

Preparation of Ni-CNT composite coatings on aluminum substrate and its friction and wear behavior^①

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Abstract: Nickel-carbon nanotube(CNT) composite coatings with a Zr-Ni interlayer were prepared by electrodeposition technique on aluminum substrate. The effects of CNT concentration in plating bath on the volume fraction of CNTs in the deposits and the coating growth rate were investigated. The friction and wear behavior of the Ni-CNT composite coatings were examined using a pin-on-disk wear tester under dry sliding conditions at a sliding speed of 0.062 3 m/s and load range from 12 N to 150 N. Because of the reinforcement of CNTs in the composite coatings, at lower applied loads, the wear resistance was improved with increasing volume fraction of CNTs. Since cracking and peeling occur on the worn surface, the wear rates of composite coatings with high volume fraction of CNTs increase rapidly at higher applied loads. The friction coefficient of the composite coatings decreases with the increasing volume fraction of CNTs due to the reinforcement and self-lubrication of CNTs.

Key words: carbon nanotubes (CNTs); composite coating; electrodeposition; friction and wear

CLC number: TG 17

Document code: A

1 INTRODUCTION

Aluminum and its alloys are attractive for many applications in automobile and aerospace industries because of their high strength-to-mass ratio and high thermal conductivities. However, poor wear resistance and low seizure load of aluminum alloys are a major drawback for applications that require sliding contact. The wear resistance of aluminum alloys can be improved by surface modification or protecting coatings. There are many technologies available to provide coatings for aluminum alloys, in particular, electrodeposited composite coating technology is of significant interest for the automotive industry. Composite coatings could be prepared by suspending micro or nano-sized particles in plating bath and co-depositing these particles with metal^[1, 2]. The particles, such as Al₂O₃, SiC, MoS₂, WC and PTFE in the deposits bring a significant improvement on the wear properties of the coatings^[3-8].

As carbon nanotubes (CNTs) have excellent mechanical properties such as high elastic modulus, bending strength and good tenacity^[9-11], CNTs have been an ideal reinforcement for composites. Recently, CNT reinforced copper matrix composites fabricated by powder metallurgy and Ni-P-CNT composite coat-

ings by electroless plating on low carbon steel were obtained^[12-15]. It is found that the wear resistance of the Cu-CNT composites and electroless Ni-P-CNT composite coatings been improved and the friction coefficient decreases due to the effect of CNTs. Because of the presence of oxide film, it is difficult to obtain an adherent electrodeposited nickel coating on aluminum substrate. In the present work, an interlayer was deposited on the aluminum substrate. The possibility of incorporation of CNTs in a nickel matrix on an interlayer was studied with a Watt's nickel bath. The effect of the concentration of CNTs in plating bath on friction and wear behavior of the composite coatings under dry sliding conditions was discussed.

2 EXPERIMENTAL

2.1 Preparation of Ni-CNT composite coatings by electrodeposition

LY12 Al alloy (Cu 4.4%, Mg 1.5%, Mn 0.6%, balanced Al, mass fraction) was used as a substrate material. The test specimens having discs of 2 mm in thickness and 20 mm in diameter were prepared. Because aluminum is an active metal, it is easy to form an oxide film on its surface. To improve the adhesion strength between Al alloy substrate and Ni

① **Foundation item:** Project(2002AA334020) supported by the Hi-tech Research and Development Program of China; project(20003009) supported by the National Natural Science Foundation of China; project(2002 - 350) supported by the Special Foundation of the Education Ministry of China for Young Teacher

Received date: 2004 - 02 - 18; **Accepted date:** 2004 - 05 - 22

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CNT composite coating, a Zn-Ni interlayer was deposited on the aluminum substrates by electroless plating. Prior to plating, all substrate surfaces were polished and degreased with acetone. The surface roughness of the substrate was about $1.0 \mu\text{m}$ (R_a). The electroless bath had the composition as follows: ZnO 5 g/L, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 15 g/L, NaOH 100 g/L, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 2 g/L, $\text{KNaC}_4\text{H}_4\text{O}_8 \cdot 4\text{H}_2\text{O}$ 5 g/L. The Zn-Ni layers were deposited on the substrates at room temperature for 20 s and with a film thickness of $3 \mu\text{m}$. After deposition, the surfaces of the Zn-Ni layers with high adhesion strength to the substrate appeared smooth and pearl blue.

