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NiP/SiC composite coatings: the effects of particles on the electrochemical behaviour

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Abstract

NiP/SiC (17 at.% P) composite coatings were prepared by electrodeposition from a Brenner type plating bath containing SiC particles. Cyclic voltammetry and immersion time were used to evaluate the electrochemical behaviour of these coatings.

The results showed that the presence of SiC particles in NiP alloy increased corrosion properties, because the exposed area of the metallic matrix was reduced due to its recovering by SiC particles. However, the current densities developed by the NiP/SiC composite coatings increased with increasing amount of incorporated particles, and such effect is more remarkable for small particles, after heat treatment and when the systems are polarized.

Keywords: Metal matrix composites; Nickel; Cyclic voltammetry; Amorphous structures

1. Introduction
2. Experimental methods
3. Results and discussion
4. Conclusions
Acknowledgements
References

1. Introduction

Several studies have been made on the NiP alloys [1], [2], [3], [4] and [5], particularly on the amorphous phases, because of their good corrosion resistance in environments containing a high concentration of Cl^-, NO_3^-, SO_4^-, or SO_3^{2-} ions. For electrodeposited NiP alloys the transition from the crystalline to amorphous structures takes place progressively over a range of several atomic percent of phosphorus and NiP coatings are amorphous when the phosphorus content exceeds 15 at.% [6] and [7].

Crystallization of the amorphous alloys can be achieved by heat treatment with subsequently decomposition to Ni_3P and f.c.c. nickel crystals at temperature above 350 °C [8].

The corrosion properties of NiP alloys, concerning the nature of its anodic dissolution, ability to passivate and susceptibility to pitting are not yet clearly established.

The NiP passivation can be attributed to the non-complete phosphorus oxidation in high potentials

and to the fact that, after polarization, the surface of the alloy becomes phosphorus-rich as result of selective dissolution of nickel during polarization. $Ni_3(PO_4)_2$ is then formed, acting as a barrier against dissolution [9]. Diegle et al. [10] suggest that NiP alloy does not developed a classical passive film and proposed that the passivation process is controlled by the formation and adsorption of hypophosphite anion, which forms a barrier layer between the alloy and the electrolyte. Schenzel et al. [11] concluded that the transformation of the amorphous NiP alloy into a continuous layer of Ni_3P containing isolated areas of nickel crystals renders electroless nickel extremely resistant to corrosion pitting. The required time and temperature depend on the phosphorus content of the coating. However, the local corrosion resistance is limited by a high chloride concentration [2], and the phosphorus quantity fluctuation on the coating may lead to the formation of microgalvanic pairs that can be the cause of the local corrosion of these alloys, when there are no macroscopic defects [12].

Krolikowski and Butkiewicz [13] showed that the anodic behaviour of NiP depends very strongly on the structural state of this alloy, and Parente et al. confirm the role of the structural condition of the alloy [4].

NiP coatings containing dispersed particles have received considerable attention lately, specially because of their resistance to wear and improved tribological properties.

The metal matrix composite coatings can be prepared either by electrodeposition or autocatalytic (electroless) deposition. The process consists of incorporating particles to the metallic matrix from an electrolyte containing particles in suspension. Convection forces move the particles straight to the surface that is to be coated, where they are adsorbed before being definitely incorporated to the growing coating.

Due to their high wear resistance and the low cost of ceramic powder, metal matrix composite coatings with SiC have been investigated for the protection of friction parts [14], [15] A. Hovestad, R.J.C.H.L. Heesen and J. Jansen, *J. Appl. Elecrochem.* **29** (1999).[15] and [16].

Many studies [7], [14], [17], [18], [19], [20], [21] and [22] concerning the incorporation of silicon-carbide particles in electrodeposited nickel matrix and about the characterization of the tribological properties have been made. Several authors expressed interest in the influence of operational parameters such as particle concentration in suspension, stirring speed, current density, effect of the addition of surfactants and others on the particle incorporation rate, based on the characteristic of volumetric fraction. However, Célis and coworkers [14], using sets of particles of different sizes, showed that the tribological behaviour of the NiP/SiC composite coating cannot be evaluated only by the volumetric fraction of incorporated particles without knowing their size exactly. Besides that, the calculation of the incorporated particles number, based on volumetric fraction divided by the particle mean volume in suspension in the electrolyte, can also be mistaken if the particles have a large grain size distribution.

