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Significance of sensitization process in electroless deposition of Ni on nanosized Al_2O_3 powders

J.N. Pang, S.W. Jiang*, H. Lin, Z.Q. Wang

Department of Materials Engineering, Key laboratory of Liaoning Provincial College for New Materials and Material Modification, Dalian Polytechnic University, Dalian, 116034, China

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Abstract

The electroless deposition of Ni on nanosized α-Al_2O_3 powders of about 150 nm diameter has been studied by employing $SnCl_2$ sensitization and $PdCl_2$ activation approach. The bath for electroless deposition was prepared by using $NiCl_2 \cdot 6H_2O$, $C_6H_5NaO_7 \cdot H_2O$, NH_4Cl and $NaH_2PO_2 \cdot H_2O$, and the deposition was carried out at a bath temperature of 70 °C with a pH value of 8.5. The morphology, microstructure and phase structure of Ni-coated α-Al_2O_3 nanopowders were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffractometry (XRD), respectively. It is found that, the sensitization process followed by repetitive resining greatly affects the morphology of Ni deposited in the form of nanoparticles onto the ultrafine alumina particles, different from the conventional continuous electroless film/coating deposited on coarser particles. The resining of the $SnCl_2$ sensitized ultrafine α-Al_2O_3 particles prior to $PdCl_2$ activation process leads to varied amount of deposited Ni particles with diameters of 50–80 nm on the Al_2O_3. It is revealed that, subsequent reduction process (activation) from Pd^{2+} to Pd is linked to the original sites of Sn^{2+} by simultaneous oxidation process from Sn^{2+} to Sn^{4+} on the previously sensitized α-Al_2O_3 nanopowders. Consequently, the form of deposited Ni correlated closely to the surface distribution of reduced Pd which may be continuous or discrete determined predominantly by the density of adsorbed Sn^{2+} on the powders during sensitization process. It demonstrates a possibility of depositing different distribution structures of metals on nanosized α-Al_2O_3 powders through controlling $SnCl_2$ sensitization process.

Keywords: Electroless deposition; Ni nanoparticles; Al_2O_3; Sensitization; Activation

1. Introduction

Ni–Al_2O_3 composite coatings have been studied widely as a promising protective material for wear and corrosion resistance, where Al_2O_3 particles in the metal matrix composites (MMCs) have been considered as one of the remarkable reinforced second phases due to the high hardness and superior chemical stability [1–3]. By far, many studies have been focusing on achieving high concentration and good dispersion structure of reinforced particles in MMCs to obtain their high performance [4–6]. Good wetting behaviors between particles and metal matrix are also desired to optimize the composite structure and properties [4]. One effective way to achieve this is to use ceramic powders covered with a metal layer as a starting material for preparation of MMCs. Owing to the isolation effect of the metal layer on the particle surface, formation of highly concentrated and well-dispersed particles distribution structures in the metal matrix will be facilitated for various available composite bulk or coating preparation techniques such as plasma spark sintering, thermal spraying, laser cladding, etc., to achieve MMCs with desired performance [7,8].

Electroless deposition is widely used to fabricate metallic coatings on various materials due to its advantage in high deposition rate, simple operation and capability of mass production [9–12]. Uysal et al. [10] prepared continuous and uniform Ni layers on SiC particles by alkaline electroless

*Corresponding author. Tel.: +86 15898196052.
E-mail address: swjiang@dlpu.edu.cn (S.W. Jiang).

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deposition, and the layer thickness of Ni was between 100 and 300 nm. Xu et al. [13] reported preparation of nickel-coated graphite by electroless deposition under mechanical or ultrasonic agitation, and found that ultrasonic agitation could promote nucleation and deposition of nickel. Michalski et al. [14] reported the electroless deposition of Ni on coarse and ultrafine Al_2O_3 powders, respectively. They found that thin Ni layers consisting of loosely agglomerated nanoparticles were chemically deposited on the surface of the coarse Al_2O_3 powders; meanwhile the sintering temperature of composite powders was about 200 °C lower than that of the pure Al_2O_3 powders. However, for ultrafine Al_2O_3 powders, no Ni could be observed on the particles.