Multiwalled carbon nanotubes (CNTs) were prepared by chemical catalytic vapor deposition. The process has been described in Ref. [12]. After purification and ball milling, the multiwalled carbon nanotubes were used to fabricate Ni-CNT composite coatings. Fig. 1 shows a TEM image of CNTs after purification.

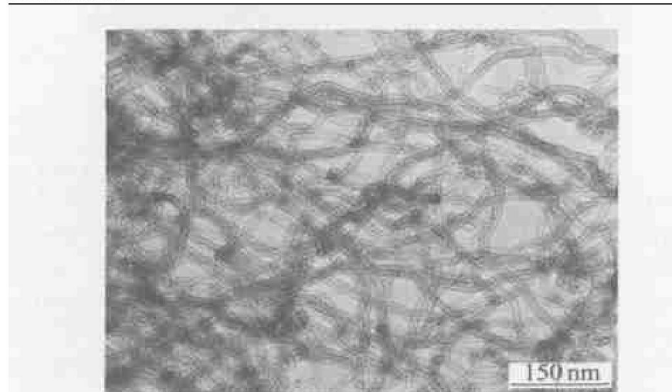


Fig. 1 TEM image of carbon nanotubes after purification

Ni-based composite coatings with different volume fraction of CNTs were deposited on the Zn-Ni interlayer by electroplating. The composition of the electroplating bath and the operating conditions are listed in Table 1. The Ni-CNT composite coatings with thickness of $12 \mu\text{m}$ were deposited under magnetic stirring. To eliminate the stress and prevent the hydrogen-induced crack, the composite coatings were heat-treated at 673 K for 2 h. By measuring the densities of the composite coatings as compared to Ni coating, filtrating and measuring the quality of CNTs in the electroplating bath after electrodeposition, the volume fraction of CNTs in the composite coatings was calculated. Microstructural analysis of the electrodeposited composite coatings was identified by X-ray diffraction (Cu K_α). The surface morphology of the as-prepared composite coatings was examined using scanning electron microscope (JEOL JSM-5600LV). Microhardness of the coatings was determined with a Vickers hardness indenter ((MT-3),

using a load of 0.49 N.

Table 1 Bath compositions and conditions for electrodepositing Ni-CNT composite coatings

Composition or condition	Value
$\text{NiSO}_4 \cdot \text{H}_2\text{O}$	250 g/L
$\text{NiCl}_2 \cdot \text{H}_2\text{O}$	30 g/L
H_3BO_3	35 g/L
CNTs	1–5 g/L
Surface agent	200–400 mg/L
pH	3.8–4.25
Temperature/ °C	55
Current density/($\text{A} \cdot \text{dm}^{-2}$)	3

2.2 Friction and wear tests

The friction and wear properties of the Ni-CNT composite coatings were investigated using a pin-on-disk wear tester (MMW-1) with the coated specimen serving as the disk under dry sliding conditions. The pin specimens (5 mm in diameter and 20 mm in height) were fabricated from a quenched and tempered steel with a Rockwell C hardness of HRC60. The surface roughness of the pin specimens was about $0.5 \mu\text{m}$ (R_a). Friction and wear tests were conducted at a sliding speed of 0.0623 m/s and at load range from 12 N to 150 N. The friction coefficient was calculated by dividing the friction force which was recorded on line via torque as measured by the strain gauge. The wear rate was defined as the mass loss of the materials per unit sliding distance. Three observations (on average) were reported in each case under steady state wear condition. The worn surfaces of the specimens were examined using a scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Microstructure and deposition rate of composite coatings

To eliminate the stress and prevent the hydrogen-induced crack, the composite coatings were heat-treated at 673 K for 2 h. Fig. 2 shows the XRD patterns of the Ni-CNT composite coatings before and after treatment. As shown in Fig. 2(a), the crystal microstructure of these electrodeposited composite coatings is mainly amorphous before treatment. The crystal structure of the nickel matrix reveals typical crystalline state after annealing treatment (Fig. 2(b)).

