



Kinetic study of electroless cobalt deposition on WC particles

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ABSTRACT

The cobalt coating with an average thickness of 15–20 nm was uniformly plated on the surface of ultra-fine WC powders by electroless plating in the present work. The effects of electroless plating condition parameters on the deposition rate were studied. It was found that the deposition rate increased with the increase of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ content, pH value, complexing agent concentration, and bath temperature, while decreased with the increase of reducing agent ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) concentration. Furthermore, the cobalt deposition rate empirical equation and activation energy were determined. The results show that the activation energy (E_a) for the electroless cobalt on WC substrates is approximately 54.65 kJ/mol.

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1. Introduction

Owing to the excellent physical and mechanical properties, ultra-fine WC-Co composite powders have been widely used for ultra-fine cemented carbides to produce wear-resistant components such as micro-drill and router for printed circuit board (PCB) manufacturing [1–3]. However, the non-uniformity distributed composite powders would induce grain growth during sintering, leading to poor properties of the cemented carbide bulks [4]. Therefore, the dispersion of WC-Co composite powders is an important factor in the microstructure and mechanical properties of ultra-fine cemented carbide bulk materials.

In recent years, plenty of techniques have been used to prepare ultra-fine WC-Co composite powders, such as high energy ball milling, hydrothermal reduction, spraying conversion process and electroless plating [5–8]. Among these techniques, electroless plating has been considered as an effective method, since the prepared composite powders not only have good dispersity, uniform thickness, homogeneous composition, but also the metal content in the powders could be controlled effectively [9,10].

Electroless plating is an autocatalytic chemical reduction

process used to deposit metal or alloy on conductive or semi-conductive material. In particular, it can be used to deposit metal coatings on the special substrate in particulate form [11]. Some researchers [12,13] reported that the electroless plated metal-coated ceramic powders could effectively inhibit grain growth during the sintering process. The effect of electroless plating conditions on the deposition rate is rather complicated. It was reported that the deposition rate is related to main salt, complexing agent, hypophosphite concentration, pH, and plating temperature [14–17].

By changing the plating conditions, a quantitative mass of cobalt coating can be obtained. Thus, cemented carbides with different cobalt content can be prepared by electroless plated WC-Co composites. In previous works, the cobalt coating prepared by electroless plating process have achieved significant results in WC surface modification [8,18]. A large amount of electroless cobalt plating bath solutions with different parameters have been tested and recommended for industrial applications, but to the authors' knowledge, there is little literature about the growth kinetics of the electroless Co-coated WC composite powders. The questions remained if the growth kinetics can adjust the cobalt content in WC/Co composite powders. The purpose of this work is, therefore, to synthesize ultra-fine WC/Co composite powders by electroless plating process, characterize the morphology and structures of WC/Co composite powders, and establish a deposition rate equation for electroless cobalt plating on WC particles which will better monitor

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and adjust the chemical deposition rate of cobalt.

2. Experimental

2.1. Pre-treatment process of WC particles

WC particles (0.2–0.3 μm , Jiangxi Jiangwu Cemented Carbide Co., LTD, China) were used as the substrate in the present study. Initially, to clean the surface, the WC powders were degreased with the nitric acid (HNO_3) solution and sodium hydroxide (NaOH) solution for 10 min and then rinsed by the deionized water. Afterwards, the cleaned WC powders were immersed in a sensitization solution, followed by activation process. The constituents of the sensitization and activation solution are shown in Table 1. The sensitization and activation process played an important role in accelerating the formation of Pd atoms on the WC Particles in the following electroless plating [19]. In order to reduce the agglomeration of the powders, all the processes were carried out with ultrasonic vibration.

2.2. Electroless cobalt plating on WC particles

The electroless plating was carried out in a cobalt electroless plating solution preheated to 60–90 °C. The bath solution contained cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hypophosphate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) and boric acid (H_3BO_3), shown in Table 2. During the electroless plating process, pH was kept at a constant value ranging between 9.0 and 11.0 by adding sodium hydroxide (NaOH). After plating, the coated WC/Co composite powders were rinsed in de-ionized water for several times and dried in a vacuum drying oven at 70 °C for 24 h.

