

High corrosion-resistant Ni–P/Ni/Ni–P multilayer coatings on steel

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Abstract

Multilayer coatings having a thickness about 20 μm and consisting of different Ni–P and Ni layers were prepared by combining electrodeposition with electroless deposition. The microstructure of the coatings was analyzed by scanning electron microscope (SEM) and X-ray diffractometer (XRD). The corrosion resistance of the coatings was estimated by electrochemical polarization measurements and salt spray test. The salt spray test showed that the three-layer coating, whose composition is Ni–P (low phosphorus)/Ni/Ni–P (high phosphorus) from surface to substrate, exhibited the highest corrosion resistance. The time of the emergence of the first red rust spot on the coating surface can reach 936 h, which is 3.5 times higher than that of the common amorphous Ni–P alloy coatings. The electrochemical analysis revealed that the difference in the corrosion potential among layers plays a very important role in protecting the substrate from rusting.

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1. Introduction

Electroless deposition technique of Ni–P alloy coatings has been a well-known commercial process that has found numerous applications in many fields due to excellent properties of coatings, such as high corrosion resistance, high wear resistance, good lubricity, high hardness and acceptable ductility [1–6]. Another advantage of the electroless deposition technique is that very uniform coatings can be obtained without special requirements for substrate geometries. In general, the electroless deposition of Ni–P alloy can be classified into three categories according to phosphorus content, i.e., low (1–5 wt.%), medium (5–8 wt.%) and high (9 wt.% and above) phosphorus deposits [7]. The Ni–P alloy deposits with different phosphorus contents have different physicochemical properties [8]. When the phosphorus contents are in low and medium levels, the as-deposited electroless plating Ni–P alloy is a mixture of

amorphous and microcrystalline nickel, but when the phosphorus content is high, a full amorphous microstructure can be formed [9–11]. Furthermore, amorphous alloys should exhibit intrinsically higher corrosion resistance than crystalline Ni since they are characterized by extreme homogeneity and thus present no defects or preferential corrosion paths, such as grain boundaries, as crystalline materials do [12–14]. According to Ref. [15], this superior corrosion resistance has also been attributed to the absence of crystalline defects and to their chemically homogeneous single-phase nature, which in turn ensures the formation of a uniform and highly protective passive film.

Since the corrosion potentials E_{corr} of the Ni and Ni–P alloy coatings on steel are more positive than that of steel substrate, the Ni and Ni–P alloy coatings are cathodic to steel substrate. When nickel is deposited as a dense, pore-free and defect-free coating on steels, it provides a physical barrier to corrosion attack unlike metals such as aluminum and zinc, which provide sacrificial protection. The substrate surface condition in controlling the porosity of electroless nickel deposition is very important. The effect of the cleaning cycle prior to the plating step was investigated

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[16], and it was found that the main factor in determining porosity was the thickness of the deposit. A dramatic reduction in porosity was found for deposits thicker than 12 μm [16,17]. A possibility for the improvement of corrosion resistance is the deposition interlayers and/or multilayered coatings. The use of multilayers or hybrid techniques in surface engineering has often been cited as the way forward to improve the mechanical, tribological and electrochemical properties of coatings [5,18–26]. A multilayer coating with layers having difference in corrosion potential has provided an effective solution to improve the corrosion resistance of the no-sacrificial coatings, and the duplex nickel coating technique has been used in industries [18,26].

In this study, the multilayer coatings having a thickness of about 20 μm and consisting of different Ni–P and Ni layers were designed. The corrosion resistance and relevant mechanisms of these coatings were analyzed based on the results of scanning electron microscope (SEM), X-ray diffractometer (XRD), electrochemical polarization experiments and salt spray tests.

