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Preparation and properties of electroless Ni–Zn–P alloy films

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Electroless deposition of Ni–Zn–P layers was studied on steel electrodes by varying the bath temperature (40–90 °C), pH and chemical composition. The deposition parameters were optimized. Alloys containing 70–86 wt % Ni, 6–20 wt % Zn and 6–10 wt % P are obtained at 20 μm h^{-1} and 85 °C. Corrosion measurements were performed in aerated 5% sodium chloride solution, the corrosion potential and current density are, respectively, −0.49 V/SCE and 2.6 μA cm^{-2}. © *1999 Kluwer Academic Publishers*

1. Introduction

The deposition process can be employed to create new alloy materials that possess novel structure and properties that are different from those obtained by metallurgical techniques [1]. Many works have reported the electroless plating processes. It was found by Saito [2, 3], Paunovic [4] and Ohno [5] that electroless plating processes can be explained by the simultaneous reaction of cathodic metal deposition and anodic oxidation of the reductant. Diverse reaction mechanisms were presented, and it was suggested that the key step in the reaction is the dissociative chemisorption to form adsorbed atomic hydrogen and adsorbed anion radical. There is, at present, an increased interest in this field of investigation, in particular, the protection of steel against corrosion. The advantage of the electroless process is that one can apply a coating over non-metallic substrates by simple immersion. The films formed are uniform over the entire substrate even when it is a complicated shape. The deposition of Ni–X–P alloys where X is rhenium, copper, molybdenum, platinum and lead, is known to exhibit a higher corrosion resistance than the binary alloys that do not contain phosphorus [6–8]. Some work has been reported on electroless and electrodeposited alloy films Ni–Zn–P [9, 10]. The film thickness prepared was of the order of 0.1–0.2 μm [11, 12]. The present work reports the effect of different solution parameters on the deposition rate, the chemical composition, the morphological and electrochemical properties of the electroless Ni–Zn–P alloys films.

2. Experimental procedure

Films were prepared using four solutions. The composition of the baths are summarized in Table I. The bath temperature was held at 85 °C and the pH of the bath was adjusted using NaOH to between 7 and 10. Steels were used as standard substrates. For electron microscope work the same substrates were used. The electron microscope used in our laboratory is a Philips XL30, equipped with a Model energy dispersive X-ray spectral analysis attachment for element analysis. Corrosion behaviour was estimated from potential and polarization measurements on the electroless films. The films were prepared directly on plates of surface area 8 cm^2 without any special preparation. The corrosion measurements were performed in aerated 5% sodium chloride solution prepared from distilled water and reagent salt at pH 8. The electrolytic cell was a Pyrex cylinder 9 cm diameter and 9 cm high. The potential of the working electrode was measured against a saturated calomel electrode (SCE) via a Lugging capillary and salt bridge. The counter electrode was a platinum plate of surface 2 cm^2. Each sample was water-rinsed and equilibrated with solution to establish a stable corrosion potential, E_{corr}. Polarization measurements were made in potentiodynamic mode with a sweep rate of 15 mV min^{-1} using a Tacussel potentiostat–galvanostat PJT24-1.

3. Results and discussion

3.1. Current–potential and impedance measurements

There have been a few reports on the polarization curves in connection with electrochemical behaviour of the electroless plating process. Brenner first described in detail the N-shaped polarization curve observed during electrochemical codeposition of zinc and nickel [1]. This fact was confirmed by other authors [13]. Lustman suggested that the curves for Zn–Ni coating

TABLE I Chemical composition of the bath

	Baths solution (g l^{-1})			
Chemical composition	A	B	C	D
$NiCl_2 \cdot 6H_2O$	7.5	8	10	47.5
$NaH_2PO_2 \cdot H_2O$	3.5	4	4	45
$H_3C_6H_5O_7 \cdot H_2O$	19.5	20	20	4
NH_4Cl	12.5	13	13	26
$ZnCl_2$	7	6	8	8

were similar to those obtained for pure nickel. Some studies demonstrated that the alloy formed is nickel rich and its structure is alpha phase [14]. In a study of Zn–Ni coatings, Brunet [15], defined three types of galvanic curves. Our case is similar to the second type, where the coating is compact and of alpha phase constitution. In this work, current–potential curves and impedance measurements have been reported using bath A (Table I). Iron was used as substrate. Figs 1 and 2 show that the alloy deposition occurs at the potential between -1.1 and -1 V/SCE. We see that the addition of sodium hypophosphite (Fig. 1) in the bath has no effect on the deposition potential. The anodic peak at -0.75 V/SCE is probably due to the anodic oxidation of the reductant. The peak current depends on sodium hypophosphite in the bath and decreases with decreasing sodium hypophosphite concentration. This peak was observed by Roev and Gudin [16] at the potential of -0.83 V/Ag/AgCl. The peak current depends on the pH of the bath and decreases with an increase in pH. At -0.435 and -0.7 V/SCE (Fig. 3), alloy deposition does not occur; it begins to grow only at -0.8 V/SCE (Fig. 4).

