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Evaluation of the corrosion resistance of electroless Ni-P and Ni-P composite coatings by electrochemical impedance spectroscopy

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Abstract Electroless Ni-P composite coatings have gained a good deal of popularity and acceptance in recent years as they provide considerable improvement of desirable qualities such as hardness, wear, abrasion resistance, etc. The disagreement among researchers on the corrosion behaviour of these coatings warrants a thorough investigation. Among the various techniques available for the determination of corrosion resistance, electrochemical impedance spectroscopy (EIS) is considered to be superior as it provides not only an assessment of the corrosion resistance of different deposits but also enables the mechanistic pathway by which the deposits become corroded to be determined. The present investigation focuses on the evaluation of the corrosion resistance of electroless Ni-P and Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ composite coatings produced using an acidic hypophosphite-reduced electroless nickel bath, using EIS. The study makes evident that the same fundamental reaction is occurring on all the coatings of the present study but over a different effective area in each case. The charge transfer resistance of electroless Ni-P and Ni-P composite deposits are in the range 32,253–90,700 Ω cm², whereas the capacitances of these coatings are in the range 11–17 μF/cm². The improved corrosion resistance obtained for electroless Ni-P and Ni-P composite coatings is due to the enrichment of phosphorus on the electrode surface, which enables the

preferential hydrolysis of phosphorus over that of nickel. The better corrosion resistance obtained for electroless Ni-P composite coatings can be ascribed to the decrease in the effective metallic area prone to corrosion. Among the three electroless Ni-P composite coatings, the corrosion resistance is in the following order: Ni-P-CeO₂ = Ni-P-Si₃N₄ > Ni-P-TiO₂.

Keywords Electroless nickel · Nickel composite coatings · Corrosion resistance · Electrochemical impedance spectroscopy

Introduction

Electroless nickel plating has a proven ability to provide improved corrosion resistance, wear and abrasion resistance and a low coefficient of friction. Electroless plating is a metal-metalloid alloy coating in which the metalloid content of the coating decides its characteristic properties. In electroless Ni-P coatings the variation in the phosphorus content influences the crystal structure of the deposit and hence its characteristic properties like corrosion resistance, wear and abrasion resistance, etc. [1, 2, 3]. Electroless Ni-P coatings are widely used for corrosion protection application in severe environments [4, 5, 6, 7, 8, 9, 10, 11, 12]. Electroless Ni-P is a barrier coating, protecting the substrate by sealing it off from the corrosive environments, rather than by sacrificial action. The corrosion resistance varies with the phosphorus content of the deposit: relatively high for a high-phosphorus electroless nickel deposit but low for a low-phosphorus electroless nickel deposit.

Electroless Ni-P composite coatings have gained a very good popularity in recent years as they provide considerable improvement of the desirable qualities such as hardness, wear and abrasion resistance, etc. [13, 14, 15]. According to one group of researchers, the corrosion resistance of electroless Ni-P composite coatings is believed to be significantly less than that of the electroless Ni-P coatings [16, 17]. The co-deposited second

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phase particles present in the electroless nickel matrix are thought to reduce both passivity and corrosion resistance. Following this premise, for applications requiring good corrosion resistance, electroless Ni-P composite coatings are not normally recommended [16]. However, the corrosion performance of electroless Ni-P composite coatings was found to be satisfactory by Hubbell [18, 19], Hussain and Such [20] and Shoeib et al. [21].

Hubbell [18, 19] studied the corrosion resistance of electroless nickel composite coatings using a neutral salt spray test and confirmed that the degree of corrosion protection offered by them is the same as that provided by the electroless Ni-P coatings having similar thickness. Hussain and Such [20] evaluated the corrosion performance of a 25- μm thick electroless Ni-P-TiO₂ composite coating, using a copper-accelerated acetic acid salt spray test (CASS test) for a duration of 16 h. According to the authors, both visual and microscopic examination made after the test indicated that the corrosion resistance of the electroless Ni-P-TiO₂ composite coating is no less than that of electroless Ni-P coatings of similar thickness. In a recent study, Shoeib et al. [21] concluded that incorporation of polymer particles, such as poly(vinyl alcohol) and poly(vinyl chloride), improves the corrosion resistance of electroless Ni-P deposits. Hence, a thorough investigation of the corrosion resistance of electroless Ni-P composite coatings is highly desirable.