2.3. Heat treatment of the WC/Co composite powders

To get the fully crystallized Co layer, the WC/Co composite powders were heat treated in a tube furnace in hydrogen atmosphere, with a heating rate of 10 °C/min at a constant temperature ranging between 400 °C and 600 °C for 1 h. Subsequently, the WC/Co composite powders were furnace-cooled down to room temperature.

2.4. Characterization of the WC/Co composite powders

The deposition rate, v , generated by the weight gain of the powders during the electroless plating, was based on the following formula:

$$v = \frac{\Delta m}{t} = \frac{m_2 - m_1}{t} \quad (1)$$

where m_1 and m_2 represent the mass of raw WC powders and coated WC/Co powders, respectively, and t is the deposition time.

The morphology of the powders was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The elemental concentration distribution of the powders was analyzed via energy dispersive X-ray spectroscopy (EDX). The structures of the powders were determined by X-ray diffraction

Table 1

The constituents of chemical reagents selected for pre-treatment process of WC powders in the present study.

Process	Component	Content	Condition
Sensitization	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + \text{HCl}$	20 g/L+40 ml/L	25 °C, 15mins
Activation	$\text{PdCl}_2 + \text{HCl}$	0.5 g/L+120 ml/L	25 °C, 15mins

Table 2

Bath compositions and operation conditions for electroless cobalt plating on WC powders in the present study.

Bath Composition	Content	Condition
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	15–30 g/L	pH 9–11 60–90 °C 8mins
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	20–50 g/L	
$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$	15–30 g/L	
H_3BO_3	25 g/L	
$\text{C}_4\text{H}_4\text{O}_4$	1.5 g/L	

(XRD) with a working voltage of 40 kV and filament current of 40 mA. The X ray diffraction angle of samples (2θ) changed from 10° to 90° with a scan speed of 8°/min. Some slow scans with a scan speed of 1°/min from 40° to 46° were also conducted to identify the presence of Co.

3. Results and discussion

3.1. Morphology of cobalt deposits

Fig. 1 shows typical SEM micrographs of WC and Co-coated WC powders. It is seen that the surface of raw WC powders were smooth, and a homogeneous coating had been achieved adhering onto the surface of WC powders. It should be pointed out that no free metal precipitated could be observed after electroless cobalt deposition. The microstructure of WC and Co-coated WC powders can be seen better from transmission electron micrograph and EDX spectrums shown in Fig. 2. It is clear from Fig. 2(a), the size of WC particle (black deeply) was about 200 nm. After electroless plating, some obvious changes in the morphology of Co-coated WC composite powders could be observed in Fig. 2(b), where a layer (light grey) with a thickness of 10–20 nm uniformly covered on WC particle. The results shown in Fig. 2(c)–(d) also give clear evidence that the plating layer is cobalt. Cu (the substrate element), W, C were presented in the EDX results of initial WC powder shown in Fig. 2(c), and Co could be observed from the plated powder as shown in Fig. 2(d), which indicated that Co had been successfully deposited on the WC particle.

Fig. 3 shows the TEM images of Co-coated WC composite powders with different plating time, where the concentration of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ were 20 g/L, 20 g/L, 30 g/L, respectively. It can be seen from Fig. 3(a) that after plated for 2 min, irregular nodules structure morphology could be observed on the WC particle surface. The large number of nodules might be attributed to the initial state of the preferred nucleation based on chemical reduction of plating. Tsai and Chao [20] found that the Co particles always firstly deposited at the catalytic site of Pd particles. When the plating time was 4 min, as shown in Fig. 3(b), more Co continuous nucleated and grew. When plating proceeds with time up to 6 min, as the deposited Co particles grew and coalesced together, the entire surface of the WC particle was covered by a continuous thin film (the thickness was about 12 nm, shown in Fig. 3(c)). Subsequently, after 8 min deposition, a thicker film (the thickness was about 20 nm) with a continuous and uniform morphology were completely distributed on the WC particle (Fig. 3(d)). What's more, it should be noted that, when further increasing the deposition time surpassed 8 min, the bubble was no longer generated in the plating bath by naked eyes. This suggested that the reaction of electroless plating process was done.

3.2. Structures of the WC/Co composite powders

Fig. 4 displays the XRD patterns of WC powders and Co-coated WC composite powders. It is seen from Fig. 4 (a) and (b) that,

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