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The Preparation of Core-Shell Al_2O_3/Cu Composite Powders by Electroless Plating in the Alkaline Solution

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In this study, Cu-coated Al_2O_3 composite powders were synthesized by using electroless plating method. The influence of the plating bath composition and ceramic powder concentration on the Cu plating was characterized by scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction techniques. The results showed that the electroless bath composition plays an important role for the structure of nano core-shell Al_2O_3/Cu composite powders. The content of copper in the composite powders could be effectively controlled by adjusting the content of copper sulfate and formaldehyde in the plating solution. Furthermore, the pretreatment of the Al_2O_3 powders is also a key factor to form a uniform shell copper layer coating on Al_2O_3 particles.

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1. Introduction

Electroless (EL) coating technique is one of the elegant ways of coating by controlling the temperature and pH of the bath. The history of EL plating began with the serendipitous discovery, by Brenner and Riddell, of EL nickel–phosphorus [1]. Electroless plating has been recognized as one of the most effective techniques for preparing metal-coated ceramics powders. In recent years, copper-coated Al_2O_3, graphite, cenospheres and SiC powders prepared by electroless copper plating have found extensive application in fields of copper matrix composites, anode material for lithium-ion batteries, high-current brush, EMI shielding, and catalysts [2]. Al_2O_3 has been widely used in many fields due to its good mechanical and anticorrosion properties, etc. However, the utility of a ceramic material in an engineering application is critically determined by its brittleness. Thus, the toughening of ceramic materials is very necessary and has been investigating for a long time. Making suitable Al_2O_3/metal composite powders is a key step for solving these kinds of problems. Metal-coated ceramic particles with a ceramic core and a metallic shell can improve as the wettability between the metal and the ceramics [3–5].

2. Experimental

The initial Al_2O_3 particles with mean particle size of 60 μm, was used as the substrate for the electroless plating process. In order to activate the surface of the substrate, the particles were subjected to coursing (HNO_3 solution) for 15 min, sensitizing in an aqueous solution of $SnCl_2$ for 20 min, activation in an aqueous solution of $PdCl_2$ for 20 min. The effect of $CuSO_4 \cdot 5H_2O$, formaldehyde and Al_2O_3 concentrations on the Cu content, morphology and coating uniformity in the plating bath was investigated. The copper plating solution is composed of copper sulfate solution 35–50 g/l $CuSO_4 \cdot 5H_2O$, 66 g/l EDTA, 18–36 ml/l formaldehyde and 12 g/l NaOH. The pH value of the plating solution was controlled continuously during the deposition of Cu. NaOH was used to adjust the pH value of plating bath. A total plating time of 20 min, a deposition temperature of $30 \pm 2\,^{\circ}$C and a pH of 12 were chosen during the electroless plating. After plating, the powder was washed with distilled water and then dried in an incubator at 60 °C. The weight of the Al_2O_3 powders was measured before and after the electroless deposition using analytical balance of 0.0001 g resolution. The surface morphology of the core-shell structured copper coated on Al_2O_3 particles were characterized by scanning electron microscopy (SEM) (JEOL 6060LV) equipped with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) analysis performed on the coated Al_2O_3 particles to determine the possible growth direction and the crystallographic relationship of the Cu deposition.

3. Results and discussions

The mechanism for the formation of Al_2O_3/Cu core--shell structure is described as follows. The pre--treatment in the $SnCl_2$ solution of Al_2O_3 surfaces enhances the adsorption of Pd ions in the subsequent activation process. After the sensitization, the Sn^{2+} is adsorbed on the Al_2O_3 surfaces. This impacts as a seed in the nuclei of Pd during activation processing, just as confirmed by Mao-Sheng [6] et al. In detail, the Sn^{2+} reacts with Pd^{2+} to form uniform Pd catalytic nuclei on the surface of Al_2O_3 particles in the activation process. The reaction was depicted by Eq. (1)

$$Pd^{2+} + Sn^{2+} \rightarrow Sn^{4+} + Pd^{0}. \qquad (1)$$

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When the Al_2O_3 particles after sensitization and activation were put into the plating solution, the copper