A variety of evaluation techniques are available for determining the corrosion resistance of electroless Ni-P deposits, namely the weight loss method, the neutral salt spray test, the CASS test, polarization studies, electrochemical impedance spectroscopic (EIS) studies, etc. Among these techniques, EIS is considered to be superior as it provides not only an assessment of the corrosion resistance of different deposits but also enables the mechanistic pathway by which the deposits become corroded to be determined. The utility of EIS in evaluating the corrosion performance of a variety of coatings is very well established [22, 23, 24, 25]. The present paper aims to evaluate the corrosion resistance of electroless Ni-P and Ni-P composite coatings using EIS.

Experimental

An acidic hypophosphite-reduced electroless nickel bath was chosen as the plating bath for the present investigation. Nickel sulfate hexahydrate was used as the source of nickel in the bath while sodium hypophosphite served as the reducing agent and source of phosphorus. Besides these, the bath also contained suitable amounts of complexing agents and stabilizers. The bath was operated at a pH range of 4.8–5.0 and at a temperature of 88 ± 1 °C with constant stirring. Medium carbon steel pieces (30 mm diameter and 5 mm thick) having a composition C 0.45%, Si 0.10%, Mn 0.68%, P 0.08%, S 0.08%, Cr 0.04%, Mo 0.002%, Ni 0.04%, Cu 0.04% and Fe (balance) were used as substrate materials. The pieces were surface ground ($R_a=0.4$), degreased with trichloroethylene and thoroughly rinsed with deionized water. They were subsequently cleaned electrolytically using an aqueous alkaline solution having a composition of 25 g/L Na₂CO₃, 35 g/L NaOH and 1 g/L sodium lauryl sulfate at 27 °C by subjecting the pieces

initially as cathodes (60 s) and later as anodes (30 s). The electrolytically cleaned specimens were thoroughly rinsed in deionized water and were used for electroless deposition without any activating metal strike plating. The electroless plating was done for 2 h. Under optimized control of bath parameters and operating conditions, the bath was capable of depositing at a rate of 10–12 $\mu\text{m}/\text{h}$. Chemical analysis of the nickel and phosphorus contents of the deposit by inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the deposits contained 89 wt% Ni and 11 wt% P. The details of the chemical composition of the electroless plating bath and its operating conditions are given in Table 1. For the preparation of electroless Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ composite coatings, 10 g/L of these second phase particles was mixed thoroughly with an aliquot of the electroless nickel plating solution using a mortar and pestle and then transferred to the plating bath. This process enables the distribution of these particles in suspended form in the plating bath. The incorporation level of the second phase particles in the Ni-P matrix was determined gravimetrically after stripping the deposit in 1:1 nitric acid. Among the three electroless Ni-P composite coatings studied, Ni-P-Si₃N₄ exhibited a higher level of incorporation (8.10 wt%), followed by Ni-P-CeO₂ (7.44 wt%) and Ni-P-TiO₂ (5.42 wt%).

The corrosion resistance of electroless Ni-P and Ni-P composite coatings was evaluated by EIS. A non-deaerated 3.5% sodium chloride solution maintained at ambient temperature was used as the test electrolyte. The thickness of the electroless Ni-P and Ni-P composite coatings used for all the experiments was 25 μm . The electroless plated substrates were degreased with acetone, washed with deionized water and dried. One square centimeter of the specimen surface was exposed to the electrolyte while the remaining area was masked using lacquer. A saturated calomel electrode with a luggin probe was used as the reference electrode, while a graphite electrode served as the counter electrode. EIS studies on electroless Ni-P and Ni-P composite coatings were performed at their respective corrosion potentials. Impedance measurements were made at a higher frequency range by performing the lock-in experiment, followed by a fast Fourier transform (FFT) experiment, which measures the impedance in the lower frequency range. In the lock-in experiment, the impedance of the sample was measured by imposing a 10 mV AC voltage (sine wave), measuring the AC current and voltage within the lock-in, then calculating the impedance of the coating at a particular frequency. The experimental details on impedance measurements are given elsewhere [22, 23, 24, 25].

