Materials Science and Engineering A 434 (2006) 319–325

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Effect of surfactant on the electrodeposition and wear resistance of Ni–Al_2O_3 composite coatings

Li Chen [a,b], Liping Wang [a,b], Zhixiang Zeng [a,b], Junyan Zhang [a,*]

[a] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China*

Received 14 March 2006; received in revised form 29 June 2006; accepted 30 June 2006

Abstract

Ni–Al_2O_3 composite coatings were electrodeposited from a Watts-type bath containing particles in suspension, which were dispersed with the aid of a cationic surfactant hexadecylpyridinium bromide (HPB). The effects of the surfactant on the zeta potential, co-deposition and distribution of Al_2O_3 particles in nickel matrix, and tribological properties of composite coatings were investigated. Experimental results showed that the addition of HPB could improve the amount of co-deposited Al_2O_3 particles, reduce the agglomeration of particles and achieve a more uniform distribution of Al_2O_3 particles in the nickel matrix. The wear resistance of the composite coatings increased with increasing concentration of HPB up to a certain optimum of 150 mg l^{-1}, beyond which a decreasing trend of wear resistance was observed under dry sliding and oil-lubricated conditions. This is probably due to the increased brittleness of metal matrix when the concentration of surfactant exceeded the optimum.

Keywords: Surfactant; Composite coatings; Zeta potential; Wear resistance

1. Introduction

Particle-reinforced composite coatings produced by electrodeposition have been widely developed over the past decades due to their high hardness, good wear resistance and corrosion resistance compared to pure metal or alloy coatings [1–3]. However, these properties mainly depend on both the matrix phases of a composite coating and the amount and distribution of co-deposited particles, which is related to many process parameters, including particle characteristics (particle shape, size, concentration and surface charge), electrolyte composition (electrolyte concentration, additives, surfactant type and concentration) and applied current (direct current, pulsed current and current density) [4]. There is a lot of research concerning the effect of operating conditions on the amount of co-deposited particles in the metal matrix [5–7].

It is well known that the ultrafine particles may agglomerate in the electrolyte bath due to high surface free energy. Furthermore, high ionic strength of electrolyte and high concentration of inert particles in electroplating bath make particles tend to get agglomerated [8]. The agglomeration of particles in coatings would bestow poor mechanical properties to composite coatings. Hence, how to increase the co-deposition content and improve the distribution of ultrafine particles in composite coatings become to a crucial problem. Attempts to alleviate the above problem, the use of various physical and chemical methods have been reported by many researchers. When pulse current (PC) and high rotation velocity of cathode were applied, compact composite deposits with high concentration of embedded WC particles and uniform distribution were obtained [7]. Qu et al. [9] reported that the use of ultrasonic vibration under PC conditions resulted in diminishing agglomeration, but the amount of Al_2O_3 nano-whiskers embedded in composite coatings was also reduced. Kuo et al. [10] demonstrated that the nano-alumina particle volume content in composite coating was increased from 8.37 vol.% to a maximum value of 26.78 vol.% and the homogeneity of the composite coating was promoted by decreasing the ionic concentration of the electrolyte solution and the use of specific ultrasonic energy treatment. Among these methods, the addition of metal cationic accelerants and organic surfactants in an electrolytic bath improved the amount and the distribution of co-deposited particles effectively [11], which was also proved in Ni–SiC electrodeposition system [12,13].

---

[*] Corresponding author. Tel.: +86 931 496 8295; fax: +86 931 496 8163.
E-mail address: junyanzh@yahoo.com.cn (J. Zhang).

0921-5093/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2006.06.098

Although many investigations have revealed that the addition of surfactants can promote the volumetric content of reinforced particles, the influence of organic surfactants on the property of metal matrix was not studied. Therefore, an attempt has been made to investigate the influence of the concentration of surfactant hexadecylpyridinium bromide (HPB) on the amount of Al_2O_3 particles in the coatings and the property of nickel matrix. The anti-wear performance of such composite coatings was also investigated.

2. Experimental procedures

The plating electrolyte was a Watts-type bath. The basic composition and the plating conditions are shown in Table 1. The average size of the α-Al_2O_3 particles used in the experiment was about 0.8 μm. To 250 ml of the nickel bath, surfactant hexadecylpyridinium bromide was dissolved followed by the addition of Al_2O_3 particles. The solution containing Al_2O_3 particles was ultrasonically dispersed for 10 min and then was stirred for 3 h before the co-deposition process.