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ions would be reduced to copper on the Al_2O_3 particles surface following Eq. (2) [7]. At the same time, the HCHO could react with OH− since the pH value was maintained at pH 13 during the electroless plating procedure, as shown in Eq. (4). Furthermore, the copper ions reacted with H_2, which was produced in Eqs. (2) and (3) on the surface of Al_2O_3, as shown in the following, Eq. (4).

$$2HCHO + Cu^{2+} + 4OH^- \rightarrow 2HCOO^- + H_2\uparrow + 2H_2O + Cu, \quad (2)$$

$$2HCHO + 4OH^- \rightarrow 2HCOO^- + H_2\uparrow + 2H_2O + 2e, \quad (3)$$

$$Cu^{2+} + H_2 \rightarrow 2H^+ + Cu. \quad (4)$$

In this way, the copper particles were deposited on the surfaces of Al_2O_3 particles and Al_2O_3-copper core-shell structures were obtained.

The coating of copper on the Al_2O_3 particles was carried out in different $CuSO_4 \cdot 5H_2O$ content in the electrolyte. Figure 1 shows the influence of $CuSO_4 \cdot 5H_2O$ and formaldehyde content in the plating solution on the Cu deposited Cu content in the produced Al_2O_3/Cu powders. It shows that the weight gain increased with the increase of $CuSO_4 \cdot 5H_2O$ and formaldehyde contents. It gives a summary that Cu content on the Al_2O_3 powder surfaces can be controlled by controlling $CuSO_4 \cdot 5H_2O$. Wang et al. [5] was studied on Cu-coated Al_2O_3 composite powders using the electroless plating method. They found that the weight increment increased with the increase of $CuSO_4 \cdot 5H_2O$ content. It can be concluded that if the coating homogeneity and continuity can be controlled for all the precursor addition, increase of $CuSO_4 \cdot 5H_2O$ content causes to control the coating thickness of the Cu on the ceramic surfaces.

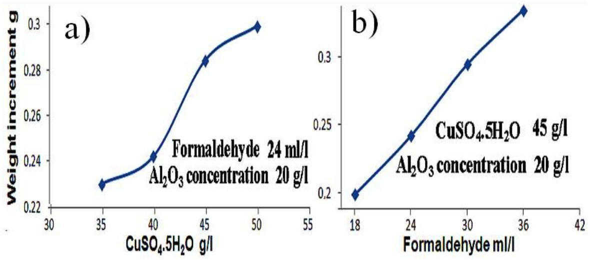

Fig. 1. Effect of the (a) $CuSO_4 \cdot 5H_2O$ and (b) Formaldehyde content in the bath solution on the weight increment in Cu coated composite powders.

The SEM micrographs of the Al_2O_3 surface-coated samples produced with different Al_2O_3 concentrations in the electrolyte are demonstrated in Fig. 2. Higher amount of copper ions can be reduced on the Al_2O_3 surfaces because the copper ion concentration was constant in the plating bath when the particle concentration was high. Another possible reason for this increase in uniform copper deposition could be the heterogeneous nucleation effect with a high particle concentration due to an increasing amount of surface area and thus an increased number of nucleation sites on the Al_2O_3 particle surfaces.

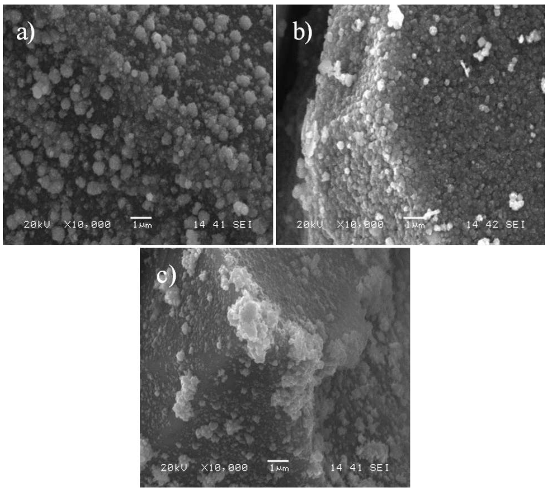

Fig. 2. SEM images of the powder with different particle loadings into electrolyte: (a) 10 g/l, (b) 20 g/l, (c) 40 g/l.