Results and discussion

Figure 1a–d shows the Nyquist plots obtained for asplated electroless Ni-P, Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ coatings, respectively, in 3.5% sodium chloride solution at their respective open circuit potentials. All the curves appear to be similar, consisting of a single semicircle in the high-frequency region. However, it

Table 1 Chemical composition of the electroless nickel plating bath and its operating conditions

Chemical composition	
Nickel sulfate (NiSO ₄ ·6H ₂ O)	23 g/L
Sodium hypophosphite (NaH ₂ PO ₂ ·H ₂ O)	21 g/L
Complexing agents and stabilizers	Proprietary
Particles in suspension (Si ₃ N ₄ /CeO ₂ /TiO ₂)	0–25 g/L
Operating conditions	
pH	4.8–5.0
Temperature	88 ± 1 °C
Plating duration	2 h
Plating rate	10–12 $\mu\text{m}/\text{h}$

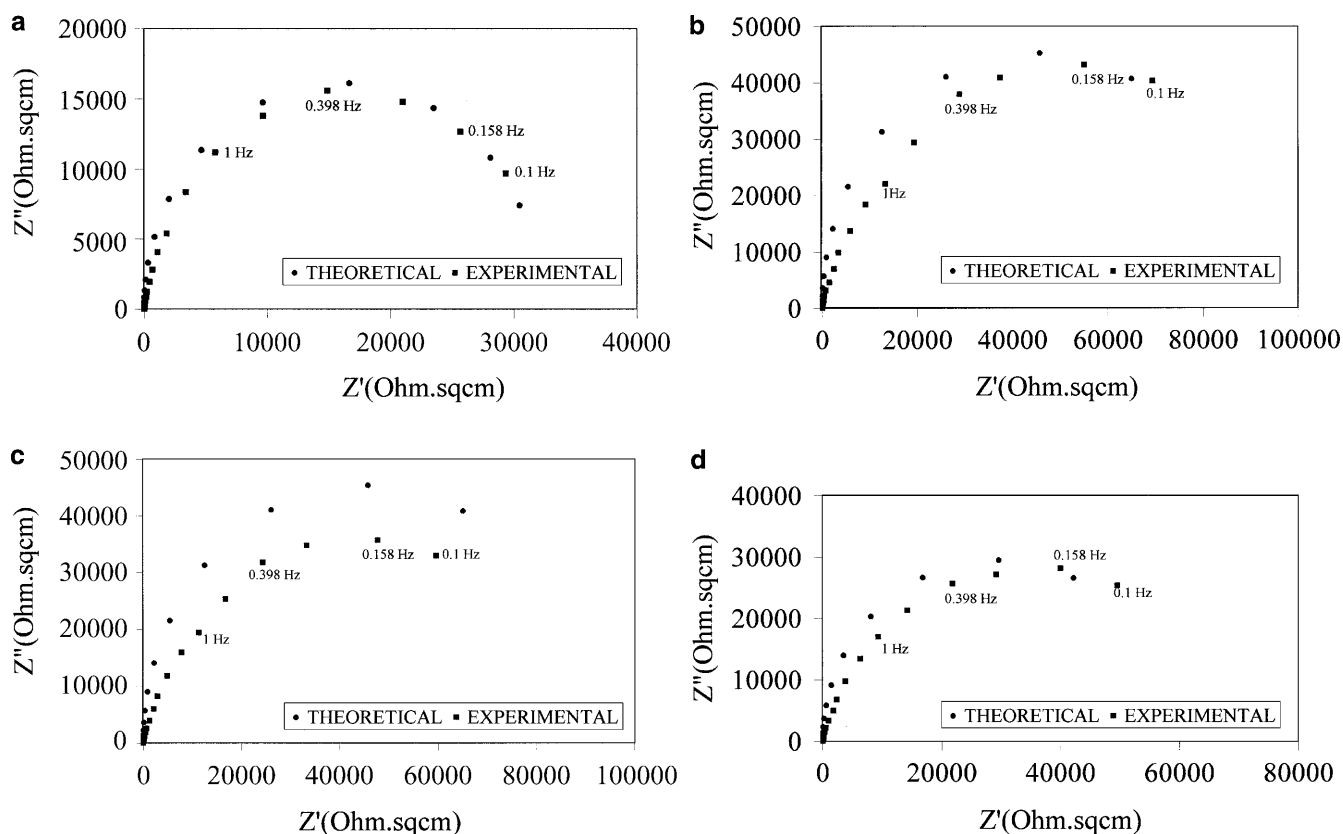


Fig. 1 Nyquist plot for electroless Ni-P and Ni-P composite coatings in 3.5% sodium chloride solution: **a** Ni-P, **b** Ni-P-Si₃N₄, **c** Ni-P-CeO₂ and **d** Ni-P-TiO₂