After ultrasonic treatment, the zeta potential of alumina particles was measured by the Zetasizer Nano Series instrument (Malvern Instruments Ltd., United Kingdom). The zeta potential was calculated automatically by the Zeta Plus instrument based on the Henry equation.

$$Z = \frac{3\eta U_E}{2\varepsilon f(\mathrm{Ka})} \qquad (1)$$

where Z is the zeta potential, η the viscosity of the suspending liquid, U_E the electrophoretic mobility, ε the dielectric constant of the suspending liquid and f(Ka) is the Henry's function. Six measurements were performed for each test using modified Watts-type bath as dispersant.

AISI-1045 steel plate with an area of 0.05 m^2 was used as the cathode; a pure Ni plate was used as the anode. Prior to electroplating, the substrates were mechanically polished to 0.08–0.12 μm surface roughness, and then a sequence of cleanings was performed to remove contamination on the substrate surface. The steel substrate was activated in a mixed acidic bath at room temperature before electroplating. During co-deposition process, the plating bath was stirred by a magnetic stirrer with stirring rate of 300 rpm. The plating time was 3 h in all the cases, and the thickness of the produced composite coatings was about 90 μm.

Table 1
Basic bath compositions and electrodeposition conditions

$NiSO_4 \cdot 6H_2O$ (g l^{-1})	300
$NiCl_2 \cdot 6H_2O$ (g l^{-1})	50
H_3BO_3 (g l^{-1})	40
Sodium dodecyl sulfate	0.1
Al_2O_3 particle (g l^{-1})	20
Hexadecylpyridinium bromide (mg l^{-1})	0–300
Temperature (°C)	40–45
pH	4
Current density (A dm^{-2})	3.0
Plating time (h)	3

The distribution of co-deposited Al_2O_3 particles in the surface and the cross-section of composite coatings were observed using a JSM-5600Lv scanning electron microscopy (SEM) instrument. The amount of co-deposited Al_2O_3 particles was determined using an energy dispersed X-ray microanalyzer (EDX) coupled to the SEM at a magnification of 50× and the dimension of region analysis was about 2.5 mm × 2 mm. The ZAF (factors of atomic number Z, absorption A, and fluorescence correction F) corrected EDX data were used to determine the atomic percentage of nickel and aluminum from the intensity of the respective Ka lines. The amount of co-deposits was examined at five different locations of each coating and the average volume percentage of these deposited elements was calculated. The hardness of the coatings was measured by using a Vicker's microhardness indenter with a load of 50 g. The final value quoted for the hardness of a coating was the average of 10 measurements.

The wear tests were performed on a reciprocating ball-on-disk UMT-2MT tribometer (Center for Tribology, Inc., California, USA) at room temperature with a relative humidity of 45–55% under dry sliding and oil-lubricated conditions. An AISI-52100 stainless steel ball (diameter 3 mm) was used as the counterpart. Dry sliding wear tests were performed under a load of 1 N with a sliding speed of 55 mm s^{-1}; oil-lubricated wear tests were performed under a load of 20 N with a sliding speed of 110 mm s^{-1}. Wear rates of all coatings were calculated on the basis of the volumetric loss, which was measured using a surface profilometer. Wear rates of all the composite coatings were calculated using the equation of $K = V/SF$, where V is the wear volume loss in mm^3, S the total sliding distance in m, and F is the normal load in N.

3. Results and discussion

3.1. Effect of HPB on co-deposition of alumina particles

Fig. 1 shows the effect of concentration of surfactant HPB on the amount of Al_2O_3 particles in composite coatings. It appeared that the volume fraction of co-deposited Al_2O_3 particles increased with increasing surfactant concentration in the

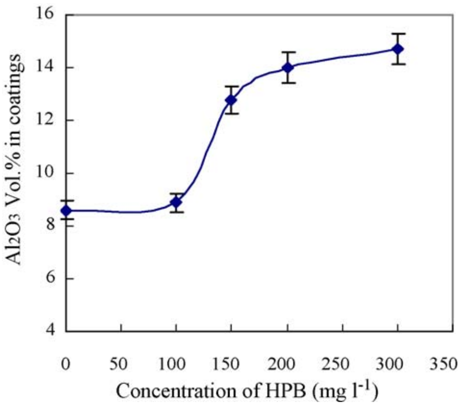

Fig. 1. The volume percentage of co-deposited Al_2O_3 particles in various concentration of surfactant (HPB).