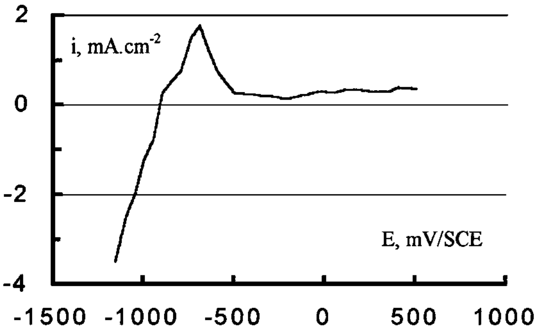

Figure 1 Current–potential curve, with sodium hypophosphite in the bath.

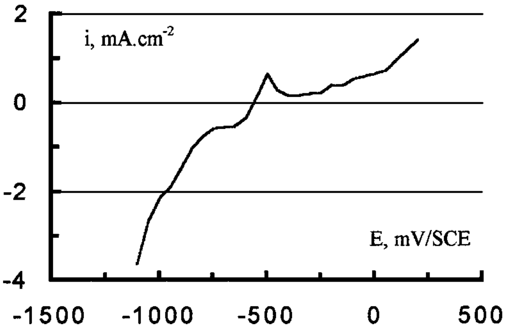

Figure 2 Current–potential curve, without sodium hypophosphite in the bath.

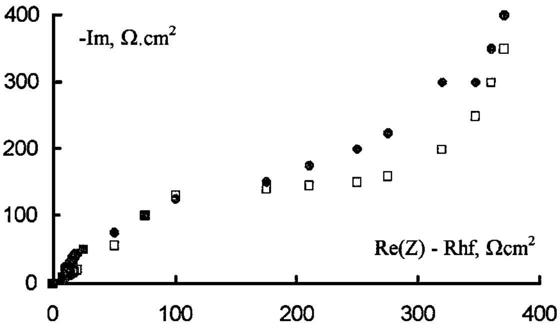

Figure 3 Impedance measurements. (●) $E = -0.435$ V/SCE, $i = 0$ mA cm^{-2}; (□) $E = -0.7$ V/SCE, $i = 0.14$ mA cm^{-2}.

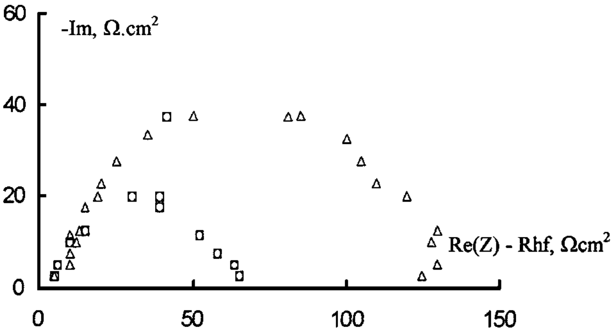

Figure 4 Impedance measurements. (△) $E = -1$ V/SCE, $i = 0.81$ mA cm^{-2}; (□) $E = -1.1$ V/SCE, $i = 2.33$ mA cm^{-2}.

For this potential, the transfer resistance which is conversely proportional to the deposition rate, was 2000 Ω cm^2. The double layer capacitance is of the order of 20 μF cm^{-2}. The form of this curve shows that no alloy deposition occurs at -0.54, -0.7 and -0.758 V/SCE. Between -0.9 and -1.1 V/SCE, the transfer resistance decreases. The impedance curves lead us to postulate a deposition process, especially at -1.1 V/SCE.

3.2. Bath temperature and pH value

The pH was fixed between 9 and 9.5 and the effect of the temperature on the film composition and the bath stability was investigated. The film composition varied slowly, but the deposition rate increase quickly when bath D was used. A film deposit was observed over the whole surface of the cell at 90 °C and pH 9.2. The bath precipitated when the temperature rose to 90 °C. The bath temperature was held constant at 85 °C while varying the pH value between 7 and 10. It should be noted that the deposition rate is very low for $pH < 9$ and the bath precipitated at $pH > 10$.

