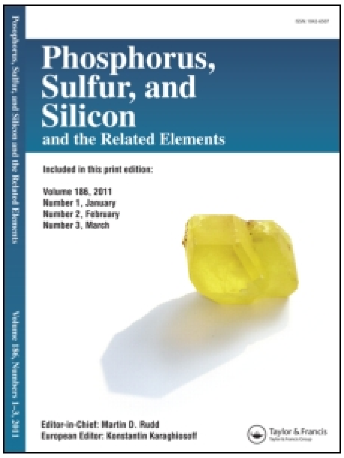

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Yin, Ping , Hu, Yucai , Zhang, Pijian , Xu, Qiang , Chen, Lei and Tang, Qinghua(2010) 'Preparation, Characterization, and Corrosion Resistance Property of a Novel Nickel Phosphorous Composite Material', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 3, 647 — 651

To link to this Article: DOI: 10.1080/10426500902915457

URL: http://dx.doi.org/10.1080/10426500902915457

Phosphorus, Sulfur, and Silicon, 185:647–651, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902915457

PREPARATION, CHARACTERIZATION, AND CORROSION RESISTANCE PROPERTY OF A NOVEL NICKEL PHOSPHOROUS COMPOSITE MATERIAL

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This article addresses the preparation, characterization, and corrosion resistance property of a Ni-P-CdO composite material. The physical chemistry, nature, and composition of the composite material were investigated by weighing method, accelerated corrosion tests, tarnish tests, scanning electron microscope (SEM), energy dispersive X-ray analysis system (EDXAS), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). The results showed that the surface of the coating was homogeneous, polished, and it had strong corrosion resistance. The coating of composite Ni-P-CdO was rather thick, about 18 μm. The elemental analysis of the composite material is Ni: 82.44%, P: 12.38%, O: 2.45%, Cd: 2.31%, and Fe: 0.42%, and 99.54% (wt.%) of the surface is composed of the Ni-P-CdO.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Characterization; corrosion resistance; nickel; phosphorous; preparation

INTRODUCTION

The advantages of nickel plating include excellent corrosion resistance, wear resistance, low porosity, uniform thickness even on complex parts, and its ability to plate on nonconductors. The nickel composite process is a useful method of preparing composite deposits on surfaces of metals, which could result in a wide variety of poly-alloy deposits with a multiplicity in deposit characteristics, and the composite deposits are usually composed of a nickel phosphorous alloy and dispersed fine powders.[1–4] Currently, many kinds of fine powders, such as SiC, BN, $ZnSnO_3$, etc., are widely used to improve the corrosion and wear resistance properties of the coating.[5–7] Although many articles have reported a composite nickel coating, there are only a few studies on oxide-dispersed nickel composite plating.[8,9]

Received 7 January 2009; accepted 23 March 2009.

We greatly appreciate the support provided by the Promotional Foundation for the Excellent Middle-Aged and Young Scientists of Shandong Province of China (2007BS08027), the Basic Project of Educational Bureau of Shandong Province of China (J07YA16), and the Foundation of Innovation Team Building of Ludong University (08-CXB001).

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Table I Results of the accelerated corrosion and tarnish tests

Coating samples	Corrosion rate ($g \cdot m^{-2} \cdot h^{-1}$) Salting water (weight lost)	Corrosion rate ($g \cdot m^{-2} \cdot h^{-1}$) H_2S tarnish (weight gained)
Pure steel plate	0.071	0.064
Ni-P	0.032	0.003
Ni-P-CdO	0.015	0.002

Shibli et al. incorporated zinc oxide particles into Ni-P plates, and found that the incorporation of ZnO particles resulted in the improvement of metallurgical and corrosion resistance characteristics of the plates.[9] In this article, cadmium oxide fine powders were co-deposited within nickel phosphorous alloys for the first time, which means a new potential application field of cadmium oxide. Although many special properties of the composite coating can be expected, corrosion resistance was investigated here, compared with that of the well-known Ni-P coating. Moreover, the composition of the composite material was also analyzed by XPS and AES.

RESULTS AND DISCUSSION

Figure 1 shows the morphology of the Ni-P-CdO composite material, and many of the particles have diameters of 2 μm in the coating. The EDXAS record for Ni-P-CdO composite material is displayed in Figure 2, and it represents that the coating contains Ni, P, O, Cd, and Fe, which indicates it has not only nickel phosphorous particles, but also CdO fine particles. The results of the accelerated corrosion and tarnish resistance of the composite material, compared to pure steel plate and Ni-P coating with similar thickness, are shown in Table I. The corrosion resistance and tarnish resistance of the composite material are better than a pure steel plate and Ni-P coating of a similar thickness. This is because the particles of CdO fine powders in the composite material have heat-resistance, and thus, slow down the crystallization of the base.

