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Competitive deposition of electroless Ni–W–P coatings on mild steel via a dual-complexant plating bath composed of sodium citrate and lactic acid

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ABSTRACT

Based on the fact that the deposition reactions for electroless Ni–W–P coatings depend on the participation of $H_2PO_2^-$, we developed a competitive deposition process that $H_2PO_2^-$ was controllably assigned to W, P and Ni deposition by the concentration ratio of dual-complexant composed of sodium citrate (NaCit) and lactic acid (Lac), namely NaCit/Lac ratio, and $NiSO_4$ concentration in plating bath. The impact of the ratio and $NiSO_4$ concentration on the deposition rate, composition, microstructure, microhardness, adhesion, corrosion resistance and wear resistance of coating was studied. The results indicate that both factors affect W codeposition through changing the deposition rate of Ni. The bath at NaCit/Lac ratio of 1:1 and $NiSO_4$ concentration of 30–40 g/L accelerates W deposition and Ni deposition, but decelerates P deposition, and thus incorporates more W (6.97–7.02 wt.%) but less P (4.87–5.03 wt.%) in coating. Furthermore, the crystalline structure, nodular morphology, microhardness and adhesion of coating also depend on both factors. The coating plated at different NaCit/Lac ratios and $NiSO_4$ concentrations demonstrates various corrosion-resistant and wear-resistant performances.

1. Introduction

By adding sodium tungstate (Na_2WO_4) accompanied with proper additives such as complexant, stabilizer and buffer into an electroless Ni–P bath, ternary Ni–W–P alloy coatings can be deposited for remarkably enhanced hardness, wear and corrosion resistance and thermal stability [1–6]. However, it is difficult to deposit tungsten (W) solely from Na_2WO_4 solution because of the relatively negative standard electrode potential of WO_4^{2-}/W (-1.05 V), compared with that of Ni^{2+}/Ni (-0.25 V), but it can be inductively codeposited with Ni [7]. In common, the codeposition can be achieved through adjusting Na_2WO_4 concentration in plating bath [8–11], adding appropriate complexants including sodium citrate (NaCit), sodium acetate, sodium pyrophosphate, lactic acid (Lac), citric acid and aminoacetic acid, etc. [12–15], or incorporating various additives like sodium carbonate, ammonium hydroxide, saccharin and selenium [12–16].

Generally, electroless Ni–W–P codeposition is determined by the reduction of Ni^{2+} and WO_4^{2-} and the oxidation of $H_2PO_2^-$ on substrate surface, as shown by the following reactions (1)–(3) [17],

$$Ni^{2+} + 2H_2PO_2^- + 2OH^- \rightarrow Ni + 2H_2PO_3^- + H_2 \quad (1)$$

$$WO_4^{2-} + 6H_2PO_2^- + 4H_2O \rightarrow W + 6H_2PO_3^- + 3H_2 + 2OH^- \quad (2)$$

$$2H_2PO_2^- \rightarrow P + H_2PO_3^- + 1/2H_2 + OH^-. \quad (3)$$

It is apparent that these reactions take place with the participation of $H_2PO_2^-$. Theoretically, 1 mol $H_2PO_2^-$ can respectively deposit 1/2 mol Ni, 1/6 mol W and 1/2 mol P. Therefore, if the proportion of $H_2PO_2^-$ to each reaction is controllable, the deposition of Ni, W and P can proceed competitively at substrate/solution interface. For instance, the more assigned $H_2PO_2^-$ there is to reaction (2), the more alloyed W there may be in coating for excellent properties.

In the present study, electroless Ni–W–P coatings were competitively deposited on mild steel in a dual-complexant bath composed of NaCit and Lac. The process was achieved by control of the concentration ratio of the dual-complexant (NaCit/Lac ratio) and $NiSO_4$ concentration. Especially, the codeposition of W notably changed with the variation of NaCit/Lac ratio or $NiSO_4$ concentration, unlike by adjusting the amount of Na_2WO_4 addition in many previous reports [8–11]. Thus, it helps develop an electroless process to effectively utilize Na_2WO_4 and to lower the cost of plating bath. Furthermore, the impact of both factors on the deposition rate, composition, microstructure, microhardness, adhesion, and corrosion and wear resistance of coating was investigated, respectively.