It can be further understood from XRD patterns in Fig. 3 that the Cu content in the surface coating decreases with the increase of the powder concentration in solution. Therefore, the Cu content in composite powder can be changed by controlling the amount of loaded powder to the bath.

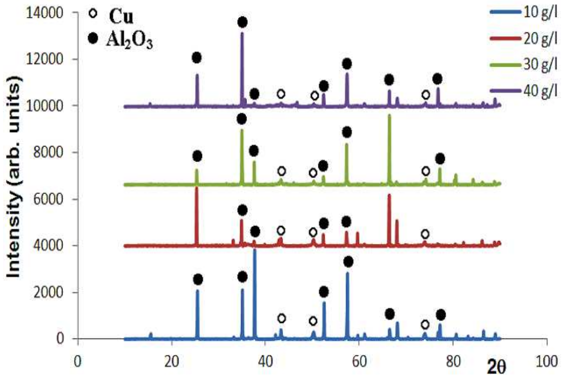

Fig. 3. XRD pattern of the powder with different load.

Figure 4a and b demonstrates the microstructures of uncoated and coated Al_2O_3 particles with core-shell structure, respectively. As can be seen from the SEM observation in Fig. 4b, homogeneous and uniform copper shell were deposited on the Al_2O_3 particles. SEM image shows nano Cu grains on the Al_2O_3 surfaces with a dense and continuous coating structure. EDS was applied to analyze the structure of the plated powders with core-shell structure and presented in Fig. 4c.

From Fig. 4c, it can be seen that Cu, O, and Al were determined in the structure. So it was considered that

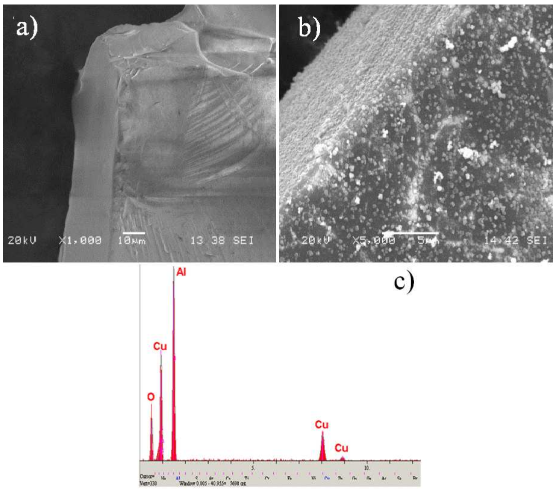

Fig. 4. SEM image of (a) uncoated Al_2O_3, (b) Al_2O_3/Cu core-shell structure, (c) EDS spectrum of the Cu coated Al_2O_3.

the powder consisted of Al_2O_3 and Cu. The uniformity of the Cu core-shell deposition and therefore, optimum process parameters were obtained for the experimental conditions of 24 ml/l formaldehyde, 20 g/l Al_2O_3 particles in the electrolyte by using a precursor of 45 g/l $CuSO_4{\cdot}5H_2O$.

4. Conclusions

The surface of Al_2O_3 ceramic powder particle has been successfully coated by copper particles by using eletroless plating and Cu core-shell structures were obtained on the Al_2O_3 surfaces. The Cu layer covering an Al_2O_3 particle was controlled by the content of $CuSO_4{\cdot}5H_2O$. The proportion between $CuSO_4{\cdot}5H_2O$ and formaldehyde as well as the powder loads were found to play an important role in the uniformity of copper layer coating Al_2O_3 particles. The full coverage of the Al_2O_3 surfaces was obtained when the particle content of the electrolyte was 20 g/l Al_2O_3, formaldehyde content of 24 ml/l and the $CuSO_4{\cdot}5H_2O$ precursor of 45 g/l.

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