The composite elements were analyzed by XPS and AES before and after sputtering by Ar^+ beam (SPT). For the Ni-P-CdO composite material, full scanning spectra of XPS show Fe 2p, Ni 2p, Ni (A), Ni 3p, Ni 3s, P 2s, P 2p, O 1s, C 1s, and Cd 3d bands clearly before SPT. The AES results also suggest the existence of Ni, P, Cd, C, Fe, and O. After

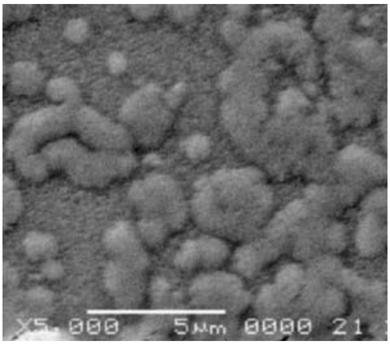

Figure 1 The SEM image of Ni-P-CdO composite material.

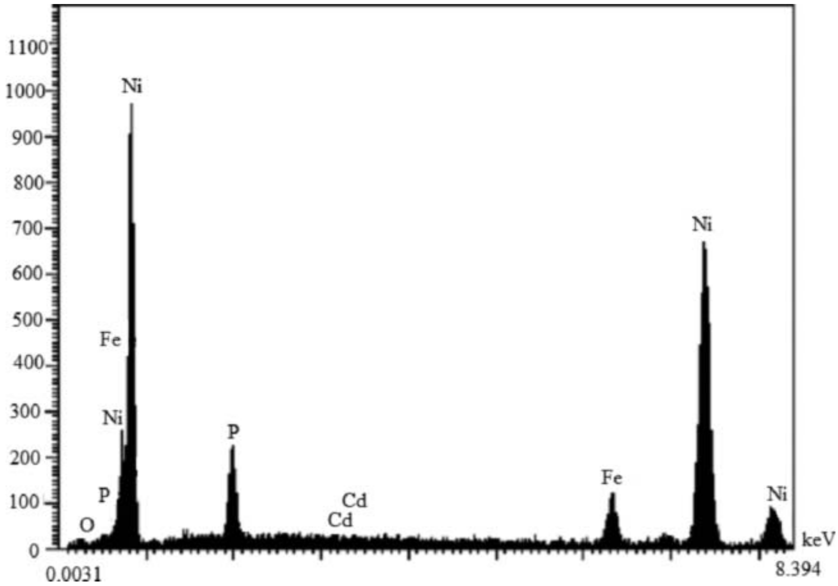

Figure 2 The EDXAS record for Ni-P-CdO composite material.

Ar$^+$ SPT, the C band disappeared, which suggests that C mostly exists as the contamination of the coating surface. The O band comes not only from CdO particles, but also from the oxidized coating surface, whose intensity becomes a little lower after a certain time of Ar$^+$ SPT. Figure 3 shows the composite of the material at different sputtering times by the AES depth profiling technique. The relative atomic content fractions (AC%) of the elements were calculated. The composite of the coating was stable after 17 min of SPT, which shows that the coating is rather thick. With a reference of Ta_2O_5 and SPT speed of 5 nm·min^{-1},

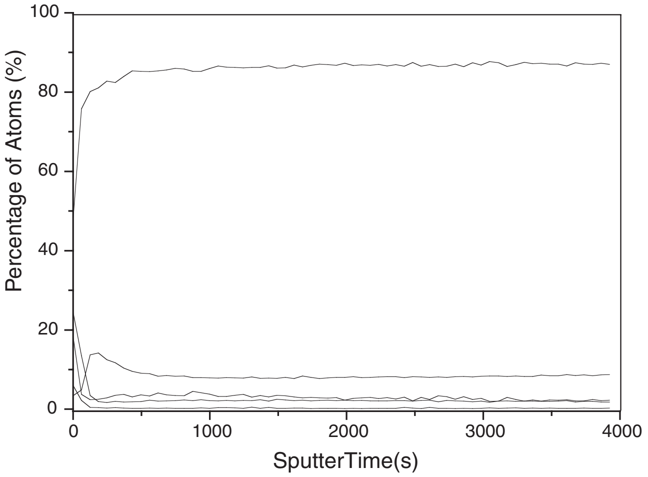

Figure 3 The composition depth profiling of the Ni-P-CdO composite material. Listed from top to bottom in the median stable area are Ni, P, O, Cd, and Fe, respectively.