Fig. 3 shows the influence of the concentration of CNTs in the plating bath on the deposition rate of the composite coating. The average deposition rate decreased with the increasing volume fraction of CNTs in the bath from $0.52 \mu\text{m}/\text{min}$ for Ni coating

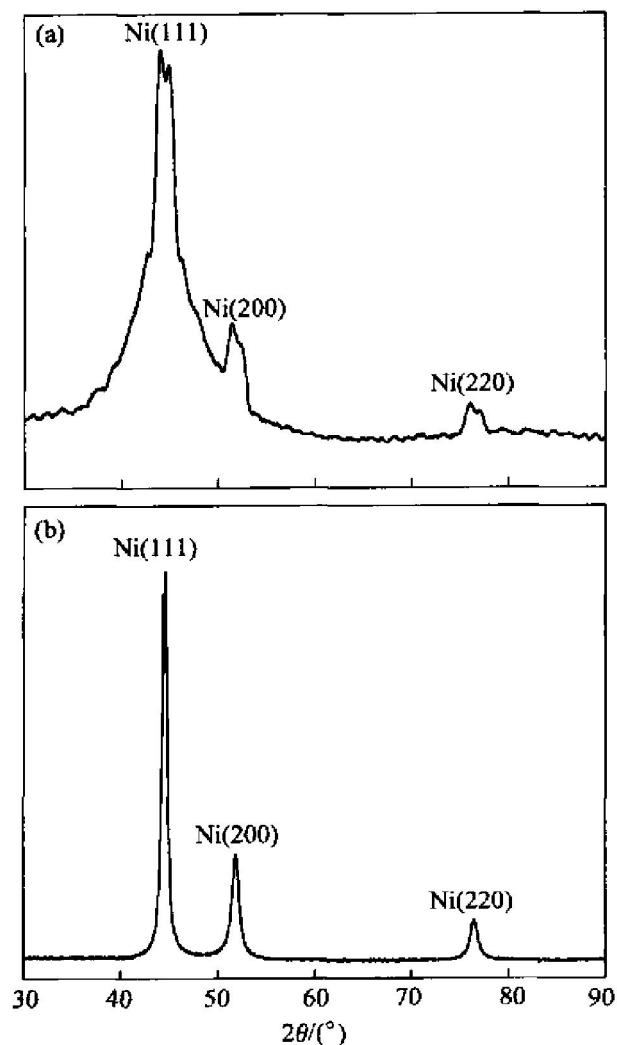


Fig. 2 XRD patterns of electrodeposited Ni/CNT composite coating before (a) and after (b) heat treatment at 673 K for 2 h

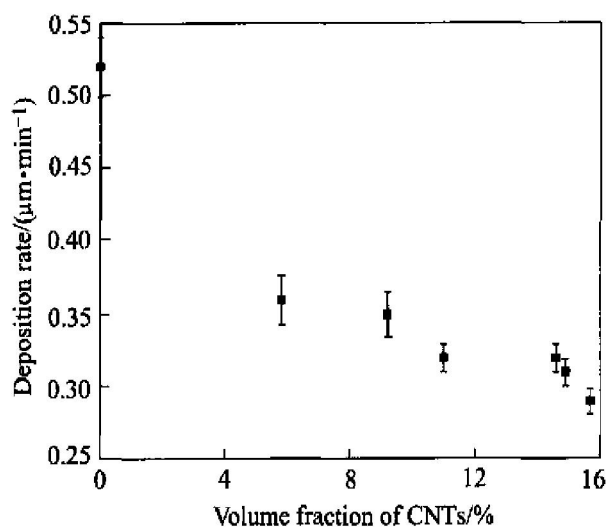


Fig. 3 Relationship of deposition rate of Ni/CNT composite coatings with concentration of CNTs in plating bath

to 0.29 $\mu\text{m}/\text{min}$ for Ni/15.3% CNT (volume fraction) coating. Explanation can be based on the catalytic redox reaction mechanism of electroplating

process^[16]. When the CNTs suspended in the plating bath, the chemically inert CNTs could occupy the catalytic sites on the substrate and decrease the contact of Ni^{2+} ions to the substrate surface. Then the amount of Ni atoms formed from the Ni^{2+} ions was reduced on the substrate surface, thereby decreasing the deposition rate. A SEM surface morphology of the Ni-based composite coating with 11.9% CNT is shown in Fig. 4. It can be found that the CNTs embedded in the nickel matrix are well dispersed.



