Corrosion Behavior of Electroless Nickel-Phosphorous and Nickel-Phosphorous-SiC Coatings

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Nickel-phosphorous (Ni-P) and nickel-phosphorous-silicon carbide (Ni-P-SiC) coatings were obtained by electroless deposition processes using laboratory made and commercial nickel/hypophosphite based baths. The characterization techniques included scanning electron microscopy (SEM), glow discharge optical emission spectroscopy (GD-OES) and X-ray diffraction (XRD). All deposits showed an amorphous micro-structure and high phosphorus content. The incorporated SiC particles (2 µm to 5 µm) constituted about 10 wt.% of the composite deposits. The techniques used to study the corrosion resistance in 3.5 wt.% sodium chloride were linear polarization resistance (LPR), Tafel plots and electrochemical impedance spectroscopy (EIS). The results showed that Ni-P-SiC deposits experienced lower corrosion currents compared with the Ni-P coatings. This fact can be ascribed to the decrease in the effective surface area available for corrosion. Concerning the mechanism by which Ni-P and Ni-P-SiC deposits become corroded, through EIS experiments and Tafel plots, it was shown that the corrosion kinetics involved a charge transfer mechanism.

Korrosionsverhalten von chemisch abgeschiedenen Nickel-Phosphor- und Nickel-Phosphor-SiC-Schichten

Untersucht wurden die Abscheideprozesse für Nickel-Phosphor und Nickel-Phosphor-Siliziumcarbid, wobei sowohl Eigenansätze als auch kommerzielle Elektrolyte auf Basis von Nickel/Hypophosphit verwendet wurden. Die Charakterisierung der Abscheidungen erfolgte mittels Rasterelektronenmikroskop (REM), Glimmentladungsspektroskopie (GD-OES) und Röntgenbeugung (XRD). Alle Abscheidungen zeigten eine amorphe Mikrostruktur und einen hohen Phosphorgehalt. Die Einbaurate der Siliziumcarbidpartikel (2 µm bis 5 µm) reichte bis zu 10 Gew.%. Die Korrosionsbeständigkeit der Schichten wurde in einer Natriumchloridlösung (3,5 Gew.%) durch Bestimmung des linearen Korrosionswiderstands, der Tafelkurven sowie unter Einsatz der elektrochemischen Impedanzspektroskopie (EIS) ermittelt. Nickel-Phosphor-SiC zeigte einen geringeren Korrosionsstrom als Nickel-Phosphor, was sich durch die kleinere, effektiv korrodierbare Fläche erklären lässt. Aus den EIS-Messungen und den Tafelkurven ist ersichtlich, dass die Auflösung der Nickel-Phosphor- und der Nickel-Phosphor-SiC-Schichten von einem durch die Kinetik bestimmten Ladungsdurchtrittsprozess beeinflusst wird.

1 Introduction

Nowadays industrial sectors such as automotive, aerospace, electronics and textile increasingly require the use of materials with suitable properties for specific applications. One possibility to improve materials performance is to protect them by coatings.

Ni-P alloys obtained by electroless plating have contributed to a significant advance in the development of protective coatings because a Ni-P coating improves basis material properties such as corrosion resistance, hardness, wear resistance and surface uniformity [1, 2]. The addition of dispersed, hard micro/nano particles into the Ni-P matrix has led to the development of composite coatings. Ni-P composite coatings exhibit an improved hardness and wear resistance. However, it is difficult to predict accurately their corrosion resistance because different parameters can influence the behaviour of these coatings. In fact, the role of dispersed particles for the corrosion properties is still controversially discussed [3, 4, 5].

This research aims to synthetize, to characterize and to evaluate the corrosion resistance in NaCl 3.5 % of as-plated Ni-P and Ni-P-SiC coatings with high phosphorus content. By using different electrochemical techniques a better understanding of the behaviour of Ni-P and Ni-P-SiC can be achieved.

2 Experimental part

2.1 Synthesis of electroless Ni-P and Ni-P-SiC coatings

Electroless Ni-P and Ni-P-SiC deposits were obtained by electroless deposition using both lab made and commercial nickel/hypophosphite based baths. The chemical

composition of the lab made plating bath consisted of:

- 30 g/L NiSO$_4$·7H$_2$O,
- 20 g/L NaH$_2$PO$_2$·H$_2$O,
- 25 g/L lactic acid,
- 5 g/L propionic acid,
- 1 mg/L Pb^{2+} (as Pb(NO$_3$)$_2$)

In the case of the plating baths used for the composite coatings, 25 g/L of SiC micro-sized particles (2 µm to 5 µm, ESK Ceramics GmbH & Co. KG, Kempten) were added to the original lab made and commercial baths. The pH value of all plating baths was adjusted to 4.8 with 5M NaOH solution. All reagents were p.a. grade.

