

Electroless plating Ni-P matrix composite coating reinforced by carbon nanotubes^①

DENG Fur-ming(邓福铭)^{1, 2}, CHEN Xiao-hua(陈小华)²,

CHEN Wei-xiang(陈卫祥)², LI Wen-zhu(李文铸)²

(1. Department of Materials Science and Engineering, Beijing Campus, China University of Mining and Technology, Beijing 100083, China;

2. Department of Physics, Zhejiang University, Hangzhou 310027, China)

Abstract: Ni-P matrix composite coating reinforced by carbon nanotubes (CNTs) was deposited by electroless plating. The most important factors that influence the content of carbon nanotubes in deposits, such as agitation, surfactant and carbon nanotubes concentration in the plating bath were investigated. The surface morphology, structure and properties of the Ni-P-CNTs coating were examined. It is found that the maximum content of carbon nanotubes in the deposits is independent of carbon nanotubes concentration in the plating bath when it is up to 5 mg/L. The test results show that the carbon nanotubes co-deposited do not change the structure of the Ni-P matrix of the composite coating, but greatly increase the hardness and wear resistance and decrease the friction coefficient of the Ni-P-CNTs composite coating with increasing content of carbon nanotubes in deposits.

Key words: carbon nanotubes(CNTs); composite coating; electroless plating; wear/friction

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1 INTRODUCTION

Electroless nickel-phosphorus plating has been exploited commercially for several decades, because it can be obtained with crystalline and/or amorphous structure over a wide range of composition^[1] and with excellent wear, corrosion resistance and other specific properties^[2]. With the increasing demands from industries for improving performances, technologies of better surface coatings, such as electroless composite coatings co-deposited with various particles have been widely employed. The main researches about these coatings published up to now, however, concentrate on two aspects. One is to enhance its wear resistance by co-depositing some hard particles, such as alumina^[3,4], silicon carbide^[5] and diamond powders^[6]. The other is to improve its friction properties by adding some lubricating materials, such as molybdenum disulfide^[7] and fluoropolymers^[8]. These composite coatings can either increase the wear resistance or decrease the friction coefficient, but few of the composite coatings could obtain the comprehensive properties with both high wear resistance and excellent lubricity.

Carbon nanotubes (CNTs) have superstrong mechanical properties^[9,10] and good lubricity of graphite^[11]. These properties of carbon nanotubes make them be useful in developing new composite

coatings with excellent comprehensive properties^[12,13]. In this paper, composite nickel-phosphorus coatings containing different contents of carbon nanotubes were deposited, the effects of agitation, surfactant and bath concentration of carbon nanotubes on the amounts of carbon nanotubes in deposits were investigated, and the morphology, structure and mechanical properties of the composite coatings were examined.

2 EXPERIMENTAL

2.1 Carbon nanotubes(CNTs)

The multi-walled carbon nanotubes(MWCNTs) with 10 - 30 nm in diameter and 10 - 20 μ m in length used in this experiment(Fig. 1) were prepared from catalytic decomposition of acetylene over SiO₂-Co catalysts in our own laboratory. The products were purified in 3 mol/L HNO₃ for about 24 h at 60 °C, and then rinsed with distilled water. Because the length to diameter ratio of the MWCNTs was too large to disperse homogeneously during plating, a planetary ball mill is employed to shorten the multi-walled carbon nanotubes to about 1 - 5 μ m.

