文章编号：1000-2618(2008)02-0195-05

【材料科学】

Fabrication and wear properties of electroless Ni-P/cenosphere composite coatings

YANG Qin-peng, TANG Jiao-ning, LI Jun-qin, and GU Kun-ming
Shenzhen Key Laboratory of Special Functional Materials
Shenzhen University
Shenzhen 518060
P. R. China

Abstract: The fabrication and wear properties of electroless Ni-P/cenosphere composite coatings on steel are investigated. X-ray diffraction analyses show that Ni-P in the as-plated composite coatings is amorphous but changes to be crystalline after heat treatment. The microhardness of the composite coatings after heat treatment is significantly increased as compared with the as-plated coatings. Tribology test indicates that the composite coatings have good tribological performance. The wear-resistance of the composite coating is about 30% higher in volume than that of the pure Ni-P coating in dry condition. Anti-corrosion properties, measured by corrosion current, increase by 77% compared with the pure Ni-P coating.

Key words: electroless coating; Ni-P; fly-ash cenospheres; wear rate
CLC number: TQ 153.1+9 **Document code**: A

Fly-ash cenospheres are primarily a by-product in power generation plants. They are composed of SiO_2 (80wt% ~ 95wt%) and Al_2O_3 (5wt% ~ 20wt%). The characters of cenosphere particles have been described in References[1-2]. Researches are in progress to use this by-product effectively to produce new usable materials because it poses major disposal and environmental problems. Using the cenospheres in the Ni-P coatings may increase tribological properties of the composite coatings and decrease air pollution. The Ni-P composite coatings were extensively investigated for practical application. The composite coatings of Ni-P-Al_2O_3 and Ni-P-SiO_2 obtained by electroless plating were also investigated[3-4]. In this work, we present a preparation of these composite coatings by electroless plating and a study of their structure, tribological and anti-corrosion properties[5-6].

1 Experiment

1.1 Electroless Ni-P/ cenospheres coating

A3 steel specimens 2 cm × 2 cm in size used for the substrates of coating were polished with emery paper and then cleaned in an acetone bath. They were etched in the mixing solution of 4% H_2SO_4 and 3% HCl in weight. The specimens were immersed levelly into an electroless bath which was vigorously agitated with a combination of a reciprocating mechanical propeller stirrer and a supersonic oscillator. The conditions of Ni-P/cenosphere coating bath were as follows: $NiSO_4 \cdot 6H_2O$ (21g/L), $NaH_2PO_2 \cdot H_2O$ (24g/L), $NaC_2H_3O_2$ (12g/L), $C_2H_6O_3$ (30ml/L), Pb^{2+} (0.002 g/L), cenospheres (10 g/L). The sizes of cenosphere particles used in this work are the mean diameter of 3 μm, 6 μm, 10 μm, and 40 μm. The coatings were obtained at 90℃ after 2 h processing.

1.2 Examination of composite coatings

The structures of the composite coatings were characterized by X-ray diffraction (Rigaku D/MAX-3A), scanning electron microscopy (SEM; JSM-5910LV) and X-ray photoelectron spectroscopy (XPS; PHI-550). Tribological performances of the composite coatings were measured using a Pin-disk tribology tester (Siland). The contact configuration is the point on flat specimen

收稿日期：2007-06-01；修回日期：2008-02-20
基金项目：清华大学摩擦学国家重点实验室基金资助项目；深圳市科技资助项目（200603）；深圳大学科研启动基金资助项目（200704）
作者简介：杨钦鹏（1976-），男（汉族），广东省梅州市人，深圳大学实验师．E-mail：yangqp@szu.edu.cn
通讯作者：汤皎宁（1961-），男（汉族），深圳大学教授、博士．E-mail：tjn@szu.edu.cn

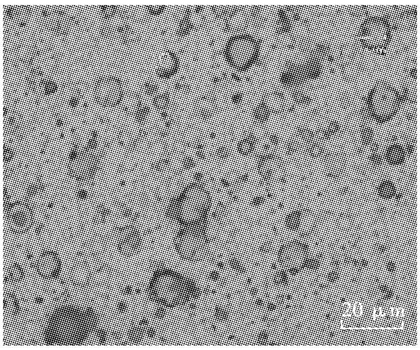
in dry condition. Al_2O_3 balls and Gr15 steel balls with Φ 5mm were used. The cross areas of the wear trace of the specimens were measured with microfigure measuring instrument (Mitutoyo SJ201P) to calculate the volume loss rate. They are average values based on 5 measurements. The wear volume was the arithmetic product of the average value of area and perimeter. The corrosion currents of the specimens were measured by an electrochemical interface system (Solartron Co. 1287).