Low carbon steel panels (2.5 x 4.5 x 0.05 cm³) were used as substrates. The pre-treatment of the substrates consisted of an electrolytic degreasing for 3 minutes at a current density of 6.5 A/dm² (cathodic mode) followed by a substrate pickling with HCl (1:1 v/v) for 3 minutes. Both procedures were done at room temperature.

In all the cases the plating was carried out by immersing the substrate into the electrolytic bath at 87 ± 1 °C immediately after the pre-treatment. The bath loading was 0.15 dm²/L and the deposition time was 2 hours. In the case of Ni-P-SiC deposits, the electroless baths containing dispersed SiC particles were mechanically stirred at approx. 500 rpm with a two-bladed glass stirring element. The sample was vertically positioned and parallel oriented to the flow direction of the bath. After the deposition process the samples were rinsed with distilled water, dried and stored in a desiccator.

2.2 Characterization of deposits

The surface morphology of deposits was studied by scanning electron microscopy (SEM) using a Philips XL 30 scanning electron microscope. The samples were examined in top and cross-sectional views. The chemical composition of deposits was determined by GD-OES with a GDA 750 Sprectruma equipped with a DC source (1000 V, 13 mA). The diameter of the exposed sample area was 2.5 mm. The microstructure of Ni-P and Ni-P-SiC deposits was studied by X-ray diffraction (XRD). An X-ray diffractometer (Bruker AXS D 5000 operating with Cu-Kα radiation) with Goebel mirror was used. The studied sample area was approx. 1 cm². The method of study was grazing incidence diffraction [6].

The coatings thickness were determined by magnetic induction method and then verified by SEM in the surface cross-section of the samples. A Deltascope MP30 (Fischer) thickness tester was used according with ASTM B 499-96 standard [7].

2.3 Corrosion resistance of deposits

All the electrochemical tests were performed using an Autolab PGSTAT 302N potentiostat/galvanostat equipped with a FRA2 impedance module and controlled with the software NOVA version 1.4. The electrochemical tests used a conventional three-electrode electrochemical cell setup: the sample (Ni-P or Ni-P-SiC deposit) as the working electrode (WE), a silver/silver chloride electrode (Ag/AgCl 3M KCl) as the reference electrode (RE) and a platinum wire as the counter electrode (AE). The electrochemical cell consisted of a glass cylinder with a PTFE bottom plate with a hole in the centre. The exposed sample area was 0.20 cm². All tests were carried out at room temperature.

The electrolytic solution was prepared by dissolving NaCl (p.a., Merck) in distilled water to give a concentration of 3.5 wt.%. In order to carry out tests with a constant concentration of oxygen in the salt solution, the electrolyte was air-saturated by bubbling air for 30 minutes. About 40 mL of electrolyte was used for each test. The OCP (open circuit potential) measurement was performed monitoring the potential of the sample (WE) in the 3.5 wt.% NaCl solution versus the reference electrode (RE) for 1 hour.

Potentiodynamic anodic polarization studies were carried out by scanning the potential +1.0 V from the OCP value. Tafel plots were obtained by scanning the potential from -0.25 V to +0.25 V from OCP. LPR plots were obtained by scanning the potential from -0.02 V to +0.02 V from OCP. All tests were carried out with a scan rate of 0.16 mV/s. EIS measurements were carried out by applying a small amplitude voltage of 10 mV (single sine wave type) to the previously determined OCP value. The frequency ranged from 10 kHz to 1 mHz. The number of frequencies was 50.

All potentials from experimental data were converted to the saturated calomel electrode (SCE) scale to facilitate the discussion.

3 Results and discussion

The Ni-P and Ni-P-SiC coatings obtained from electroless plating process were classified according to the baths employed for their synthesis. The used nomenclature of the samples is summarized in *Table 1*.