2.2 Bath composition and plating conditions

The composite coating was deposited from acid hypophosphite bath, containing nickel sulphate

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Correspondence: DENG Fur-ming, Associate professor, PhD; Tel: + 86-10-82385919; E-mail: dfm@cumt.edu.cn

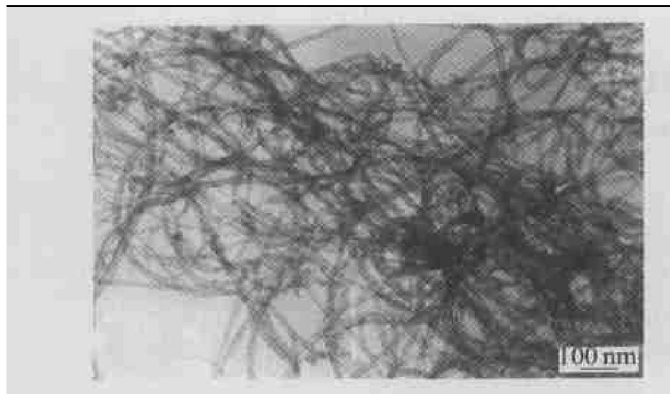


Fig. 1 TEM image of purified multi-walled carbon nanotubes

($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), 25 g/L; sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 22 g/L; and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), 10 g/L; sodium ethane acid ($\text{NaC}_2\text{H}_3\text{O}_2$), 16 g/L; lactic acid ($\text{C}_3\text{H}_6\text{O}_4$), 30 g/L; carbon nanotubes, 0–10 mg/L; and lead nitride [$\text{Pb}(\text{NO}_3)_2$], 2 mg/L with three different surfactants. The co-depositing was held for 3 h at 84 °C with pH value of 4.6 to 4.7 and stirred with four types of agitation.

2.3 Plating procedure and measurements

The substrate of the coating was prepared from 45[#] steel with dimensions of 12 mm × 12 mm × 20 mm. The pre-cleaned substrates were sensitized in a stannous chloride solution (0.1 mol/L SnCl_2 and 0.1 mol/L HCl) then activated in palladium chloride solution (0.01 mol/L PdCl_2 and 0.25 mol/L HCl) for 1 min prior to plating. The substrates were rinsed by distilled water before and after cleaning, sensitization and activation. For the sake of the strong bonding of the composite coating to the substrate, a thin layer of about 1–3 μm nickel-phosphorus coating was firstly deposited on the substrate, and then nickel-phosphorus-carbon nanotubes (Ni-P-CNTs) coating was deposited. The composite coating was subsequently annealed at 400 °C for 1 h and then cooled in air.

The amount of the carbon nanotubes in deposits was analyzed on model Lecor-334 carbon-sulphur analyzer. In order to collect about 5–10 g powder of the Ni-P-CNTs composite, several Ni-P-CNTs composite coatings were deposited directly to the substrate and then were peeled off from the substrate. The surface morphologies in as-deposited state and after annealing and the worn surface after sliding test were observed by SEM. The structure of the coating was determined by X-ray diffraction with CuK_α irradiation. The microhardness test was carried out by Vickers hardness tester with a load of 1 N, and the wear / friction test was carried out by a model MM-200 wear testing machine at a speed of 800 r/min with a load of

750 N and an engine oil (20[#]) for lubrication.

3 RESULTS AND DISCUSSION

3.1 Effect of agitation

Table 1 shows the effect of agitation methods and rates on the deposited amount of carbon nanotubes. The results show that the amount of carbon nanotubes co-deposited by ultrasonic agitation is greater than that by other agitation methods (mechanical stirring, magnetic stirring and nitrogen bubbling). Of the four agitation methods the amount of the deposited carbon nanotubes changes only a little with increasing agitation rate under the experimental conditions. The probable reasons for these were that, on one hand, in order to get Ni-P-CNTs composite coating with better distribution of carbon nanotubes, a stronger stirring method needs to be employed since carbon nanotubes that tangled together as clusters during growing process (Fig. 1) are much more difficult to disperse than other ultrafine particles; on the other hand, the strong stirring of the plating bath will wash the just deposited carbon nanotubes away from the depositing surface, so the moving velocity of the plating bath near the depositing surface must be controlled in a rational range.