3.3. Microstructure

The most important feature of electroless chemical deposition is the regularity of the coating thickness. The technique for obtaining this type of coating has the advantage of a uniform deposition rate on all areas of the substrate, and overflows at the corners (point effect) are not present. The micrographs in Fig. 5, show the cross-section of a coating obtained from bath D. This coating is composed of crystallite areas having slightly different diameters. The chemical analysis of these crystallites

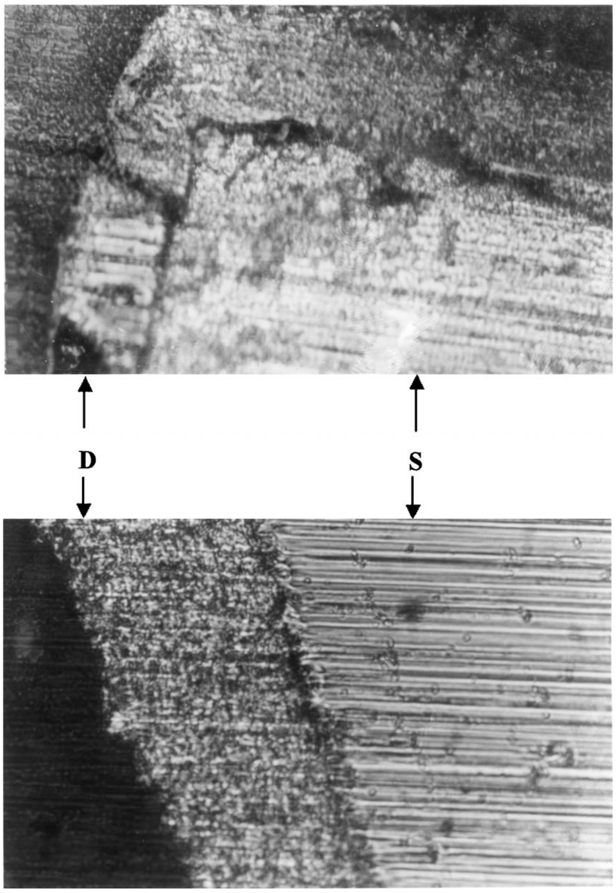

Figure 5 Cross-sectional view of a Ni–Zn–P coating: **S**, substate; **D**, deposit.

is more or less the same as that of the coating. From the work of Snyder *et al.* [11], the crystallite diameter varies with bath pH, and is of order of 0.02 μm for pH 6.3 and of the order of 0.05 μm for a coating obtained at pH 11.4. The scanning electron microprobe analysis, showed that the distribution of all the elements is dense, homogeneous and uniform, with a higher density for nickel.

3.4. Electrochemistry

The electrochemical parameters of the films obtained are summarized in Table II. As shown in this table, the corrosion potential of all samples is approximately the same. The current density is of the order of 2.6 μA cm^{-2}. The coating thickness of the sample selected for corrosion testing is between 2 and 9 μm. From the results in Table II, the film thickness does not seem to influence the electrochemical parameters. These values are less noble than those obtained by Snyder [11]. This could be due to the microstructure and the porosity of the coating studied. It could be very interesting to determine the electrochemical parameters after homogenizing heat treatment of the different coatings.

TABLE II Electrochemical parameters

Sample	Film layer (μm)	E_{corr} (V/SCE)	i (μA dm^{-2})	Chemical composition (wt %)		
				Ni	Zn	P
S_1	—	−0.69	4.5	—	—	—
1	1.8	−0.495	2.6	80	13	7
2	2.1	−0.485	2.6	82	12	6
3	2.2	−0.5	2.7	83	11	6
4	2.6	−0.485	2.7	78	16	6
5	3.3	−0.49	2.6	82	12	6
6	4.3	−0.49	2.4	80	14	6
7	4.8	−0.48	2.7	82	12	6
8	5.0	−0.48	2.7	82	12	6
9	9.0	−0.49	2.5	79	14	5

4. Conclusion

Optimal preparation conditions for alloy films of Ni–Zn–P, by an electroless process, containing 70%–86% Ni, 6%–20% Zn and 6%–10% P were obtained. Compact Ni–Zn–P layers were deposited. The baths containing hypophosphite as reducer gave a high film quality of alloy Ni–Zn–P. These conditions are related to the chemical composition, pH value and temperature of the bath. The best films were obtained with bath D, and the deposition occurred at potentials close to −1.1 V/SCE. The depositior were made directly on the steel without any special preparation of the substrate surface. The deposition rate was about 20 times more important than that obtained with less concentrated baths. With this deposition rate it was possible to obtain relatively thicker films. The corrosion potential of the various fimls obtained with a thickness between 2 and 9 μm was of the order of −0.49 V/ECS and the corrosion densities of 2.6 μA cm^{-2}. These values are less noble than those of zinc but close to those of the Ni–P alloy.

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