

Electrochemical behavior of electroless Ni-P-SiC nano-composite coatings

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ABSTRACT. Ni-P-SiC nano-composite coatings were successfully fabricated on a P20 plastic die steel surface by combining acid etching and electroless plating process. Electrochemical behavior of coatings and substrate has also been studied by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). Results demonstrated that the SiC-doped Ni-P coating possessed excellent anti-corrosion property with i_{corr} ($0.813\mu Acm^{-2}$) about 6% that of steel substrate, the Ni-P-SiC nano-composite coating exhibited good corrosion resistance properties in protecting the P20 plastic die steel.

1. Introduction

Electroless plating is a chemical process, which involves the catalytic reduction of metallic ions in an aqueous solution and their subsequent deposition without using electrical energy. This method has many advantages over other coating methods (such as electrodeposition), owing to the homogeneous deposition onto irregular substrate surfaces, simplicity, and absence of special equipment. Since the invention of the electroless plating technology in 1946 by Brenner and Riddell, electroless Ni coatings have attracted significant interest due to their high corrosion resistance, thickness uniformity, and specified hardness as well as strong wear resistance and high cohesion to the substrate surface [1-4]. As a result, electroless Ni deposition has been widely used in many practical applications including electronic boards, automotive parts, oil and gas equipment, and corrosion resistance coatings. In order to tune specific coating properties, it was suggested to codeposit the main composite layer with various second-phase particles via the same method [5]. Several factors influence the incorporation of hard and soft particles into the electroless Ni-P matrix, including their size and shape, relative density, charge, degree of inertness, concentration in the plating bath, compatibility with the matrix, part orientation, and degree of agitation [6,7].

S.R. Allahkaram et al. performed the deposition, characterization, and electrochemical evaluation of Ni-P nanodiamond composite coatings [8]. In their work, the composites were deposited on steel substrates, and the optimum concentration of diamond nanoparticles was determined via hardness measurements, linear polarization studies, and electrochemical impedance spectroscopy (EIS). The obtained results demonstrated high corrosion resistance and hardness of the produced composite coatings as compared to those of the deposited Ni-P films. A.S. Hamdy et al. studied the corrosion resistance of electroless deposited Ni-P alloy coatings on low carbon steel supports containing tungsten (Ni-P-W) and nano-scattered alumina (Ni-P-Al₂O₃) components as well as the effect of the heat treatment on the coating characteristics [9]. S. Alirezai et al. investigated the hardness and wear resistance of electroless Ni-P and Ni-P-Al₂O₃ coatings on AISI 1045 steel discs, which were



significantly increased by the presence of alumina particles in the Ni-P coating matrix, while their maximum values were obtained after the heat treatment at a temperature of about 400 °C [10]. C. Dehghanian et al. discussed the effects produced by the addition of three types of surfactants (cationic, anionic, and non-ionic ones) with different concentrations into the plating bath on the deposition rate, polytetrafluoroethylene (PTFE) content, and surface morphology of electroless Ni-P/PTFE composite coatings [11]. They demonstrated that the presence of cationic and non-ionic surfactants created a uniform distribution of PTFE particles in the coating matrix, which in turn increased the corrosion resistance of the produced material.

The addition of SiC particles into the Ni-P coating matrix can potentially increase its hardness; however, the effect produced on the corrosion resistance of the resulting nanocomposite has not been investigated in sufficient detail [12-15]. In this work, we report the electrochemical behavior of Ni-P-SiC electroless composite coatings, which exhibited good corrosion resistance properties in protecting the P20 plastic die steel.

2. Experimental

2.1. Preparation of Ni-P-(nano-SiC) composite coatings

Commercial plastic die steel P20 specimens with dimension of $\Phi 14 \times 2$ mm, and SiC powder, with an average size of 40 nm, were used as substrate and reinforcement particles, respectively. To prepare the substrates and make them ready for pretreatment and coating process, they were mechanically polished with emery papers of up to No. 1500 and washed with acetone, ethanol and deionized water several times in an ultrasonic cleaner.

Table 1. Chemical composition of the electroless deposition bath used.

Bath constituents and parameters	Quantity	Bath constituents and parameters	Quantity
NiSO ₄ ·6H ₂ O	25g/L	KI	2mg/L
NaH ₂ PO ₄ ·H ₂ O	30 g/L	SiC concentrated solution	100ml/L
NaCH ₃ COO	20 g/L	Temperature	87 ± 2°C
CH ₃ CH(OH)COOH	20ml/L	pH value	4.5 ± 0.2
C ₆ H ₈ O ₇ ·H ₂ O	8g/L	Time	180min

Subsequently etched in a solution of 20% (v/v) H₂SO₄ for 2 min to remove the oxide layer and obtain a homogeneous micropitted surface, then rinsed by immersion in distilled water at room temperature for 2 min, followed by activated in a 5% (v/v) H₂SO₄ solution for 30 s. The samples were rinsed using distilled water after different steps of the pretreatment process. Fig. 1c shows the chemical composition of the pretreated P20 was used. Following the pretreatment operation, the specimens were immersed in electroless bath, with chemical composition stated in Table 1, for 3 h. In order to produce a composite coating, the SiC concentrated solution with a certain concentration of SiC nanoparticles were added to the bath and uniformly dispersed in the solution using a magnetic stirrer.