Table 1 Effect of agitation on depositing amount of carbon nanotubes (CNTs 5 mg/L, $\text{C}_{12}\text{H}_{25}\text{O}_4\text{SNa}$ 0.01 g/L)

Agitation type	Agitation condition	CNTs content in deposits/ %
Mechanical stirring	80–200 r/min	0.11–0.16
Magnetic stirring	200–400 r/min	0.21–0.24
Nitrogen bubbling	3.0–4.5 L/min	0.12–0.13
Ultrasonic vibrating	10–25 kHz, 150 W	0.47–0.52

3.2 Effect of surfactant

Table 2 shows the effect of different surfactants on content of carbon nanotubes in the deposits. It is clear from Table 2 that the coatings using anionic surface active agent ($\text{C}_{12}\text{H}_{25}\text{O}_4\text{SNa}$) and nonionic surface active agent [$(\text{C}_2\text{H}_4\text{O})_x$] contain higher depositing amount of carbon nanotubes than that of the coating using cation surface active agent ($\text{C}_{19}\text{H}_{42}\text{NBr}$). This indicates that anionic and nonionic surfactants possess better wetting, emulsifying and dispersing effect on carbon nanotubes, thus it will be easily entrapped on the depositing surface of the substrate.

Table 2 Effect of surfactants on depositing amount of carbon nanotubes (CNTs 5 mg/L; Ultrasonic vibrating)

Surfactants (0.01 g/L)	Cetyl trimethyl ammonia bromide (C ₁₉ ⁺ H ₄₂ NBr)	Sodium lauryl sulfate (C ₁₂ ⁻ H ₂₅ O ₄ SNa)	Polyvinyl alcohol [(C ₂ H ₄ O) _x]
w (CNTs) / %	0.21	0.52	0.44

3.3 Effect of carbon nanotubes concentration

The depositing amount of carbon nanotubes versus concentration of carbon nanotubes in the plating bath is shown in Fig. 2. The results show that the amount of carbon nanotubes in the deposits increases as carbon nanotubes concentration in the plating bath increases from zero to 5 mg/L, but it increases as much as about 0.52% tending to saturation when carbon nanotubes concentration in the bath is up to 5 mg/L. This implies that carbon nanotubes in the deposits are independent of carbon nanotubes concentration after up to 0.52%.

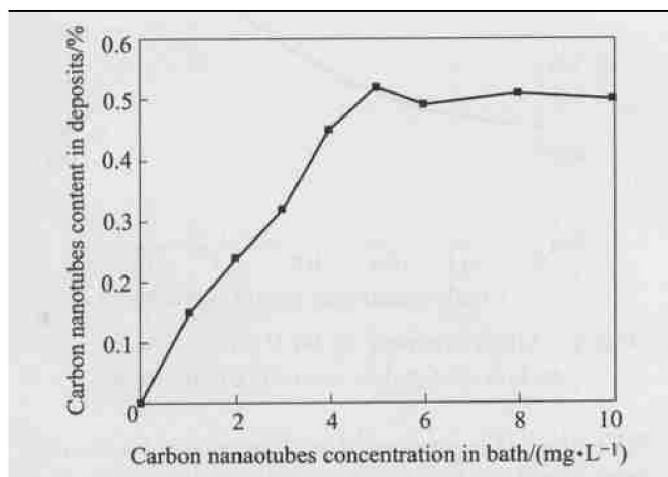


Fig. 2 Effect of CNTs concentration in plating bath on CNTs content in deposits

From the above experimental results it can be concluded that the depositing amount of carbon nanotubes mainly depends on the surface properties of carbon nanotubes and the fluid velocity of the plating bath near the depositing surfaces of the coating. However, of all the surfactants and the agitation methods studied in this paper the maximum content of carbon nanotubes in the deposits is still low with only 0.52%. Therefore, it is significant to further study an effective surfactant and agitation method for preparation high performance of electroless plating Ni-P-CNTs coating.

