

Electrochemical behavior of Ni-P-SiC composite coatings: Effect of heat treatment and SiC particle incorporation

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Abstract

This paper describes the effects of heat treatment and of SiC particle incorporation on the electrochemical behavior and physical structure of Ni-P (17 at% P) composite coatings. The deposits were obtained by electrodeposition with various contents of SiC particles in the plating bath and heat treated at 420 °C. The physical structure was investigated by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM – image analysis). The electrochemical behavior of the resultant composite coatings was determined by chronopotentiometry and electrochemical impedance spectroscopy in 0.6 M NaCl solution at pH 6. Heat treatment showed a positive effect on the electrochemical behavior of Ni-P coatings, shifting the open circuit potential towards less active potentials. The incorporation of SiC particles inhibited pit nucleation on the Ni-P composite coating, with or without post heat treatment. However, heat treatment in the Ni-P-SiC seemed to induce cracks in the metallic matrix, initiating at the SiC particles, possibly caused by the contraction in the metallic matrix. The cracked structure promoted localized corrosion, while coatings without heat treatment resulted in a general and uniform corrosion.

Keywords: composite materials, corrosion, electrochemical reactions, Ni-P-SiC.

Introduction

Ni-P alloys have been studied in the last few decades due to their characteristics concerning the effect of phosphorous content on its crystal structure [1,2]. Crystalline Ni-P structures can be obtained, though, by heat treatment above 350 °C [1]. It has been reported that the amorphous form, containing no grain boundaries and structure defects, results in coatings with outstanding mechanical and corrosion properties. Ni-P alloys, however, present low hardness and consequently low wear resistance, restraining their application in industry. Structures with better wear resistance have been successfully achieved by the incorporation of ceramic particles in the metallic matrix, such as SiC, Al₂O₃, Cr₂O₃ and TiO₂ [3-9]. A remarkable improvement in the resistance to localized corrosion of Ni-SiC composite coatings was observed with alloys containing sub-micron SiC particles [10]. This work aims at studying the effects of heat treatment and of the particle incorporation on the electrochemical behavior of Ni-P and Ni-P-SiC (17% at. P) composite coatings containing various amounts of embedded SiC particles, in 0.6 M NaCl.

Experimental

Ni-P and Ni-P-SiC (17 % at. P) composite coatings with varying amounts of incorporated SiC particles were obtained by electrodeposition. The plating bath consisted of NiSO₄ 50 g·L⁻¹, NiCl₂·6H₂O 60 g·L⁻¹, H₃PO₃ 20 g·L⁻¹, H₃PO₄ 50 g·L⁻¹, Na₂SO₄ 50 g·L⁻¹, containing 0, 40, 80 and 200 g·L⁻¹ of SiC particles (with a mean diameter of 600 nm [11]) in suspension, at pH 2. The substrate and counter electrode were made of copper and nickel, respectively. Electrodeposition was carried out at 0.1 A·cm⁻² (which resulted in 50 μm thick coatings, measured by optical microscopy). After the process, the specimens were heat treated at 420 °C for 1 h in N₂ atmosphere. The concentration of SiC embedded in the Ni-P matrix (volume %) was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), with an error of 2 wt.%. The number of incorporated particles per unit area (particles/μm²) was determined by image analysis using Scanning Electron Microscope (SEM - JEOL JSM 6400). The crystalline state and thickness of the deposits were obtained by X-Ray Diffraction analysis (XRD), using CuKα (λ=1,5418Å) radiation in the Phillips X'Pert diffractometer, and by optical microscopy, respectively. Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) were performed in 0.6 M NaCl solution (pH 6) using an EG&G PAR 273 potentiostat and a Solartron 1250 frequency response analyzer. The EIS measurements were carried out at the OCP using a perturbation of 10 mV amplitude signal and frequency range of 100 kHz to 10 mHz. After 1200 h of immersion in the NaCl solution, the coatings were observed in the SEM.

Results and Discussion

The correlation between the amount of SiC in the coating, expressed in volume percent and number of incorporated particles per unit area (particles/μm²), and the concentration of particles suspended in the solution showed that the volume of SiC particles (vol. %) embedded in the metallic matrix increased with increasing particle concentration in the solution, reaching a saturation point at about 17 vol.% under the conditions used. The increase of particles concentration in the electroplating bath induced a selective phenomenon, promoting smaller particle embedded in the coating (Figs. 1a, b and c).