Table II Composition and conditions of composite Ni-P-CdO coating material

Composition and condition of the plating bath	
$NiSO_4 \cdot 6H_2O$ (A.R.)	0.20 mol/L
$NaH_2PO_4 \cdot H_2O$(A.R.)	0.24 mol/L
$Pb(Ac)_2$ (A.R)	5×10^{-5} mol/L
1-Hydroxyethylidenediphosphonate ligand	0.10 mol/L
CdO	0.15 mol/L
Surfactant	10 mol/L
pH	5–5.5
T (°C)	80
t (Plating time)	30 min

we estimated the coating thickness to be over 325nm (0.325 μm). The atomic percentages in the median stable area during the SPT are Ni: 82.44%, P: 12.38%, O: 2.45%, Cd: 2.31%, and Fe: 0.42%.

High resolution XPS of the Ni-P-CdO composite material is shown in Table S1 (available online in the Supplemental Materials). The binding energies of Ni 2p from the high resolution XPS before and after SPT could be seen. Peaks at about 857.199 and 853.414 eV indicate that Ni exists in oxidation states of 2 and 0, respectively.[10] Thus, there are two oxidation states of nickel on the surface of the material, but only one in the interior. Phosphorous also exists in two oxidation states, 0 and 3, on the coating surface, indicated by the two different binding energies, 129.796 and 132.893 eV before SPT, while only elemental P exists in the inner coating to form Ni-P-CdO co-deposit. Little change in Cd 3d binding energy before and after SPT was observed, which indicates that Cd only exists in the form of CdO in the coating.[10] It was also found that O exists in the –2 oxidation state. Fe is in the oxidation state of 3 on the coating surface, and in the state of 0 and 2 in the interior of the coating. The studies of Hur et al., working on the microstructure of nickel plating, explained that the elemental iron was from the steel substrate.[11] The Fe^{2+} comes from oxidation in the coating forming procedure, while the Fe^{3+} on the surface is oxidized from Fe^{2+} by the O_2 in the air. A main part of O exists in CdO, and only a little O exists in the iron oxides. The atomic/molecular ration of Ni, P, and CdO is 82.44: 12.38: 2.31, and the Ni-P-CdO alloy composes 99.54% (wt.%) of the material.

CONCLUSIONS

In summary, we have successfully prepared a Ni-P-CdO composite material under mild conditions. The material formed possesses with strong corrosion and tarnish resistance properties; the material was mostly composed of Ni-P-CdO alloys; its atomic percentages of the material are Ni: 82.44%, P: 12.38%, O: 2.45%, Cd: 2.31%, and Fe: 0.42%; and 99.54% (wt.%) of the surface is composed of the Ni-P-CdO.

EXPERIMENTAL

The morphology of the composite material was examined on a JSF5610LV scanning electron microscope, JEOL Co., Japan. The EDXAS was performed on a Noran Lever-2 EDX analytical instrument. The XPS and AES measurements were made on a Perkin-Elmer PHI 550—ESCA/SAM photoelectron spectrometer operated at 10 kV and 30 mA. High resolution XPS spectra were generated with the analyzer pass energy setting at 10 and 50 eV, respectively. The voltage and current of the electron beam for AES analysis were 3 kV and 10 μA, respectively. An argon ion gun with a voltage of 4 kV, an emission current of 15 mA, and a scan area of 5 mm × 5 mm were used for depth profiling studies.

Monodispersed fine powders of cadmium oxide were mixed with surfactant and treated in an ultrasonic bath for 10 min, then mixed with Ni-P plating solutions ultrasonically for 30 min. Steel specimens (2×5 cm^2) were polished and buffed with SiC sandpaper and MgO powder. They were etched at 25°C in 10% H_2SO_4 solution and rinsed with distilled water, dried with cool air, then rinsed with acetone and dried again before being placed in the plating bath. The bath was stirred electrically during the plating course, and the whole plating time was 30 min. The specimens were then thoroughly rinsed with distilled water and dried with cool air. The bath composition and operating conditions are shown in Table II.

Accelerated corrosion tests of the coating were performed in 10% NaCl solution. The appearance of the solutions was recorded at certain time intervals. The tarnish tests were carried out in a glass vacuum desiccator with 1% H_2S (volume ratio) gas atmosphere. The time for the specimens to become faintly tarnished (with visible little spot tarnished) in H_2S was measured and recorded. The corrosion and tarnish tests were both performed at 25°C.

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