3.4 Surface morphologies and structure

The introduction of carbon nanotubes into the deposits results in obvious change in surface color of the Ni-P-CNTs composite coatings. The original

shining Ni-P coatings have changed to dull and black. SEM observation on the black dotted area of the surface in as-deposited state (Fig. 3 (a)) reveals that most carbon nanotubes are co-deposited at the coarse grain boundary in the form of clusters and part of them are well dispersed in the form of single fiber at its voids filling up with tinny grain Ni-P particles. It is clear that most of the carbon nanotubes are embedded deeply in the Ni-P matrix and part of them are protruded from the surface of the composite coating.

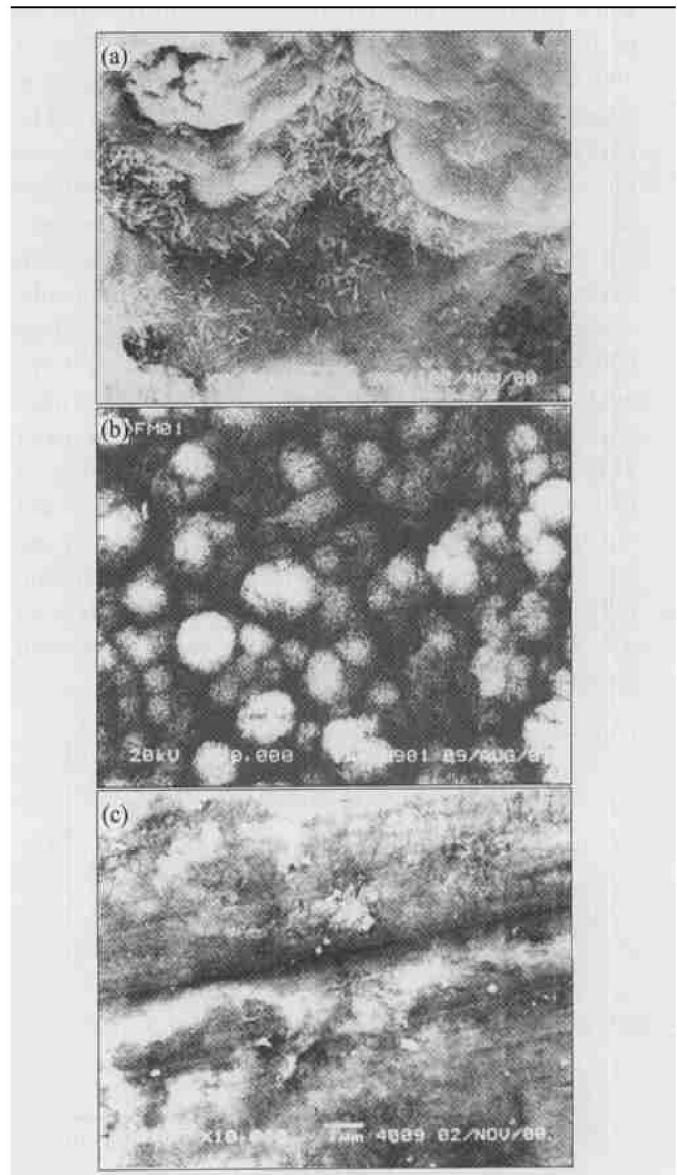


Fig. 3 SEM morphologies of Ni-P-CNTs composite coating

- (a) —In as deposited surface;
- (b) —After annealing at 400 °C for 1 h;
- (c) —Worn surface after sliding test under load of 750 N at speed of 800 r/min for 10 h (20[#] engine oil for lubrication)

Obviously, the surface structure of the coating might be of high wear resistance and excellent anti-friction property because of the superstrong mechanical properties^[9, 10] and self-lubrication of the carbon nanotubes^[11]. Energy dispersive spectrum (EDS)