The present work is an extension of Vaillant's study [7] and [21], which observed aspects such as electrolyte/particle interaction, effect of H_3PO_3 variation on the NiP metallic matrix composition from electrolytes with and without SiC_{600} particles, structure, microstructure, thermal stability and mechanical properties of the NiP and NiP/SiC_{600} composite coatings. In that work, Vaillant observed weak acid–basic and chemical variations between SiC particles and the electrolyte, concluding that the NiP/SiC_{600} electrolyte system is steady. When considering mechanical properties, it was observed that coatings may be divided in three ranges according to the phosphorus contents: 0–7 at.% P—crystallized state; 7–15 at.% P—microcrystallized state; over 15 at.% P—amorphous state.

It was also verified that NiP/SiC_{600} coatings (>15 at.% P), after heat treatment (at 420 °C), show the same hardness (1100 Hv) and mass loss than that obtained for hard chromium.

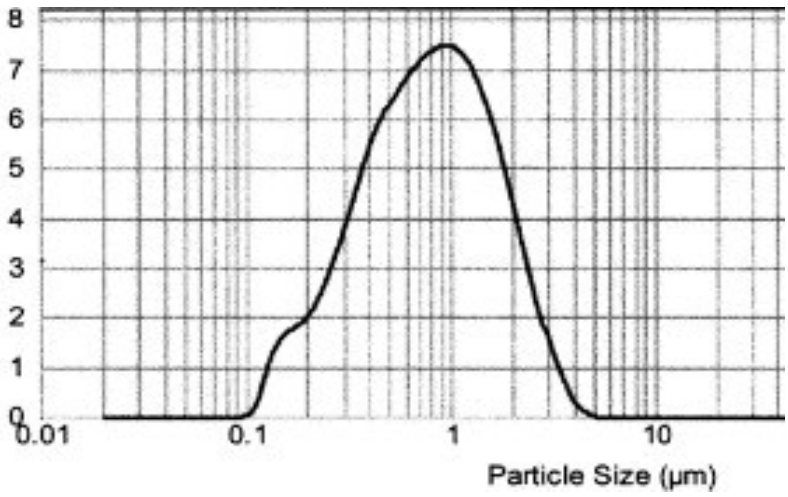
The aim of the present work is to study the influence of the amount and distribution of SiC incorporated particles on the NiP metallic matrix, and heat treatment on the electrochemical behaviour of the NiP/SiC (at 17 at.% P) composite coatings. The purpose is to study the effect of particle considering the incorporated % volume of SiC (as reported in literature) and the incorporated number of particles by area unit (new purpose). Cyclic voltammetry and immersion time were used to evaluate the electrochemical behaviour of these coatings.

2. Experimental methods

NiP/SiC (17 at.% P) composite coatings were prepared by electrodeposition from a Brenner type plating bath [23] containing $NiSO_4 \cdot 6H_2O$ 210 g l^{-1}; $NiCl_2 \cdot 6H_2O$ 60 g l^{-1}; H_3PO_3 20 g l^{-1}; H_3PO_4 50 g l^{-1}; Na_2SO_4 50 g l^{-1} and SiC particles 0–200 g l^{-1}. The pH of the solution was 2 at 80 °C.

SiC_{600} particles were used to obtain NiP/SiC composite coatings. Grannulometry measurements using Malvern Mastersize 2000S apparatus gave a large particle distribution size (between 100 and 5000 nm), with an average particle size of 600 nm (Fig. 1).

Fig. 1. SiC_{600} size distribution.