should be noted that although these curves appear to be similar with respect to their shape, they differ considerably in their size. This indicates that the same fundamental processes must be occurring on all these coatings but over a different effective area in each case.

To account for the corrosion behaviour of as-plated electroless Ni-P and Ni-P composite coatings in 3.5% sodium chloride solution at their respective open circuit potentials, an equivalent electrical circuit model given in Fig. 2 has been utilized to simulate the metal/solution interface and to analyze the Nyquist plot. A similar analysis has been carried out by Lo et al. [26] to study

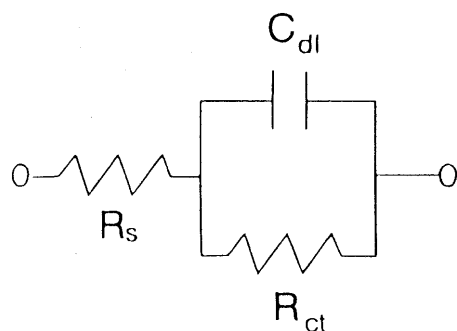


Fig. 2 Equivalent electrical circuit model used to analyze the EIS data of the electroless Ni-P and Ni-P composite coatings

the impedance behaviour of electroless Ni-P coatings in 1 M NaOH solution at -1.2 V.

The charge transfer resistance R_{ct} and double layer capacitance C_{dl} obtained for electroless Ni-P and Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ composite coatings are compiled in Table 2. The open circuit potential (OCP), a reliable parameter that indicates the tendency of these systems to corrode, is also included in the same table, along with R_{ct} and C_{dl} values for an effective comparison.

The occurrence of a single semicircle in the Nyquist plots (Fig. 1a–d) indicates that the corrosion process of electroless Ni-P and Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ composite coatings involves a single time constant. A similar conclusion of the existence of a single time constant has been reported by Lo et al. [26], Zeller [27] and Van Der Kouwe [28] for the corrosion of electroless Ni-P coatings in sodium chloride and sodium hydroxide solutions at the respective open circuit potentials. To further validate this view, the calculated R_{ct} and C_{dl} values are substituted for the proposed equivalent electrical circuit to obtain theoretical impedance values [29], which are also plotted along with the experimental impedance values in Fig. 1a–d. The mean percentile deviation between experimental and theoretical impedance data was found to be 11.69% for electroless Ni-P, 30.93% for electroless Ni-P-Si₃N₄, 30.38% for electroless Ni-P-CeO₂ and 37.88% for electroless Ni-P-TiO₂ coatings. The higher degree of deviation resulting in the case of electroless Ni-P composite coatings might possibly be due to the decrease in the available

Table 2 Electrochemical parameters estimated from EIS data of as-plated electroless Ni-P and Ni-P composite coatings in 3.5% sodium chloride solution

Type of coating	OCP (mV vs. SCE)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	i_{corr} ($\mu\text{A}/\text{cm}^2$)
Ni-P	-320	32,253	12	1.66
Ni-P-8.10 wt% Si_3N_4	-275	90,525	11	0.33
Ni-P-7.44 wt% CeO_2	-292	90,700	11	0.37
Ni-P-5.42 wt% TiO_2	-310	58,991	17	0.66

metallic area for the charge transfer reaction, although the apparent area (1 cm^2) remains equal to that of the electroless Ni-P coating.