2. Experimental details

Mild steel samples, with dimensions of 20 mm in diameter and 3 mm in thickness, were used as substrates for electroless Ni–W–P

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coatings. The sample surface was pretreated with grinding (SiC abrasive paper), degreasing (acetone), etching (20 wt.% H_2SO_4 solution, 3 min) and activating (5 wt.% H_2SO_4 solution, 5 min), and was rinsed with deionized water after each step. Subsequently, the pretreated samples were dipped in electroless bath to plate Ni–W–P coatings. The bath contained 10–50 g/L $NiSO_4$ for Ni source, 50 g/L Na_2WO_4 for W source, 30 g/L NaH_2PO_2 as reductant, NaCit and Lac with a constant total concentration of 90 g/L as dual-complexant, and 20 g/L $(NH_4)_2SO_4$ as buffer. The operating conditions were bath pH at 9.0 ± 0.2, plating temperature at 90 ± 2 °C and plating time of 1 h. Due to the differences of NaCit/Lac ratio and $NiSO_4$ concentration, nine types of electroless Ni–W–P coatings were prepared, denoted from S1 to S9 as listed in Table 1.

An Oxford INCA energy dispersive spectroscope (EDS) attachment on JSM-6700F field-emission scanning electron microscope (FESEM), operated at accelerating voltage 20 kV, was used to study the content of Ni, W and P elements in electroless Ni–W–P coating. The values reported in this work are the average values of three measurements. The coating structure was analyzed using an XRD-7000 X-ray diffractometer (XRD) with CuK_{α} radiation ($\lambda = 1.54060$ Å) in the range of 20–90°. The surface and cross-sectional morphologies of coating were observed by use of FESEM with model of JSM-6700F and ZEISS MERLIN.

The deposition rate of coating was characterized by the weight gain on unit surface area of samples per hour, and expressed in mg/cm^2 h, as shown in Ref. [18]. Samples were weighed by ALC210-4 electronic balance with precision of 0.1 mg. The coating hardness was measured via a TUKON-2100 Vickers microhardness tester with a load of 20 g for 10 s. Moreover, a WS-2005 automatic scratch tester was applied to determine the adhesion between coating and substrate under the loading rate of 100 N/min, ultimate load of 100 N, scratching rate of 4 mm/min and scratch length of 4 mm.

Electrochemical tests were conducted in a conventional three-compartment glass cell on a CHI660D electrochemical workstation. Ni–W–P coatings with an exposed area of 1 cm^2 served as the working electrode, while a platinum electrode and a saturated calomel electrode (SCE) were respectively used as the counter electrode and the reference electrode. The electrode potential of the polarization curve was recorded from −1 to 1 V (scanning rate 1 mV/s) in 3.5 wt.% NaCl solution at room temperature. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the curves to evaluate the electrochemical corrosion resistance of coating.

The tribological behavior of coating was investigated on a home-made ball-on-disk tribo-tester using a Φ2-mm-sized GCrl5 steel ball as friction pair under dry condition. The experiments were conducted under 2 N load and 300 rev/min for 16 min at ambient temperature (20 ± 3 °C). Furthermore, the wear rate was calculated from the mass loss of three replicate test results to evaluate the wear resistance of coating.

3. Results and discussion

3.1. Deposition rate of Ni–W–P coating

Fig. 1 shows the dependence of the deposition rate of coating on NaCit/Lac ratio and $NiSO_4$ concentration. The rate increases from 6.8 mg/cm^2 h at NaCit/Lac ratio of 0.2 (coating S1) to 13.7 mg/cm^2 h at the ratio of 1.0 (coating S3) but then decreases to 7.4 mg/cm^2 h at the ratio of 5.0 (coating S5). The variation range of the rate is within 6.9 mg/cm^2 h as the ratio changes from 0.2 to 5.0. Similarly, the rate increases from 6.3 mg/cm^2 h at $NiSO_4$ concentration of 10 g/L (coating S6) to 14.3 mg/cm^2 h at the concentration of 40 g/L (coating S8) but then decreases to 5.4 mg/cm^2 h at the concentration of 50 g/L (coating S9). It is seen that the variation range of deposition rate reaches 8.9 mg/cm^2 h with $NiSO_4$ concentration increasing from 10 to 50 g/L, while the maximum rate (coating S8) is nearly two times larger than the minimum rate (coating S9). Hence, both NaCit/Lac ratio and $NiSO_4$ concentration affect the deposition rate of coating, and the latter plays a more notable role, indicated by the much higher variation range of the rate.