3.1 Morphology

The scanning electron micrographs of the deposits in top and cross sectional view are shown in *Figure 1* and *Figure 2*. For both Ni-P deposits S1 (*Fig. 1a*) and S2 (*Fig. 1c*), a regular, continuous and relatively smooth
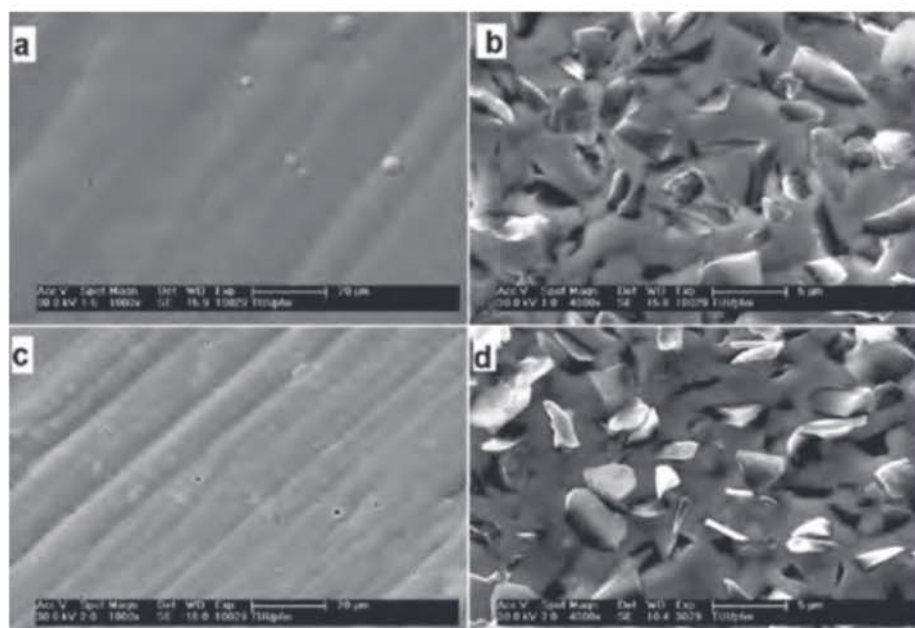

Fig. 1: SEM micrographs in top view of Ni-P and Ni-P-SiC deposits: a) S1 (1000X), b) C1 (4000X), c) S2 (1000X) and d) C2 (4000X)

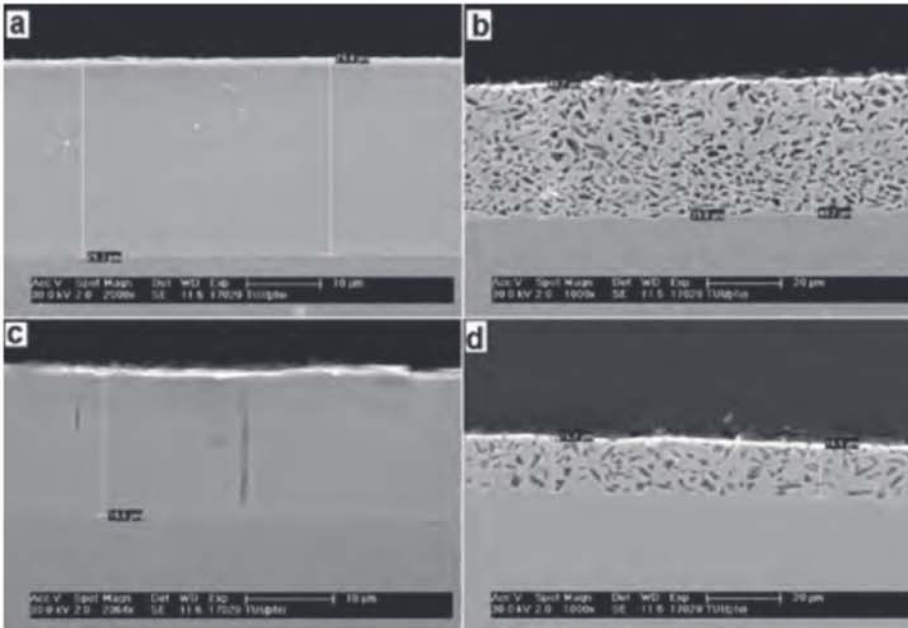Fig. 2: SEM micrographs in cross sectional view of Ni-P and Ni-P-SiC deposits: a) S1 (2000X), b) C1 (1000X), c) S2 (2364X) and d) C2 (4000X)

Tab. 1: Classification of electroless Ni-P / Ni-P SiC deposits

	Ni-P	Ni-P-SiC
Lab made baths	S1	C1
Commercial baths	S2	C2

morphology is observed. Deposit S2 shows the presence of micro-pores uniformly distributed over the surface (*Fig. 1c*). Cross sectional view (*Fig. 2c*) also confirmed the presence of pores.

In the case of the Ni-P-SiC composite deposits C1 (*Fig. 1b* and *2b*) and C2 (*Fig. 1d* and *2d*), a coarse morphology with uniform distribution of SiC particles can be observed. There are neither agglomerated nor depleted zones of particles. The incorporation of dispersed SiC micro-particles seems to prevent the growth of pores as well.