analysis of the black dotted area (Fig. 4) shows that the Ni-P-CNTs composite coating contains carbon nanotubes 6.47% which is much greater than the average content of carbon nanotubes in the deposits (Tables 1 and 2). The contradictory results can be only explained that most of the deposited carbon nanotubes are not in dispersed single tubules but in cluster form, even though the carbon nanotubes are shortened by ball milling for decades of hours and dispersed by ultrasonic agitation. Further observation on the surface of the Ni-P-CNTs coating after heat treatment at 400 °C for 1 h shows that the surface morphology is quite different from that in deposit state. The coarse grain Ni-P deposits disappear, the second phase Ni₃P (black areas) disperses at the interfaces of the α -Ni matrix (bright and slightly dim areas), the carbon nanotubes are embedded under the α -Ni matrix (slightly dim areas) and therefore can be observed indistinctly (Fig. 3 (b)). X-ray diffraction (XRD) analysis of the Ni-P-CNTs coating after annealing shows that only nickel, iron and Ni₃P phases are present and no graphite and carbide exist (Fig. 5). These indicate that the introduction of carbon nanotubes in the composite coating does not change the structure of Ni-P matrix, and that the amorphous to crystalline structure transformation takes place with the precipitation of Ni₃P phase as it is similar to the Ni-P coating when it is annealed at 400 °C for 1 h^[14].

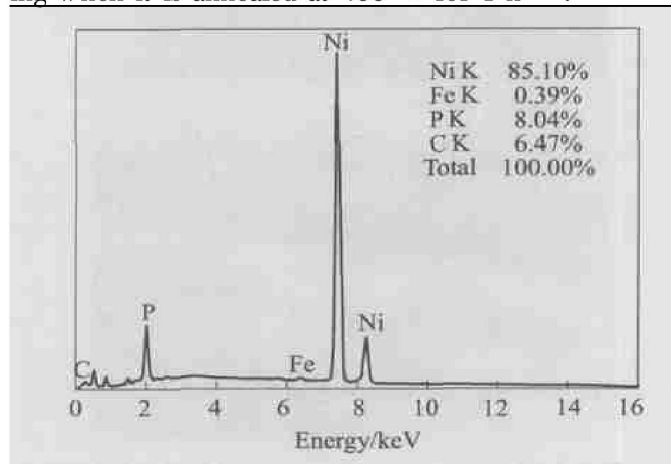


Fig. 4 EDS analysis of Ni-P-CNTs composite coating at black dotted area in Fig. 3(a)

3.5 Hardness, wear resistance and friction coefficient

Microhardness as a function of the content of carbon nanotubes in deposits is shown in Fig. 6. It is shown that the hardness of the Ni-P-CNTs composite coatings increases with the increasing amount of carbon nanotubes in deposits, average microhardness value changes from HV610 to HV880 as the content of carbon nanotubes varies from zero to 0.52%. These indicate that the introduction of carbon nanotubes to the composite coating greatly reinforces the Ni-P matrix of the composite coating.

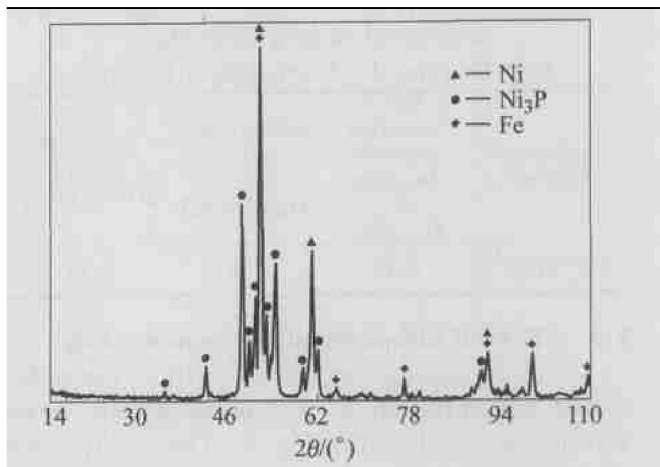


Fig. 5 XRD pattern of Ni-P-CNTs composite coating (CNTs content 5 mg/L; Ultrasonic vibrating; C₁₂H₂₅O₄SNa 0.01 g/L) annealed at 400 °C for 1 h