Table 1
Bath composition for electroless Ni–W–P coatings S1–S9.

Samples	NaCit/Lac ratio	$NiSO_4$ concentration (g/L)
S1	0.2 (1:5)	30
S2	0.3 (1:3)	30
S3	1.0 (1:1)	30
S4	3.0 (3:1)	30
S5	5.0 (5:1)	30
S6	1.0 (1:1)	10
S7	1.0 (1:1)	20
S8	1.0 (1:1)	40
S9	1.0 (1:1)	50

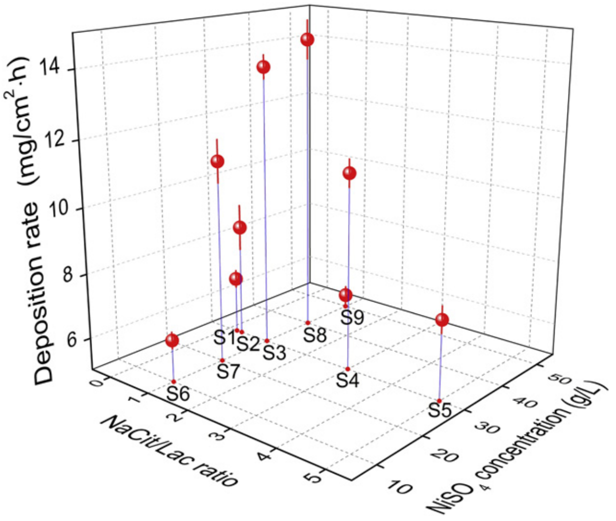

Fig. 1. Effect of NaCit/Lac ratio and $NiSO_4$ concentration on the deposition rate of electroless Ni–W–P coatings S1–S9.

3.2. Chemical composition of Ni–W–P coating

Figs. 2(a), (b) and (c) present the atomic percent (at.%) of W, P and Ni elements in coatings S1–S9, derived from the corresponding EDS spectra. Obviously, as NaCit/Lac ratio increases from 0.2 to 5.0 (coatings S1–S5), W content increases from 0.56 at.% (2.21 wt.%, coating S1) to 2.37 at.% (6.97 wt.%, coating S3) and then decreases to 1.13 at.% (3.69 wt.%, coating S5); but P content changes with a contrary trend, which decreases from 15.56 at.% (8.78 wt.%, coating S1) to 9.46 at.% (5.03 wt.%, coating S3) and then increases to 14.69 at.% (8.11 wt.%, coating S5). Correspondingly, the content of Ni base increases from 83.88 at.% (coating S1) to 88.17 at.% (coating S3) and then decreases to 84.18 at.% (coating S5). On the other hand, with an increase of $NiSO_4$ concentration from 10 to 50 g/L (coatings S6, S7, S3, S8 and S9), W content increases from 0.17 at.% (0.64 wt.%, coating S6) to 2.40 at.% (7.02 wt.%, coating S8) and then decreases to 0.58 at.% (1.68 wt.%, coating S9); but P content continuously decreases from 14.89 at.% (8.29 wt.%, coating S6) to 7.74 at.% (4.04 wt.%, coating S9); and furthermore, Ni content increases from 84.94 at.% (coating S6) to 91.95 at.% (coating S9). It can be seen that without changing Na_2WO_4, NaH_2PO_2 or $NiSO_4$ concentration in plating bath, NaCit/Lac ratio affects the chemical composition of electroless Ni–W–P coatings, while under a constant addition of Na_2WO_4, NaH_2PO_2 as well as NaCit and Lac, the variation of $NiSO_4$ concentration in bath also influences W and P content in coating. Since Ni content in Ni–W–P coatings is larger than 87 wt.% as above indicated, the deposition rate of Ni base mainly contributes to the deposition rate of the coating; and the deposition rate of coating in turn primarily reveals the deposition rate of Ni. It is therefore found that, associated with Fig. 1, higher content of W in coating corresponds to