The eletrodeposition was carried out in a thermostatic cell (140 ml), where both static vertical electrodes were immersed. A combined stirring system allowed keeping the particles in suspension and moving them towards the cathode. The substrate was a copper disk (A = 1.76 cm^2) and a nickel sheet (A = 4 cm^2) was used as a soluble anode. The electrodeposition was carried out with a 0.1 A cm^{-2} current density, what resulted in a 50 μm thickness composite coating (measured by optical microscopy cross-sections). After electrodeposition, the specimens were cleaned by ultrasound for 2 min, and some of them were heat treated at 420 °C for 1 h in a N_2 atmosphere.

The structure of alloy deposits was analysed by X-ray diffraction (XRD) and the chemical composition (P and SiC ($*_v$)) of composite coatings was determined by energy dispersion

spectroscopy (EDS).

The number of incorporated particles by area unit ($*_{pn/A}$) was evaluated by image analysis of micrographs obtained by scanning electron microscopy (JEOL 6400).

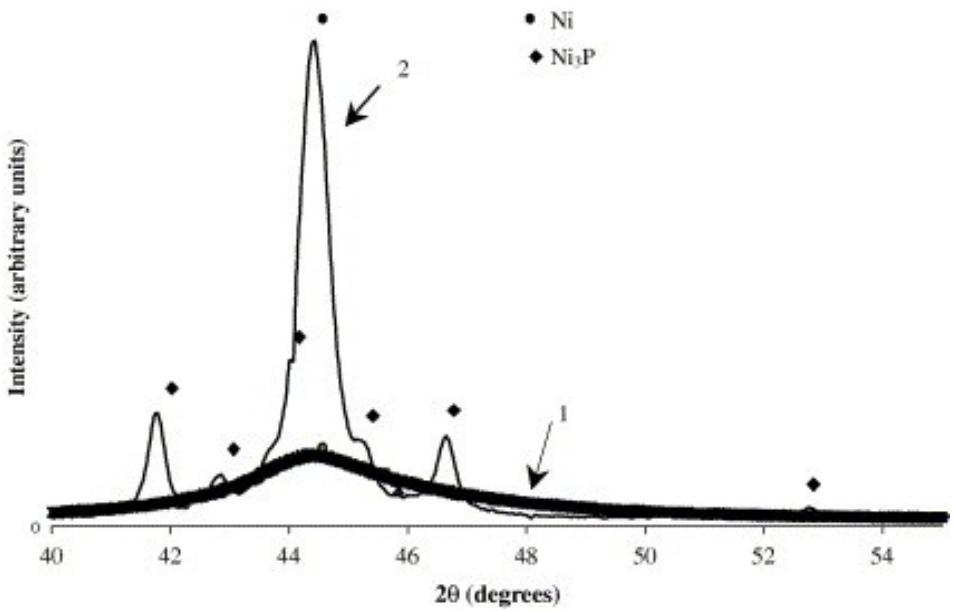
The electrochemical behaviour of obtained composite coatings was investigated by cyclic voltammetry. Measurements were performed using a computer-controlled potentiostat EG&G PAR model 273 in a conventional three-electrode cell. Platinum was used as a counter electrode and a saturated calomel as a reference electrode. A Haber–Luggin capillary was placed in front of the disk electrode. Potentiodynamic polarization was measured with a scan rate of 0.5 mV s^{-1}, the first cycle being the from −400 to +200 mV (SCE) and the second cycle from −400 to +500 mV (SCE). The electrolyte was a 0.6 M NaCl solution and the exposed area of the working electrode was 0.64 cm^2.

The evolution of the corrosion potential against the immersion time was measured in 0.6 M NaCl solution, and saturated calomel was used as a reference electrode.

3. Results and discussion

XRD analysis showed that as-plated NiP coatings are amorphous and the structure of the heat-treated samples became crystalline (Fig. 2). Before heat treatment, only one broad peak could be clearly seen in the diffractogram of the sample, indicating an amorphous structure. On the other hand, heat-treated samples showed a typical diffractogram of a crystalline structure (Ni_3P and f.c.c. nickel crystals).