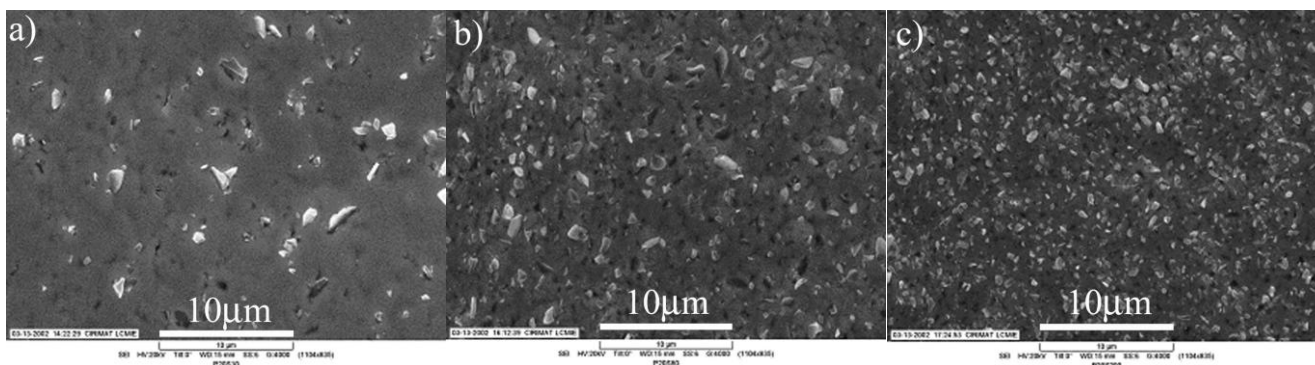


Fig. 1: SEM micrographs of composite Ni-P-SiC coatings obtained from electrolytes with different concentrations of SiC particles: a) 10 g.L⁻¹; b) 80 g.L⁻¹ and c) 200 g.L⁻¹.

This phenomenon, also observed by other authors in similar systems [5,11], may be based upon the probability of mechanical interaction between the cathode and the suspended particles. The particle is completely incorporated into the metallic matrix only when the deposit reaches a certain thickness, so that the ejection, caused by the arriving particles, is restrained. The time required for complete particle incorporation is, therefore, a size function, *i.e.*, bigger particles need longer periods for their complete incorporation into the metallic matrix [12]. The incorporation of particles must not affect phosphorous content in the deposit, which remained constant at about 17 at.%. Heat treatment at 420 °C for 1 h in N₂ atmosphere resulted in the crystallization of nickel followed by precipitation of nickel phosphide, Ni₃P (Ni → Ni_(cfc) + Ni₃P), obtained by the X-ray diffraction measurements results. A transition from amorphous to crystalline structure is accompanied by a volume contraction. This is in agreement with the observations for this system, that the coatings suffered about 5 % reduction in thickness with thermal treatment. This structural change and associated contraction, may influence cohesion between the SiC particles and the metallic matrix and, therefore, affect properties such as corrosion resistance.

Open circuit potential measurements with time showed that thermal treatment of Ni-P coatings (without particles) displaced the OCP towards less active values compared to the as-plated specimens. Heat treatment also caused the shift of the OCP to less active values in the first 100 hours. After this period of time, it showed similar behavior as that of the specimens without thermal treatment, *i.e.* with a stable OCP.

The electrochemical impedance results exhibited one time constant and the fitting parameters were equivalent to the circuit Rs(RpCdl) where Rs is the solution resistance, Rp the polarization resistance, and Cdl the double layer capacitance. The results are presented using Nyquist diagrams, Figs. 2 and 3. The spectra obtained for Ni-P and Ni-P-SiC coatings without thermal treatment in the first hour of immersion in 0.6 M NaCl, pH 6, showed very similar values of polarization resistance (40 kΩ·cm² - 45 kΩ·cm²), Fig. 2a. The same behavior was observed for the heat treated specimens (Fig. 2b), having in this case polarization resistance of the order of 20 kΩ·cm². After 1200 hours of immersion, while the as-plated Ni-P coatings (without particles) showed polarization resistance of the order of 100 kΩ·cm² (Fig. 3a), the heat treated specimens exhibited 13 kΩ·cm² (Fig. 3b).

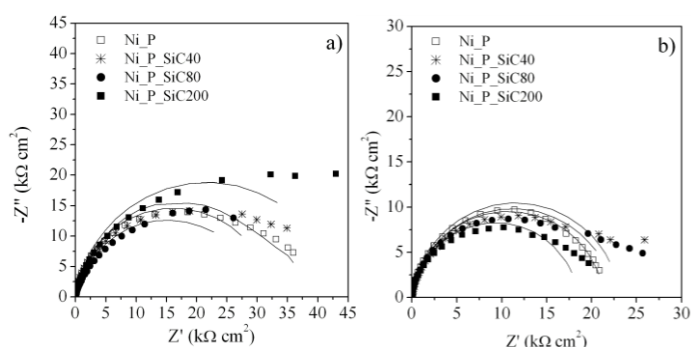


Fig. 2: Nyquist plots for Ni-P, Ni-P-SiC40, Ni-P-SiC80, Ni-P-SiC200 coatings at the OCP, after immersion in 0.6 M NaCl, pH 6, for 1 hour: a) as-plated and b) heat-treated.