2.2. Coating corrosion resistance

The electrochemical investigations were performed with Corrosion Test Electrochemical Workstation (CHI660D, Shanghai CH Instruments, Inc.) coupled to a computer, and the test system was controlled and experimental data recorded by the Corrosion Test software package. The measurement was carried out using a conventional three-electrode cell with platinum foil as the auxiliary electrode, saturated calomel electrode (SCE) as the reference electrode, and the samples with an exposed area of 1 cm² as working electrode. 3.5 wt % NaCl aqueous solution maintained at ambient temperature was used as the test electrolyte. Prior to the beginning of the EIS measurements the sample was immersed in the corrosive medium for about 30 min to establish the steady state potential. The EIS

measurements were performed for corrosion potential at sinusoidal voltage excitation with perturbation amplitude of 5 mV in a frequency range from 100 kHz to 0.01 Hz. All the recorded impedance spectra were displayed as Nyquist and Bode diagrams. After EIS measurements, the system was allowed for 1 h to reach its steady open circuit potential. The potentiodynamic polarization tests of samples were performed successively at a sweep rate of 0.33 mVs^{-1} in the applied potential range from -400 mV to 400 mV. The electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated using the Tafel extrapolation method. The working electrode cleaned in acetone, rinsed in deionized water before the electrochemical test.

3. Results and discussion

3.1 Potentiodynamic polarization studies

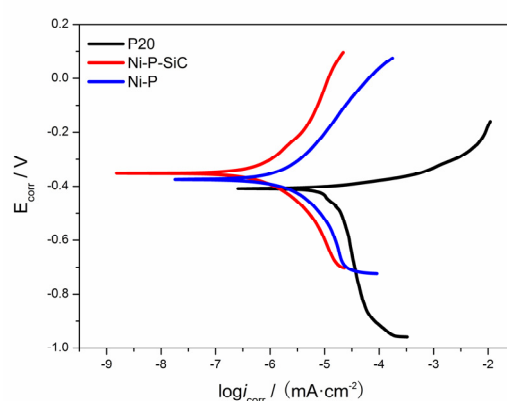


Figure 1. Potentiodynamic curves of P20 plastic die steel, electroless Ni-P coating and Ni-P-SiC composite coatings immersed in 3.5 wt.% NaCl solution.

The corrosion behaviors of P20 plastic die steel, Ni-P and Ni-P-SiC composite coatings immersed in 3.5 wt.% NaCl solution were investigated by potentiodynamic polarization method. Figure 1 shows the potentiodynamic curves of three samples in 3.5 wt.% NaCl solution. The electrochemical corrosion parameters derived from the potentiodynamic polarization curves are tabulated in Table 2, respectively.

Table 2. Corrosion characteristics of P20 plastic die steel, electroless Ni-P coating and Ni-P-SiC composite coatings immersed in 3.5 wt.% NaCl solution by potentiodynamic polarization technique.

Type of coating	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)
P20 plastic die steel	-409	13.06
electroless Ni-P coating	-375	2.369
Ni-P-SiC composite coating	-352	0.813

It was found that both coatings exhibited more positive corrosion potentials (E_{corr}) and dramatically lower corrosion currents (i_{corr}) than those of the steel substrate. As it can be seen, coating the substrate alloy can extensively improve the corrosion resistance in corrosive media. The corrosion potential of Ni-P coated specimen (-375 mV) is almost 34 mV more positive than that of the P20 plastic die steel (-409 mV), the corrosion current densities has decreased from $13.06 \mu\text{Acm}^{-2}$ for P20 plastic die steel down to $2.369 \mu\text{Acm}^{-2}$ for Ni-P coated specimen, from which it could be deduced that the tendency towards corrosion has decreased through applying Ni-P coating. In addition, the corrosion potential of Ni-P-SiC nano-composite coated specimen (-352 mV) is almost 23 mV more positive than that of Ni-P coated specimen, meanwhile corrosion current densities obtained through the extrapolation of the linear portion of cathodic and anodic polarization curves has decreased to $0.813 \mu\text{Acm}^{-2}$ from $2.369 \mu\text{Acm}^{-2}$ for Ni-P coated alloy. It means the corrosion resistance of Ni-P-SiC coatings is better than that of Ni-P coatings in 3.5 wt.% NaCl solution. The existence of SiC nanoparticles decreased the porosity