Fig. 2. XRD patterns of as-plated and after heat treatment NiP coating with P content 17 at.%: (1) as-plated; (2) after heat treatment at 420 °C.



In previous work [24], it was showed that the microhardness of a crystalline structure (after heat treatment) is much greater than that of the amorphous NiP. After heat treatment the microhardness of NiP coatings can be increased in about 500 Hv.

It was verified [24] and [25] that, as shown in Fig. 3, the incorporated particle in volumetric fraction ($*_v$), evaluated by chemical analysis, increased very fast, starting from low suspension particle concentration, then reaching a plateau (which shows the saturation of the incorporation phenomena), agreeing with the results reported in literature [26]. However, the incorporated particle number by coating area unit ($*_{pn/A}$) continued to increase with the quantity of particles in suspension. This effect was followed by the reduction of the incorporated particle size, as can be seen in Fig. 4.

Fig. 3. Amount of SiC particles in the NiP/SiC_{600} composite coatings as a function of the particle concentration in the suspension [24] and [25].

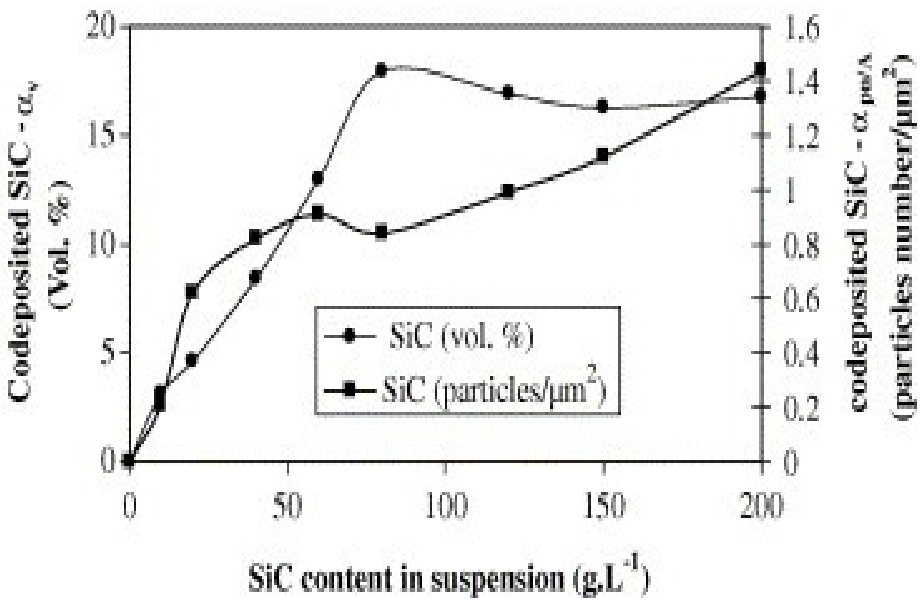
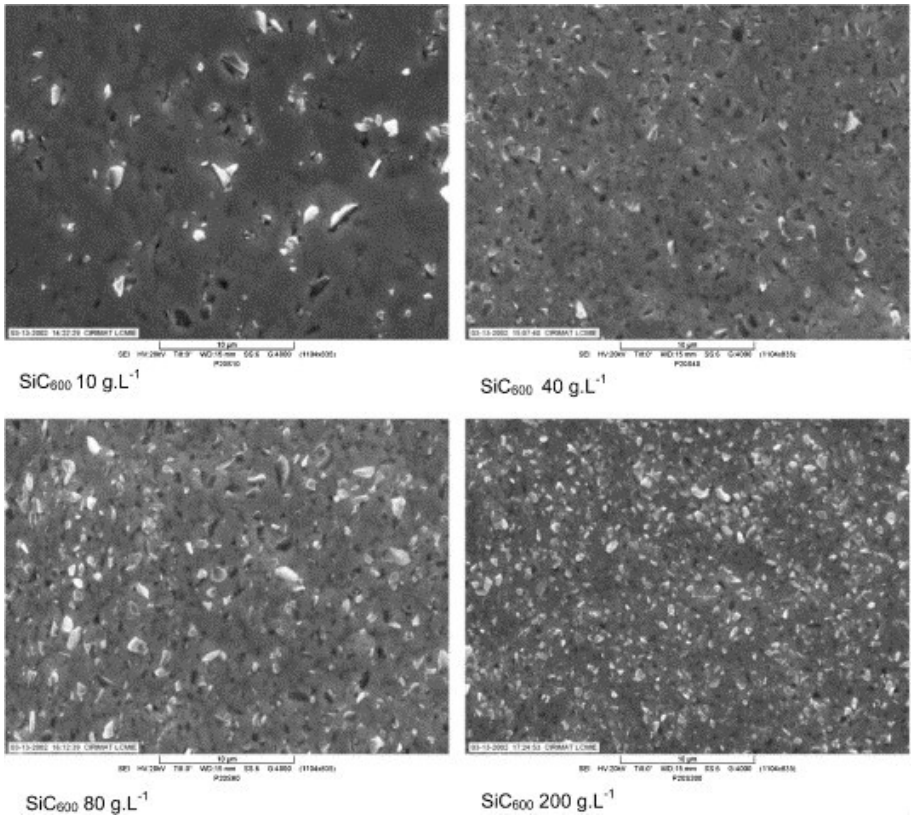