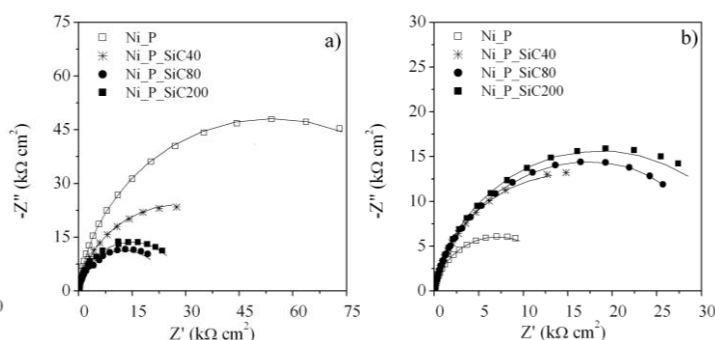


Fig.3: Nyquist plots for Ni-P, Ni-P-SiC40, Ni-P-SiC80, Ni-P-SiC200 coatings at the OCP, after immersion in 0.6 M NaCl for 1200 hours: a) as-plated and b) heat-treated.

Other author [13] have also observed, by impedance studies, higher polarization resistance for the non-treated Ni-P alloys compared to the heat treated specimens and attributed this effect to the crystal structure of the coating. Specimens without thermal treatment are amorphous and are supposed to exhibit better corrosion resistance. Nevertheless, the resistance values for the as-plated Ni-P coatings oscillated with time of immersion in NaCl solution, indicating that this system is less stable than the others. Pitting corrosion was observed, by SEM micrographs, on the as-plated Ni-P coatings (Fig. 4a and b), which was not observed for the heat-treated specimens (Fig. 4c). For other coatings, except for the as-plated Ni-P, the Rp values, with or without heat treatment, were very unstable up to 100 hours of immersion, in the same manner as obtained for the OCP. After this time, a dark grey film formed on the surface and more stable values of polarization resistance were obtained. Similar results were documented by Krolkowski *et al.* [14] and Diegle *et al.* [15].

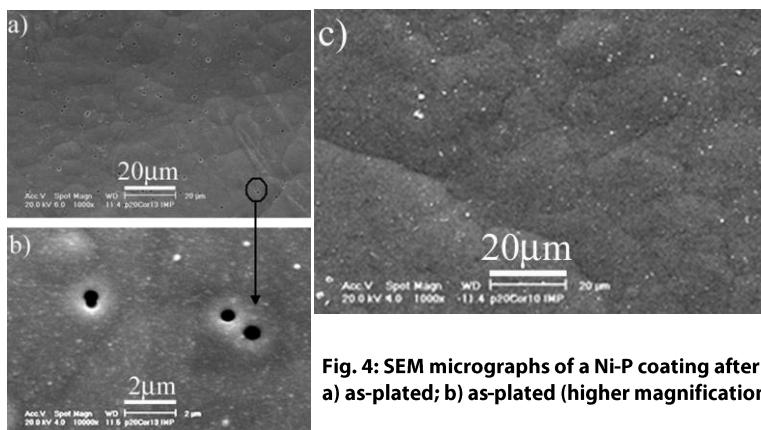


Fig. 4: SEM micrographs of a Ni-P coating after 1200 hours immersed in 0.6 M NaCl, pH 6: a) as-plated; b) as-plated (higher magnification) and c) heat-treated.

The incorporation of SiC particles in the Ni-P coatings affected the polarization resistance (Figs. 3a and b). Lower Rp values were obtained for the as-plated Ni-P-SiC specimens, and higher values for heat treated Ni-P-SiC, compared to the Ni-P coatings. Higher values, with increasing SiC content in the coating, were also obtained by other author [10]. Variations in electrochemical activity of Ni-P-SiC coatings may be related to the surface area effectively exposed to the electrolyte, which is the Ni-P area, once SiC particles are electrochemically inactive. Structural changes in the Ni-P matrix itself with the incorporation of particles are less likely.

The as-plated Ni-P-SiC coating, immersed in NaCl solution for 1200 h, exhibited general corrosion on the surface of the Ni-P matrix (Fig. 5a), while the heat treated Ni-P-SiC specimens showed localized corrosion at the interface between Ni-P and SiC particles (Fig. 5b). With thermal treatment, structural change and contraction may occur. The contraction, which cannot be accommodated by the embedded particles, can result in fissures initiating at the particles, contributing to localized corrosion at the interface Ni-P-SiC.