of Ni-P coating, and lent to an increase of the anti-corrosion ability. This conclusion is different from some scholars' reports, such as X.G. Hu et al.[16] summarized that the corrosion mechanism of the Ni-P-MoS₂ composite coatings was mainly ascribed to the formation of microcells around the nanosized MoS₂ particles, and the active ion-like Cl⁻ destroyed the surface film and induced the corrosion on the inside part of the coating. Moreover, M.H. Paydar et al.[17] also concluded that the presence of the B₄C particles in the Ni-P-B₄C coating has a decreasing effect on its corrosion resistance due to the creating micro cracks in the coated microstructure. Besides, many scholars have come to the similar conclusion [18, 19, 20].

3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy method is one of the powerful techniques to investigate the corrosion resistance of different coatings on P20 plastic die steel. Figure 2 shows the Nyquist and Bode plots obtained for the bare P20 plastic die steel substrate, as-plated Ni-P and Ni-P-SiC composite coatings immersed in 3.5 wt.% NaCl solution at their respective open circuit potentials (OCP).

The Nyquist plots obtained for P20 plastic die steel substrate, as-plated Ni-P and Ni-P-SiC composite coatings appear to be similar, consisting of only one capacitive loop in the high frequency region. Although these Nyquist plots appear to be similar with respect to their shape, they differ appreciably in the diameter of the loops. This indicates that the corrosion resistance of the bare P20 plastic die steel substrate, as-plated Ni-P and Ni-P-SiC composite coatings in 3.5 wt.% NaCl solution were different. The capacitive loop diameters can be used to calculate the impedance value. The bigger the capacitive loop diameters, the better the corrosion resistance of the coatings. So, it is evident that the corrosion resistance obtained from EIS measurements is increased in the order P20 plastic die steel < Ni-P coating < Ni-P-SiC composite coating, which accords with the results obtained from the polarization tests. As shown in Fig. 6(b), it can be seen that Bode plots of as-plated Ni-P and Ni-P-SiC composite coatings revealed higher impedance value and broader phase angle than P20 plastic die steel, which could be ascribed to the good corrosion resistance of electroless Ni-P and Ni-P-SiC composite coatings deposited on the P20 plastic die steel substrate. Comparing the Bode plots of electroless Ni-P and Ni-P-SiC composite coatings, the corrosion process of both coatings involves a single time constant and the Ni-P-SiC coating appears to offer better corrosion protective ability.

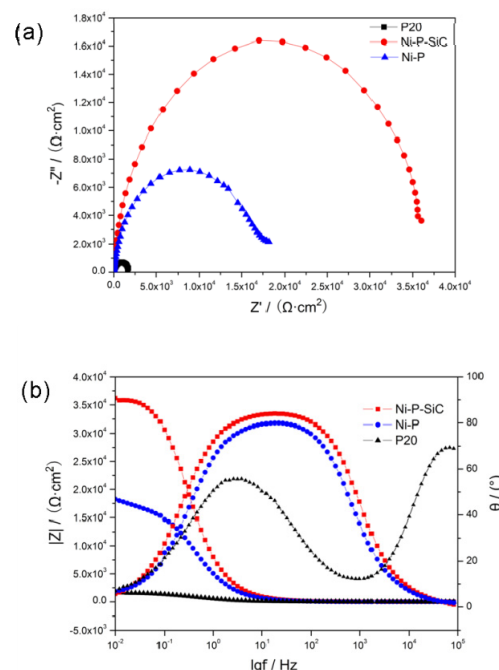


Figure 2. Nyquist plots (a) and Bode plots (b) for P20 plastic die steel, electroless Ni-P coating and Ni-P-SiC composite coatings immersed in 3.5 wt.% NaCl solution.

4. Conclusion

The linear polarization and electrochemical impedance spectroscopy (EIS) tests demonstrated that both coatings exhibited more positive corrosion potentials (E_{corr}) and dramatically lower corrosion current densities (i_{corr}) than those of the steel substrate, the Ni-P coating shows excellent anti-corrosion property with i_{corr} ($2.369 \mu\text{Acm}^{-2}$) about 18% that of P20 plastic die steel (i_{corr} $13.06 \mu\text{Acm}^{-2}$), meanwhile the SiC-doped Ni-P coating also possesses better anti-corrosion property with i_{corr} ($0.813 \mu\text{Acm}^{-2}$) about 6% that of steel substrate. It can be concluded that the Ni-P-SiC nano-composite coating exhibited better corrosion resistance properties than Ni-P coating in protecting the P20 plastic die steel.

Acknowledgments

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