The Ni-P/cenospheres composite coatings using cenospheres with a particle size of 10 μm were annealed under a nitrogen flow at 200℃, 400℃, 600℃, 800℃ for 2 h. Microhardness measurements (HV100, 15Sec) of these samples were also performed.

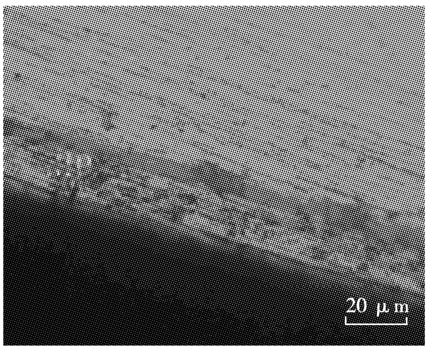
2 Results and discussions

2.1 Phase analysis and microstructure

Ni-P/cenosphere composite coatings are fabricated by electroless chemical deposition. The thickness of the composite coatings is about 40 μm. The microstructure for a typical composite coating is shown in Fig. 1. There are some agglomerations of the cenospheres within the coating. The distribution of the cenospheres varies from one area of the coating to another, but it is obvious that the cenospheres enchase into the composite coatings.



(a)surface

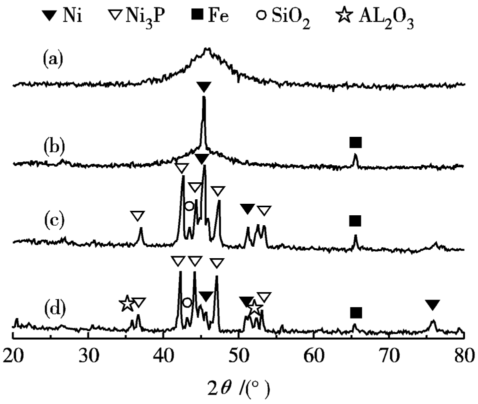


(b)section

Fig. 1 Microstructures images of the Ni-P/cenosphere composite coating

图 1 Ni-P/空心微珠复合镀层的显微结构图

X-ray diffraction patterns of the composite coatings with 10 μm cenospheres are shown in Fig. 2. The results indicate that the composite coating consists of the amorphous phase of Ni-P for the as-prepared composite coating (Fig. 2 (a)). However, the amorphous phase decreases in the composite coating after heat treatment. The Ni and Ni_3P phases appear in the sample annealed at 400℃ for 2 h (Fig. 2 (c)). All amorphous phases disappear when the annealing is performed above 600℃ for 2 h (Fig. 2 (d)).



(a) as-plated coating, (b) after heat treated at 200℃,
(c) after heat treated at 400℃, (d) after heat treated at 600℃

Fig. 2 X-ray diffraction patterns for the composite coatings using cenospheres with 10 μm

图 2 空心微珠复合镀层的 X 射线图（直径 10 μm）

EDX analysis of the composite coating indicates that the composite coating consists of 17.06% O, 8.36% Al, 11.33% Si, 6.35% P, 1.47% Fe and 55.43% Ni in weight. XPS spectra, shown in Figs. 3, exhibit that phosphorus exists in the form of simple phosphorus, nickel exists in the form of Ni^{3+} or Ni^{2+}, whereas silicon and oxygen exist in the form of SiO_2 on the surface of the composite coating.