2. Experiments

The substrates used were 5.0×2.5×0.1 cm steel sheets (C1008, AISI). Before depositing, the substrates were first cleaned with trichloroethylene, rinsed with deionized water, degreased with methylbenzene and propanone agitated ultrasonically for 5 min, acid-cleaned with 0.1 M HCl for 2 min and thoroughly rinsed again with deionized water. The multilayer coatings were obtained by combining electrodeposition with electroless deposition. For comparison, six samples were designed, which are given in Table 1. The thickness of the Ni–P or Ni layers during the deposition was ensured using the Coulometric method by anodic dissolution (according to ISO 2177:1985). For convenience, samples 1–6 are denoted by Ni–P with low phosphorus, Ni–P with medium phosphorus, Ni–P with high phosphorus, Ni–P (low phosphorus)/Ni–P (high phosphorus), Ni–P (medium phosphorus)/Ni–P (high phosphorus) and Ni–P (low phosphorus)/Ni–P (high phosphorus) coatings, respectively. The samples were thoroughly cleaned with deionized water between any two steps of the deposition to

Table 1
The designed six samples in the present experiments

Sample	Coatings (μm) (from surface to substrate)
1	20 (low phosphorus deposits)
2	20 (medium phosphorus deposits)
3	20 (high phosphorus deposits)
4	6.5 (low phosphorus deposits)/ 13.5 (high phosphorus deposits)
5	9.5 (medium phosphorus deposits)/1 (electroplated Ni)/ 9.5 (high phosphorus deposits)
6	9.5 (low phosphorus deposits)/1 (electroplated Ni)/ 9.5 (high phosphorus deposits)

Table 2

Bath compositions and plating conditions of electroless Ni–P depositions

Chemical compounds (g/L)	Low-phosphorus deposits [27]	Medium-phosphorus deposits	High-phosphorus deposits
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	20	15	15
$\text{Na}_2\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	10	14	26
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	10	–	–
$\text{NaC}_2\text{H}_3\text{O}_2$	15	13	13
pH	6.48	4.95	5.00
Temperature ($^\circ\text{C}$)	90	72	95

avoid the contamination of the bathes. Times spent between any two different plating solutions were kept to an absolute minimum. The bath compositions and deposition conditions of three electroless plating Ni–P alloy depositions are shown in Table 2. The Ni layer in sample 5 or 6, sandwiched by two electroless plating Ni–P alloy layers, was obtained by electroplating from an acid solution of composition: $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ 650 g/L, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 6 g/L and H_3BO_3 36 g/L, with pH 4.0 at temperature of 60 $^\circ\text{C}$ and current density of 2 A/dm^2 for 15 min, which gives a Ni layer with a thickness of about 1 μm . All the chemicals used in the experiments were AR grade.

To determine the contents of nickel and phosphorus in the coatings, the Ni–P alloy coatings were peeled from the substrates and then dissolved in nitric acid to form ion solution. The concentration of the nickel ion in the solution was determined by the titrimetric method. Through this method, the content of nickel in the coatings was obtained, and the remnant was considered as the phosphorus content.

Crystallographic structure was studied by the X-ray diffractometer (XRD; Rigaku Dymax) with a Cu target and a monochromator at 50 kV and 300 mA. The scanning rate and step were fixed at 4 $^\circ$ /min and 0.02 $^\circ$, respectively. The scanning region (2 θ) was ranged from 10 $^\circ$ to 90 $^\circ$. The morphology and the energy-dispersive X-ray (EDX) analysis of the cross-section of sample 6 were examined by using a JEOL scanning electron microscope (SEM).

The salt spray tests were performed on all the coatings using the NSS cabinet of SF850 (Atlas Electric Devices). The area fraction of the red or gray rust on the coating surface was determined by the counting point method.

The major drawbacks to the salt spray tests are restricted reproducibility and difficulties in quantitatively interpreting the results. Recently, a number of electrochemical and microscopy techniques have been established for corrosion resistance and porosity of electroless nickel coatings on steel [28,29]. In this paper, electrochemical measurements were performed on an LK98 Microcomputer-based Electrochemical System (LANLIKE, Tianjin, China), which was controlled by a computer and supported by self-designed software. Electrochemical tests were carried out in a 3 wt.% NaCl aqueous solution using a classic three-electrode cell with a platinum plate (Pt) as counterelectrode and an Ag/AgCl electrode (+207 mV vs. SHE) as reference. Before testing, the working electrode was cleaned in acetone

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