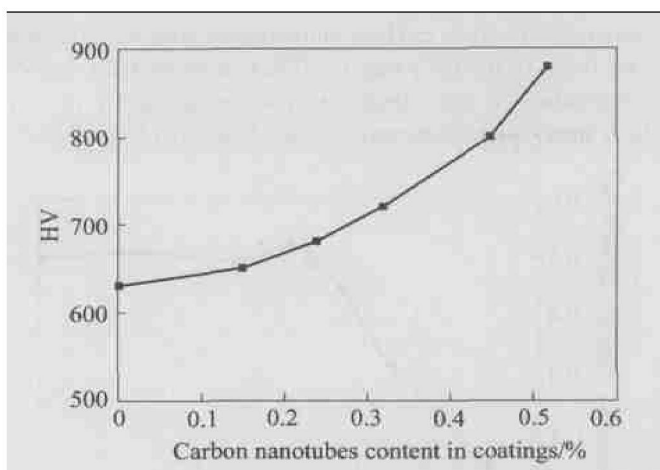


Fig. 6 Microhardness of Ni-P-CNTs coatings vs carbon nanotubes content in coatings

The wear resistance of the Ni-P-CNTs composite coatings (Fig. 7) show that the wear volume approximately decreases linearly with increasing content of carbon nanotubes in deposits under the experimental conditions, and the minimum wear volume of the Ni-P-CNTs composite coatings occurs at the maximum content of carbon nanotubes in deposits (about 0.52%), which is about one sixth of that of the conventional Ni-P coating. The friction coefficient test results (Fig. 8) show that the friction coefficient of the Ni-P-CNTs coatings ranges from 0.25 to 0.10 as the carbon nanotubes content varies from zero to 0.52%.

SEM examination of the worn surface of Ni-P-CNTs coating (Fig. 3(c)) shows that most of the worn surface become flat and smooth except for a little adhesive wear vestiges and very small scratches even though sliding under the load of 750 N at 800 r/min for 10 h with 20# engine oil for lubrication. These indicate that the carbon nanotubes deposited in the composite coating can greatly enhance the load

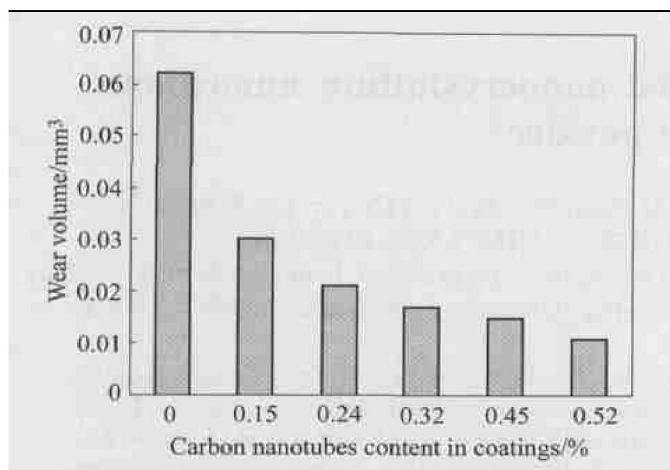


Fig. 7 Wear volume of Ni-P-CNTs coatings vs carbon nanotube content in coatings (sliding load of 750 N, sliding speed of 800 r/min, 20# engine oil for lubrication)

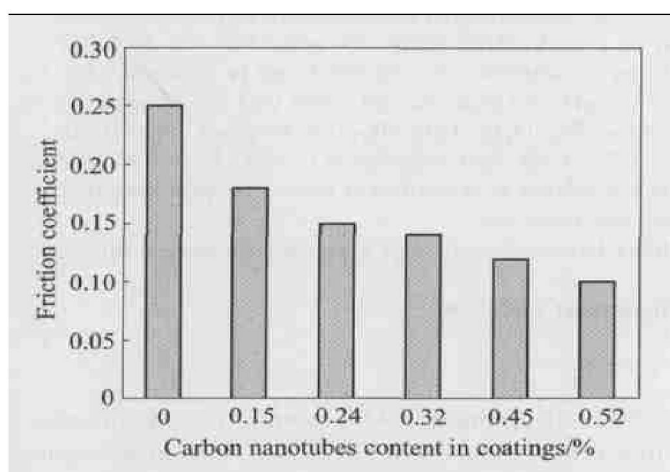


Fig. 8 Friction coefficient of Ni-P-CNTs coatings vs carbon nanotubes content in coatings (sliding load of 750 N, sliding speed of 800 r/min, 20# engine oil for lubrication)