Fig. 4. Surface morphology of NiP/SiC_{600} composite coatings at different particles (SiC_{600}) concentration in suspension in the electrolyte.



In order to study the influence of particles concentration in the incorporation rate and its effect on the electrochemical behaviour of the composite coatings by means of cyclic voltammetry and immersion time, the conditions indicated in Table 1 were chosen.

Table 1.

SiC_{600} particles quantity in suspension related to % vol. SiC_{600} ($*_{\%\ vol.\ SiC}$) incorporated, and the number of particles incorporated by area unit ($*_{np/A}$)

Type of coating	**SiC (g l^{-1}) in suspension**	**SiC incorporated**	
		SiC_{600} ($*_{\%\ vol.\ SiC}$) % volume SiC	**SiC_{600} ($*_{np/A}$) (particles/µm^2)**
NiP	0	0	0

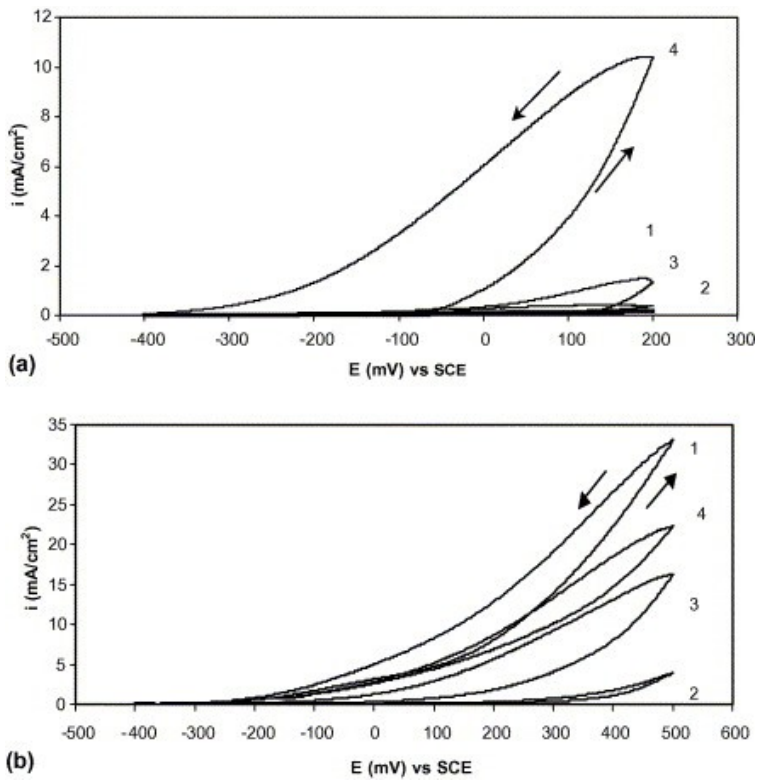
Type of coating	SiC (g l^{-1}) in suspension	SiC incorporated	
		SiC_{600} (*% vol. SiC) % volume SiC	SiC_{600} (*np/*A*) (particles/μm^2)
NiP/SiC40	40	8.4	0.82
NiP/SiC80	80	17.9	0.84
NiP/SiC200	200	16.7	1.44