2.2 Microhardness, wear and corrosion examination

The microhardness of the surface of the composite coating is related to the distribution of cenospheres. The average value of microhardness is acquired through measuring 5 points randomly on the surface of the coating. Table 1 shows the microhardness of the Ni-P/cenospheres composite coatings with different particle sizes of cenospheres. It can be seen that all the Ni-P/cenospheres composite coatings are harder than the pure Ni-P coatings. The hardness of the composite coating increases as the particle size and the volume fraction increase in the coating. The microhardness of the top surfaces for the Ni-P/cenospheres composite coatings is always higher than those of the bottom surfaces due to the higher cenospheres content on the top surfaces.

Table 2 shows the relationship of microhardness and heat treatment temperature for the composite coatings with 10 μm cen-

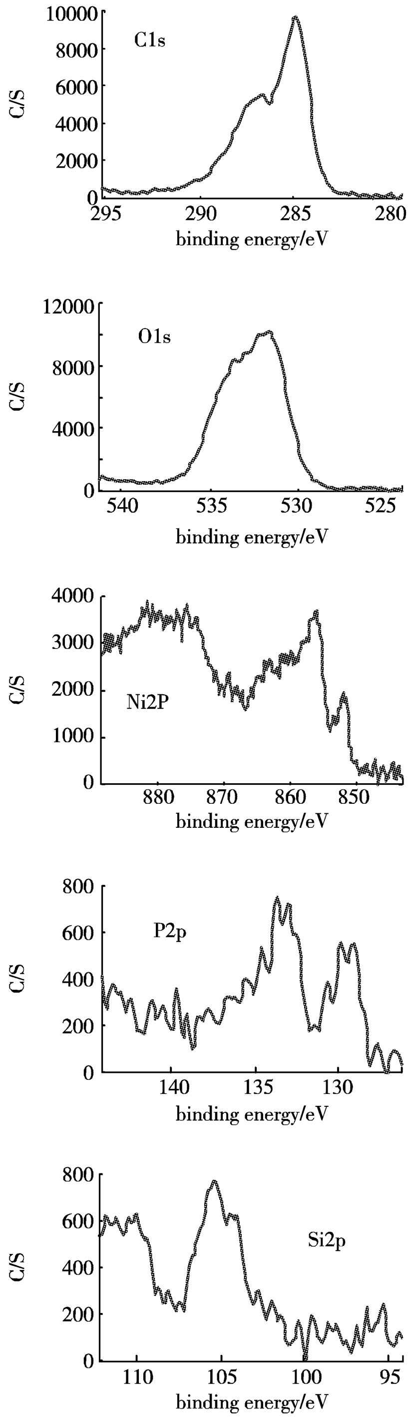


Fig. 3　XPS spectra of the elements on the composite coatings surface.

图 3　复合镀层表面各元素的 XPS 谱图

ospheres. The highest microhardness presents in the composite coating treated at 400℃. It is just the temperature at which the transformation from amorphous phase to crystalline phase finishes. It is shown that the bonding between the metal and ceramic phase in the coating becomes the strongest at this temperature.

Table 1　The microhardness of the composite coatings using different particle sizes of cenospheres

表 1　不同直径空心微珠复合镀层的显微硬度

type	microharsness（HV100）	
	upon the specimens	down the specimens
3 μm	715	657
6 μm	693	492
10 μm	785	586
40 μm	1044	569
Ni-P coating	591	590

Table 2　Relationship between the microhardness and the heat treatment temperature for the composite coatings using cenospheres with 10 μm

表 2　直径 10 μm 的空心微珠复合镀层在不同热处理温度下的显微硬度

t/℃	microharsness（HV100）	
	upon the specimens	down the specimens
200	963	418
400	1113	605
600	998	397
800	1030	421

The relationships between the friction coefficient and the particle size of cenosphere, and the relationship between the friction coefficient and the heat treatment temperature are given in Tables 3 and 4, respectively. The Al_2O_3 balls and steel balls counter faces were used in this examination. The load of 15 N, and the rev of 120 r/m were used in this examination. The medium value of the friction force in steady-state was used to determine the friction coefficient ($\mu = F/15$ N).