Fig. 4 SEM image of Ni/CNT composite coating

Compared with the density of Ni/CNT composite coating and the quality of CNTs in the electroplating bath after electrodeposition, the volume fraction of CNTs in the composite coatings was calculated. Table 2 lists the corresponding volume fraction of CNTs in the composite coatings. The volume fraction of codeposited CNTs in the coatings increases with the increasing concentration of CNTs in the plating bath. When the concentration of CNTs in the plating bath is higher than 4 g/L, the increase in volume fraction of CNTs in the composite coating is slow. It indicates that the volume fraction of CNTs in the composite coating tends to become full state when the concentration of CNTs in the plating bath is higher than a constant value.

Table 2 also lists the Vickers hardness of Ni/CNT composite coatings. Microhardness of the composite coatings have been determined with a Vickers hardness indenter using a load of 50 g. As shown in Table 2, the Vickers hardness of all Ni/CNT coatings prepared is higher than that of pure electrodeposited nickel. And the hardness of the composite coatings increases with increasing volume fraction of CNT. It has been theoretically and experimentally demonstrated that CNTs have excellent mechanical properties, such as high elastic modulus and high strength and toughness^[9-11].

Table 2 Relationship of CNT concentrations in plating bath with volume fraction of CNTs and hardness of composite coatings

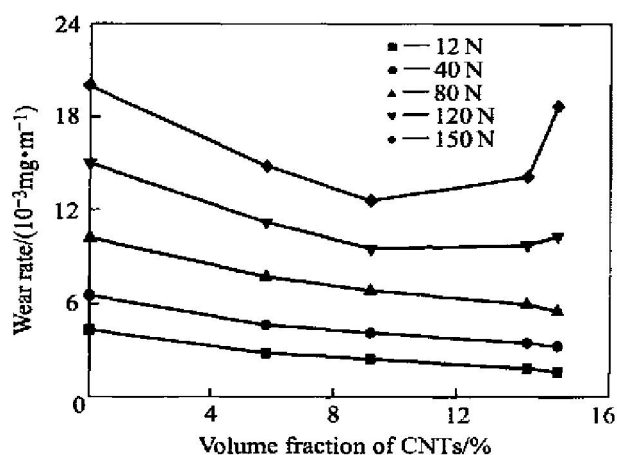
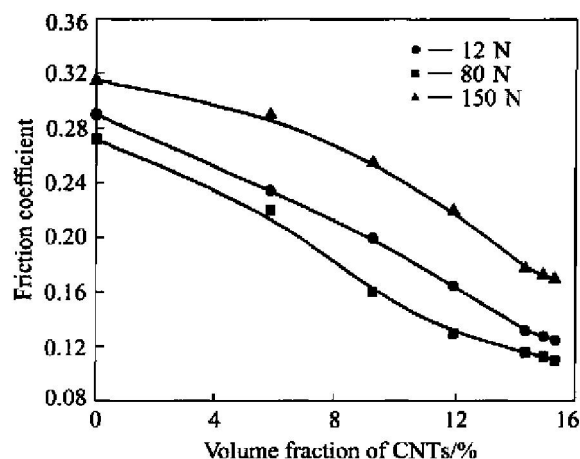
CNT concentrations in plating bath/ ($\text{g} \cdot \text{L}^{-1}$)	Volume fraction of CNTs in coatings/ %	Vickers hardness
0	0	564
1	5.8	653
2	9.2	711
3	11.9	756
4	14.3	793
5	14.9	807
6	15.3	822

The hardness increase of these composite coatings can be attributed to the dispersion-strengthening of the CNTs in the deposits.

3.2 Friction and wear behavior of electrodeposited Ni-CNT composite coatings

Fig. 5 shows the wear rates of the composite coatings versus volume fraction of CNTs at a sliding speed of 0.062 3 m/s. As the applied load increases, the wear rate of the electrodeposited composite coatings increases. Due to the effect of the reinforcement, CNTs can be used to fabricate the composites and electroless composite coatings with excellent wear resistance^[12, 13]. In this work, for the test coatings, the observed wear rates did not vary in a simple manner with the applied load range from 12 N to 150 N. As shown in Fig. 5, for the composite coating with volume fraction of CNTs less than 14.3 %, the wear rate shows a steadily decreasing trend with the increasing volume fraction of CNTs at the same applied load. For the composite coatings with the volume fraction of CNTs more than 14.3 %, the wear rates also decrease increasing with the volume fraction of CNTs at lower applied loads. However, the wear rates of composite coatings increase rapidly at applied loads above 120 N. Increasing the applied load results in cracking and spalling of the flake layer on the worn surface of composite coatings with higher volume fraction of CNTs, thereby increasing the wear rate considerably.

