h. This indicates that most of the inner surface of lotus-type porous Cu specimens has been covered by Zn coatings after 1.5 h, and the role of the rest of time was to assure the uniformity of coatings on the inner surface of pores. Therefore, in the following discussion, all electroless plating times are set at the maximum value of 2.5 h to assure uniformity of the obtained alloy layers.

Fig. 2(a) has shown the variation trend of plating thickness at the distance of 0.5 mm from pore openings with electroless plating time increase by measuring the alloy layer thickness in FESEM images. The main difficulty for the test method is how the surficial metal on the