Table 3　Relationship between the friction coefficient and the particle size of cenospheres

表 3　不同粒度空心微珠复合镀层的摩擦系数

type	friction coefficient	
	Al_2O_3 ball	steel ball
3 μm	0.591	0.725
6 μm	0.572	0.773
10 μm	0.711	0.720
40 μm	0.737	0.713
Ni-P coating	0.354	0.621

Table 4 Relationship between the friction coefficient and the heat treatment temperature for composite coatings using cenospheres with 10 μm

表4 直径10 μm的空心微珠复合镀层在不同热处理温度下的摩擦系数

temperature/℃	friction coefficient	
	Al_2O_3 ball	steel ball
200	0.632	0.527
400	0.593	0.597
600	0.680	0.582
800	0.633	0.734

The friction coefficients of the composite coatings are larger than those of the pure Ni-P coatings, due to the presence of cenospheres at the surface of the composite coatings. The friction coefficient increases with the size of cenopheres when the Al_2O_3 balls are used, and it is almost unchanged when the steel balls are used (Table 3). The friction coefficient of the composite coating with the 10 μm cenospheres will decrease after heat treatment for both kinds of balls. The lowest friction coefficient is found after a heat treatment at the temperature of 400℃ (Table 4).

The wear amount of composite coating is lower than that of the pure Ni-P coating, and higher than that of the composite coating after heat treatment (Table 5). The Ni-P/cenospheres composite coatings have better tribological properties because cenospheres are inserted into the matrix of the electroless nickel. The wear amount of the composite coating is about 30% in volume lower than that of pure Ni-P coating with the counter face of Al_2O_3 balls, and about 2 times higher than that of the composite coating after heat treatment. The wear amount of the composite coating is 16% in volume lower than that of pure Ni-P coating with the counter face of steel ball and hardly invariable after a heat treatment at 400℃. But the friction coefficients of the composite coatings with different cenospheres are larger than that of the pure Ni-P coatings.

Table 5 The wear amount for the samples prepared in different conditions

表5 不同镀层磨损量比较

type	wear volume/($mm^3 \cdot N^{-1}$)	
	Al_2O_3 ball	steel ball
Ni-P coating	0.2815	0.0215
composite coating(10 μm)	0.1998	0.0180
composite coating after heat treated	0.0621	0.0166

Anti-corrosion examinations of the composite coatings were carried out in a 3% HCl bath. The corrosion current of the composite coating with 10 μm cenospheres is the lowest. That means the anti-corrosion properties of the composite coatings with 10 μm cenospheres is the best, with the corrosion current 77% lower as compared with the pure Ni-P coatings.

Conclusions

The Ni-P/cenospheres composite coatings were fabricated in this work. It consists of Ni and cenosphere phases and Ni3P after heat treatment. Phosphorus exists in the simple phosphorus form, nickel in the Ni^{3+} or Ni^{2+} form, whereas silicon and oxygen exist in the form of SiO_2 on the composite surface. The dispersion of cenospheres in the composite coating increases its microhardness. For the composite coating with 10 μm cenospheres, the wear amount of composite coating is about 30% in volume lower than that of pure Ni-P coating with the counter face of Al_2O_3 ball, and about 2 times higher than that of the composite coating after heat treatment. The wear amount of the composite coating is 16% in volume lower than that of pure Ni-P coating with the counter face of steel ball and hardly invariable after a heat treatment at 400℃. However, the friction coefficients of the composite coatings are larger than those of the pure Ni-P coatings. The lowest corrosion current is found in the composite coating with 10 μm cenospheres. The corrosion current of this composite coating is 77% lower than that of the pure Ni-P coating in a 3% HCl bath.

References:

[1] ZENG Ai-xiang, XIONG Wei-hao, XU Jian. Electroless Ni-P coating of cenospheres using silver nitrate activator [J]. Surface and Coatings Technology, 2005, 197: 142-147.

[2] Marshall G. W, Lewis D B, Clayton D. The electrodeposition of Ni-P-Al_2O_3 deposits [J]. Surface and Coatings Technology, 1997, 96: 353-358.