Fine ceramic powders, especially those in nanosize, have been recognized as effective strengthening second phases for MMCs [15,16]. However, successful electroless deposition of metals on ultrafine powders was rarely reported. The electroless deposition of metals on ultrafine powders may be very different from that on coarse powders due to that ultrafine powders have high specific surface area with tendency of agglomeration by van der Wals forces between them. In this work, the electroless deposition of Ni on nanosized α-Al_2O_3 powders has been studied through a traditional method at different sensitization conditions. The influence of sensitization on the Ni deposition were discussed for understanding the mechanisms of electroless nickel deposition on ultrafine α-Al_2O_3 particles.

2. Experimental

2.1. Raw materials

Nanosized α-Al_2O_3 powders with an average size of 150 nm and purity of 99.99% were used for the experiment. Typical parameters of the α-Al_2O_3 nanopowders are listed in Table 1.

2.2. Experimental procedure

The electroless plating bath and the deposition parameters are shown in Table 2. A conventional nickel deposition method with $SnCl_2$ sensitization and $PdCl_2$ activation was employed in this work [10,17]. The bath of electroless nickel is composed typically of a source of nickel ions, a reducing agent, a complexing agent and a stabilizer or inhibitor [18,19]. $NiCl_2$ is chosen as the source of nickel ions, while hypophosphite as the reducing agent in the bath. In the sensitization process, Sn^{2+} ions are absorbed on the surface of the Al_2O_3 powders, which could facilitate attracting of Pd^{2+} ions onto the surface of particles. Then the reactions of Eq. (1) may happen, where the Pd^{2+} is reduced to Pd^0, while the Sn^{2+} is oxidized to Sn^{4+}. When the activated α-Al_2O_3 powders are added to the bath, the reactions of Eqs. (2) and (3) will happen, where the Pd^0 acts as catalyst [10]. The Ni^{2+} ions will be reduced to metallic nickel and the metallic Pd^0 oxidized to Pd^{2+} during the subsequent Ni deposition process. As the reaction continues, the metallic nickel could be deposited and become denser and thicker on the α-Al_2O_3 powders.

Table 1
Characteristics of the Al_2O_3 powders used in this experiment.

Characteristics	
Crystallinity	α-Al_2O_3
Purity	99.99%
Mean particle size	150 nm
Specific surface area	12.54 m^2/g

Table 2
Composition of the electroless Ni plating bath and the deposition parameters.

Chemical composition and operating conditions	
$NiCl_2 \cdot 6H_2O$	45 g/L
$Na_3C_6H_5O_7 \cdot 2H_2O$	120 g/L
NH_4Cl	40 g/L
$NaH_2PO_2 \cdot H_2O$	8 g/L
pH	8.5
Temperature	70 °C
Stirring speed	250 r/min

Table 3
Sensitization conditions of electroless Ni depositied samples.

Samples	Powder weight (g)	Rinse conditions after $SnCl_2$ sensitization
A	0.05	5 times
B	0.1	3 times
C	0.1	1 time

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

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2 + Ni^0\downarrow \quad (2)$$

$$Pd + Ni^{2+} \rightarrow Pd^{2+} + Ni \quad (3)$$

In this experiment, in addition to adopting the $SnCl_2$ sensitization and $PdCl_2$ activation process in Ref. [10], rinsing of the sensitized Al_2O_3 powders was intentionally applied for the Ni electroless deposition. Firstly, the Al_2O_3 powders were immersed in acetone solution with ultrasonic agitation for 20 min to clean the surface. Secondly, the powders were sensitized in an aqueous solution of 10 g/L $SnCl_2 \cdot 6H_2O$ and 30 ml/L HCl for 10 min. Finally, the Al_2O_3 powders were activated in an aqueous solution of 0.25 g/L $PdCl_2$ and 3 ml/L HCl for 10 min. The powders were rinsed with distilled water in each step and dried in oven after the pretreatment processes. In order to investigate the effect of Sn^{2+} absorption behaviors on electroless nickel plating, different $SnCl_2$ sensitization conditions were controlled to prepare powders, as given in Table 3. For sample A, the sensitization condition is that 0.05 g Al_2O_3 powders were immersed in 80 ml $SnCl_2$ solution followed by rinsing for five times with 100 ml distilled water in ultrasonic cleaner. Sample B and C are both with 0.1 g Al_2O_3 powders and rinsed in 100 ml distilled water, but different in rinsing times. Each rinsing lasted for 5 min.