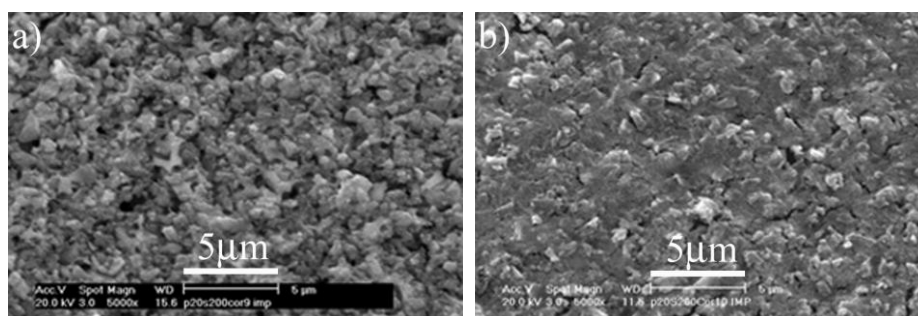


Fig. 5: SEM micrographs of a Ni-P-SiC200 coating after 1200 hours immersed in 0.6 M NaCl, pH 6: a) as-plated and b) heat-treated

Conclusions

The results obtained in this work showed that thermal treatment causes microstructural changes in the Ni-P matrix, going from amorphous to crystalline, followed by a slight contraction in the metallic matrix (5 %). These changes impact the electrochemical behavior of Ni-P coatings. Heat treatment at 420 °C for 1 hour shifts the open circuit potential towards less active values, preventing pit formation. The concentration of particles in the solution affects the particle size incorporated in the coating. The higher the concentration in solution, the smaller the particle embedded in the coating. Phosphorous content in the deposit is not affected by the embedded particles, and remained constant at about 17 %. The higher Rp observed on the as-plated Ni-P (without particles) was not related to a better corrosion resistance but with some other phenomenon occurring during the attack. The incorporation of particles in the coating results in higher polarization resistance, compared to the coatings containing only the metallic matrix (Ni-P), for heat treated specimens. Heat-treated Ni-P-SiC composite coatings, despite particle concentration or particle size, exhibit higher polarization resistance than the Ni-P coatings. The lower electrochemical activity has been associated with the smaller active surface area established by the non-conductive SiC particles.

References

1. J.-P. Bonino, S. Bruet-Hotellaz, C. Bories, P. Pouderoux, A. Rousset, *J. Appl. Electrochem.* **1997**, 27, 1193.
2. S. Vaillant, *PhD thesis*, Université Paul Sabatier, Toulouse, France, **2002**.
3. Y. Li, *Plat. Surf. Finish.* **1997**, 84, 77.
4. S. Shawki, Z.A. Hamid, *Anti-Corr. Meth. Mater.* **1997**, 44, 178.
5. A. Grosjean, *PhD thesis*, Université de Besançon, Besançon, France, **1998**, 215.
6. S. Vaillant, L. Datas, J-P Bonino, *Matériaux et Techniques* **2001**, 89, 47
7. P. Lima Neto, F. J. B. Rabelo, A. M. M. M. Adam, L. A. Avaca, E. R. Gonzalez, *Interfinish* **1988**, 92, 385.
8. H. G. Schenzel, H. Kreye, *Plating Surf. Finish.* **1990**, 77, 50.
9. I. Apachitei, F. D. Tichelaar, J. Duszczuk, L. Katgerman, *Surf. Coat. Technol.* **2002**, 149, 263.
10. I. Garcia, A. Conde, G. Langelaan, J. P. Celis, *Corrosion Science* **2003**, 45, 1173.
11. C.F. Malfatti, J. Z. Ferreira, C.B. Santos, B.V. Souza, E.P. Fallavena, S. Vaillant, J.-P. Bonino, *Corrosion Science* **2005**, 47, 567.
12. J.P. Celis, J. R. Roos, C. A Buelens, *J. Electrochem. Soc.* **1987**, 134, 1402.
13. M.M.V. Parente, O.R. Mattos, S.L. Díaz, P. Lima Neto and F.J. Fabri Miranda, *J. Appl. Electrochem.* **2001**, 31, 677.
14. A. Królikowski, P. Butkiewicz, *Electrochimica Acta* **1993**, 38, 1979.
15. R. B. Diegle, N. R. Sorensen, G. C. Nelson, *J. Electrochem. Soc.* **1986**, 133, 1769.

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