The high values of the charge transfer resistance (R_{ct}), in the range $32,253\text{--}90,700 \Omega \text{ cm}^2$, obtained for the coatings of the present study imply a better corrosion protective ability of electroless Ni-P composite coatings than the electroless Ni-P coating. Van Der Kouwe [28] recommended that an intact electroless Ni-P coating should have a charge transfer resistance above $45,000 \Omega \text{ cm}^2$. The capacitance values obtained for electroless Ni-P and Ni-P composite coatings are very low, of the order of $11\text{--}17 \mu\text{F}/\text{cm}^2$. These values are highly comparable to those obtained for similar coatings reported elsewhere [26, 27, 28]. Lo et al. [26] reported C_{dl} values in the range $100\text{--}120 \mu\text{F}/\text{cm}^2$ for electroless Ni-P (11.8–12.8 wt% P) in deaerated 1 M NaOH solution at -1.2 V . Zeller [27] reported a value of $28 \mu\text{F}/\text{cm}^2$ for a electroless Ni-P (10–11 wt% P) coating having a thickness of $50\text{--}60 \mu\text{m}$ in 5% NaCl solution. Van Der Kouwe [28] also reported C_{dl} values of 30 and $42 \mu\text{F}/\text{cm}^2$ for electroless nickel high-phosphorus coatings having a thickness of greater than $20 \mu\text{m}$ in 3% NaCl solution. The C_{dl} value is related to the porosity of the coating [30]. The low C_{dl} values confirm that the electroless Ni-P and Ni-P composite coatings of the present study are relatively less porous in nature. The i_{corr} values of electroless Ni-P and Ni-P composite coatings of the present study calculated using the corresponding R_{ct} values (Table 2) are comparable to those of similar deposits reported elsewhere [27].

It is evident from literature reports on Ni-P coatings that preferential dissolution of nickel occurs at open circuit potential, leading to the enrichment of phosphorus on the surface layer [31, 32, 33, 34, 35, 36]. The enriched phosphorus surface reacts with water to form a layer of adsorbed hypophosphite anions (H_2PO_2^-). This layer in turn will block the supply of water to the electrode surface, thereby preventing the hydration of nickel [34, 37], which is considered to be the first step to form either soluble Ni^{2+} species or a passive nickel film. Van Der Kouwe [28], using glow discharge optical emission spectrometry (GDOES), confirmed the presence of a phosphorus-rich surface layer in a high-phosphorus (8 wt% P) electroless nickel deposit even before it is subjected to any corrosive environment. Accordingly, such a condition of phosphorus enrichment at the surface would enable hydrolysis of phosphorus and retard hydrolysis of nickel. Hence the better corrosion resistance obtained for electroless Ni-P and Ni-P composite coatings is due to the enrichment of phosphorus on the electrode surface.

Comparing the corrosion resistance of electroless Ni-P and Ni-P composite coatings, the latter coatings appear to offer better corrosion protection. This seems to be logical, because even though the apparent area remains the same, the effective metallic area prone to corrosion is decreased considerably in the case of electroless Ni-P composite coatings. Among the electroless Ni-P composite coatings, the R_{ct} values of electroless Ni-P- Si_3N_4 and Ni-P- CeO_2 are very similar, but higher than Ni-P- TiO_2 .

Conclusions

From the present study it can be concluded that during the corrosion process of electroless Ni-P and Ni-P composite coatings, the same fundamental reaction is occurring on all the coatings but over a different effective area in each case, thus causing a larger variation in the size of the semicircle in the Nyquist plot. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of the coatings of the present study involves a single time constant. The charge transfer resistance of the electroless Ni-P and Ni-P composite deposits are in the range $32,253\text{--}90,700 \Omega \text{ cm}^2$, whereas the capacitances of these coatings are in the range $11\text{--}17 \mu\text{F}/\text{cm}^2$. These charge transfer resistance and capacitance values are comparable to those obtained for similar coatings. The low capacitance values suggest that the electroless Ni-P and Ni-P composite coatings of the present study are relatively less porous in nature. The i_{corr} values calculated using the charge transfer resistance are also comparable to those obtained for similar deposits. The corrosion resistance observed for electroless Ni-P and Ni-P composite coatings is due to the enrichment of phosphorus on the electrode surface, which causes preferential hydrolysis of phosphorus over that of nickel. The better corrosion resistance obtained for electroless Ni-P composite coatings over electroless Ni-P coatings can be ascribed to the decrease in the effective metallic area available for corrosion. Among the three electroless Ni-P composite coatings, corrosion resistance is in the following order: Ni-P- $\text{CeO}_2 = \text{Ni-P-Si}_3\text{N}_4 > \text{Ni-P-TiO}_2$.

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