bearing capability and decrease the friction coefficient of the composite coating. Apparently, the carbon nanotubes in the deposits can suppress the plastic deformation and enhance the mechanical properties of the Ni-P matrix since the fiber strengthening effect of carbon nanotubes^[13], especially part of the extruding carbon nanotubes embedded parallel to the coating surface can protect the surface of the matrix from wearing and decrease the contact area between the tribo-surfaces. Moreover, the carbon nanotubes dislodged from the matrix can act as a micro-rolling

bearing between the tribo-surfaces, thus further decrease the friction coefficient of the composite coating. Therefore, it is deduced that the high wear resistance and excellent friction property of the Ni-P-CNTs composite coating can be attributed to the superstrong mechanical properties of the carbon nanotubes embedded in the Ni-P matrix and its fiber strengthening effect.

REFERENCES

- [1] Sampath K P, Nair P K. Structural transformations in electroless Ni-P-B deposits[J]. *Plating and Surface Finishing*, 1994, 71(5): 96-100.
- [2] Spencer L F. Electroless nickel plating—a review[J]. *Metal Finishing*, 1974, 72(11): 50-54.
- [3] ZHONG Hua xiang. Study on the process for composite plating of Ni-P-Al₂O₃[J]. *Surface Technology*, 1991, 20(6): 8-12. (in Chinese)
- [4] WANG Guo bing. Mechanism of composite Ni-P-Al₂O₃ electroless plating[J]. *Journal of Northeast University of Technology*, 1991, 74(5): 548-552. (in Chinese)
- [5] LI Yong jun. Investigation of electroless Ni-P-SiC composite coatings[J]. *Plating and Surface Finishing*, 1997, 84(11): 77-81.
- [6] Reddy V V N, Ramamoorthy B, Nair P K. A study on the wear resistance of electroless Ni-P/Diamond composite coatings[J]. *Wear*, 2000, 239: 111-116.
- [7] YU Guang. Study on the electroless Ni-P-MoS₂ composite coatings[J]. *Surface Technology*, 1996, 25(1): 12-14. (in Chinese).
- [8] Runcan R. Hardness and wear resistance of electroless Nickel/Teflon composite coatings[J]. *Metal Finishing*, 1989, 87(9): 35-39.
- [9] Tracy M M J, Ebbesen T W, Givson J M. Exceptional high Young's modulus observed for individual carbon nanotubes[J]. *Nature*, 1996, 381: 678-680.
- [10] Wong E W, Sheehan P E, Lieber C M. Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes[J]. *Science*, 1997, 277: 1971-1975.
- [11] Sinnott S B, Shenderova O A, White C T, et al. Mechanical properties of nanotubule fibers and composite determined from theoretical calculations and simulations[J]. *Carbon*, 1998, 36(1-2): 1-9.
- [12] CHEN X H, DENG F M, WANG M, et al. Carbon nanotube-Ni composite coating with high wearability [A]. GAO Warr zhen, LI Jian. *Proceeding of III International Symposium on Tribology-Fatigue*[C]. Chansha: Hunan University Press, 2000. 529-531.
- [13] CHEN X H, Peng J C, Deng F M, et al. Tribological behavior of carbon nanotubes-reinforced nickel matrix composite coatings[J]. *J of Materials Science Letters*, 2001, 20(22): 2057-2060.
- [14] REN X F, LIU Y X. Microstructure of Ni-P chemical coating layer[J]. *Metal Physics Examination and Testing*, 1998, 90(1): 8-10.

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