Fig. 6 shows the variation of friction coefficient for the composite coatings with the volume fraction of CNTs. At the same applied load, the friction coefficient of the composite coatings is lower than that of pure electrodeposited nickel. The values of friction coefficient are in the range of 0.12 to 0.29. It is found that the friction coefficient decreases with the increasing volume fraction of CNTs in the deposits. The incorporation of CNTs in the nickel deposits served as spacers, preventing the rough contact between the mating me-

**Fig. 5** Variation of wear rate of composite coatings with volume fraction of CNTs at different loads**Fig. 6** Variation of friction coefficient of composite coatings with volume fraction of CNTs at different loads

tal surface. In addition, the short and tube shape of the CNTs spalled at higher loads would slide or roll more easily between the mating steel surface, resulting in the great decrease in friction coefficient.

The worn surfaces of the electrodeposited composite coating with 14.3% CNTs (volume fraction) at loads of 40 N and 150 N are shown in Fig. 7. The plastic deformation with characteristic grooves and a little degree flake formation can be observed on the worn surface of the composite coatings. Because of the high hardness and wear resistance of the CNTs in the composite coatings, the local plastic deformation on the worn surfaces of the composites was thus greatly reduced. It is suggested that the addition of CNTs can strengthen the electrodeposited coatings and improve the wear resistance of composite coatings on aluminum substrate at lower applied load. At higher load, as shown in Fig. 7(a), the worn surfaces reveal continuous grooves and flakes. Additionally, cracking

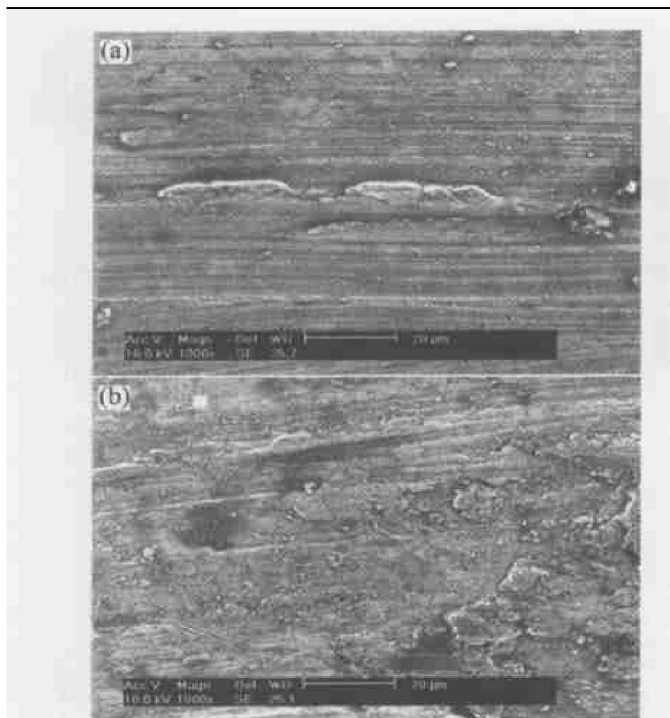


Fig. 7 Worn surfaces of electrodeposited Ni-14.3% CNT composite coating under dry sliding condition and different loads
(a) -40 N; (b) -150 N

and peeling can also be seen on the worn surface. In contrast, localized fracture occurs easily at CNT-Ni matrix interface, and the flake is fractured and debonded at the worn surface under the high load conditions, resulting in an increase in wear rate for the composite coating with high volume fraction of CNTs. Because of the lubricant effect, the debonded CNT between the mating surfaces can also decrease the friction coefficient.

4 CONCLUSIONS

1) Nickel-carbon nanotube composite coatings with a Zn-Ni interlayer were deposited on aluminum substrate by electroplating. With the increasing concentration of CNTs in plating bath, the volume fraction of codeposited CNTs in the coatings increases, while the deposition rate of composite coating decreases.

2) The friction and wear properties of composite coatings were shown to depend on the volume fraction of CNTs and applied load. At lower applied loads the wear resistance was improved with increasing the volume fraction of CNTs due to the reinforcement of CNTs. Increasing the applied load resulted in cracking and peeling of the flake layer on the worn surface, the wear rate of com-

posite coatings with higher volume fraction of CNTs increased considerably.

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(Edited by LONG Huai-zhong)