[3] Shukla S, Seal S, Akesson J. Study of mechanism of electroless copper coating of fly-ash cenosphere particles [J]. Appl Surf Sci, 2001, 181(1): 35-50.

[4] Shukla S, Seal S, Rahaman Z. Electroless copper coating of cenospheres using silver nitrate activator [J]. Mater Lett, 2002, 57: 151-156.

[5] Stephen F, Rudy. Surface preparation of various metal sand alloys before plating and other finishing applications [J]. Metal Finishing, 2001, 99: 191-205.

[6] ZHANG Shu-sheng, HAN Ke-jiang, CHENG Lin. The effect of SiC particles added in electroless Ni-P plating solution on the properties of composite coatings [J]. Surface and Coatings Technology, 2008, 202(12): 2807-2812.

Abstract：1000-2618(2008)02-0199-EA

镍、磷和空心微珠复合镀层摩擦磨损性能研究

杨钦鹏，汤皎宁，李均钦，谷坤明

（深圳市特种功能材料重点实验室，深圳 518060）

摘　要：运用化学镀方法，把空心微珠作为第二相加入化学镀镍和磷镀液中，制得以镍、磷和空心微珠为主的复合镀层. X 射线分析显示，复合镀层经过热处理后由非晶态变成晶态. 复合镀层经过热处理后显微硬度及摩擦学性能提高. 复合镀层耐磨性比纯镍和磷镀层提高约 30%，抗腐蚀性提高 77%. 运用 SEM 和 XPS 等对复合镀层性能和结构进行分析.

关键词：化学镀；镍-磷；空心微珠；磨损率

中图分类号：TQ 153.1 +9　　　**文献标识码**：A

参考文献：

[1] ZENG Ai-xiang，XIONG Wei-hao，XU Jian. 用硝酸银为活化剂制备空心微珠的 Ni-P 镀层［J］. 表面与涂层技术，2005，197：142-147（英文版）.

[2] Marshall G W，Lewis D B，Clayton D. 电化学沉积 Ni-P-Al_2O_3 镀层［J］. 表面与涂层技术，1997，96：353-358（英文版）.

[3] Shukla S，Seal S，Akesson J. 粉尘煤灰空心微珠粒子的化学镀铜层机理研究［J］. 应用表面科学，2001，181(1)：35-50（英文版）.

[4] Shukla S，Seal S，Rahaman Z. 用硝酸银为活化剂在空心微珠表面化学镀铜［J］. 材料快报，2002，57：151-156（英文版）.

[5] Stephen F，Rudy. 在电镀和其它表面应用之前，不同金属砂合金的表面制备［J］. 金属精饰，2001，99：191-205（英文版）.

[6] ZHANG Shu-sheng，HAN Ke-jiang，CHENG Lin. 化学镀 Ni-P 溶液中加入 SiC 粒子对复合镀层性质的影响［J］. 表面与涂层技术，2008，202(12)：2807-2812（英文版）.

【中文责编：坪　梓；英文责编：卫　栋】

·简　讯·

2007 年深圳高新技术产值突破 7000 亿元

据深圳市科技和信息局介绍，2007 年深圳市高新技术产品产值首次突破 7000 亿元，产值规模、自主知识产权产值比例和占 GDP 比例等主要指标均居全国前列. 2007 年深圳共实现高新技术产品产值 7598.76 亿元，比上年增长 20.49%，占深圳市 GDP 的 32.46%，占工业总产值比例继续超过 50%. 其中，具有自主知识产权的产值达 4454.39 亿元，占全部高新技术产品产值的 58.62%. 在产业快速做大的同时，深圳市高新技术企业数量也迅速发展，截至 2007 年底，深圳经认定的高新技术企业已增至 2748 家，产值过亿元的企业由 2006 年的 390 多家，迅速增至 547 家，其中，高新产值超百亿元的有 11 家，超 200 亿元的企业有 6 家，超 500 亿元的有两家，超 1000 亿元的有 1 家. 这些数据充分显示了高新技术产业作为第一支柱产业，对深圳市经济发展的支撑和在全国产业中的地位.

（坪　梓）