Full-size table

View Within Article

Fig. 5(a) shows that at the first cycle, from (−400 to +200 mV (SCE)), NiP/SiC200 (SiC_{600} 200 g l^{-1}) coating developed higher current densities, when compared to the other coatings, followed by NiP, NiP/SiC40 (SiC_{600} 40 g l^{-1}) and NiP/SiC80 (SiC_{600} 80 g l^{-1}), which developed very low current densities.

Fig. 5. Voltammogram in 0.6 M NaCl solution, scan rate 0.5 mV s^{-1} of composite coatings NiP and NiP/SiC, as deposited: (a) first cycle (−400 to +200 mV (SCE)) and (b) second cycle (−400 to +500 mV (SCE)), (1) NiP, (2) NiP/SiC40 (SiC_{600} 40 g l^{-1}), (3) NiP/SiC80 (SiC_{600} 80 g l^{-1}) and (4) NiP/SiC200 (SiC_{600} 200 g l^{-1}).



However, at the second cycle, from (−400 to +500 mV (SCE)), when the systems were polarized to more positive potentials, as shown in Fig. 5(b), the coatings with incorporated particles developed lower current densities compared to NiP coating. This effect can be attributed to the partial coating of silicon carbide particles on composite coatings surface, which is more important in higher polarizations. Garcia et al. [27] verified that the presence of inert particles in nickel metallic matrix (in Ni/SiC (SiC 5 μm)) improved the corrosion resistance, since the exposed area of the nickel metallic matrix was reduced thanks to the surface covering by SiC particles, shifting the corrosion potential to more positive values.

In the present work it was observed any relationship between the corrosion potential and the quantity of incorporated particles in the composite coatings (Table 2). However, the current densities increased with increasing amount of particles on NiP/SiC composite coatings, as seen in Fig. 5(b), and this effect is probably due to the size reduction of the incorporated particles. It was showed (Fig. 4 and Table 1) that the incorporated particle quantity ($*_{pn/A}$) increased with SiC_{600} concentration in suspension. The incorporation process became selective and the small particles were preferentially incorporated (Fig. 4).

Table 2.

E_{corr} for NiP and NiP/SiC coatings, as deposited and after heat treatment in 0.6 M NaCl

Type of coating	E_{corr} (mV) vs SCE	
	Coating as deposited	**Coating after heat treatment**
NiP	−350	−269
NiP/SiC40	−358	−259
NiP/SiC80	−346	−269
NiP/SiC200	−362	−271

Full-size table

View Within Article

The composite coatings NiP/SiC200 developed higher current density than NiP/SiC80 but both had the same quantity of incorporated SiC_{600}, in volumetric fraction ($*_v$). On the other hand, for the NiP/SiC200 composite coatings, the particle number by area units is about 50% higher than in the case of NiP/SiC80, due to size reduction of the incorporated particle. This behaviour indicates that the composite coatings containing small particles developed higher current density.

It was observed that the current densities developed by the as-plated NiP/SiC composite coating increased with increasing amount of the incorporated particle and their size reduction. Furthermore, the size reduction of the incorporated particle increased the metallic matrix/particle interface area; hence, the composite coating has a tendency to diminish its resistance against local corrosion, because of the voids produced by discontinuous interface around the particles.

It was reported in the literature that there are voids in the composite coatings, producing discontinuous particle/matrix interfaces. Verelst [28] and [29] observed the formation of an interface between the nickel matrix and alumina particles.

In the present work the results agree with the results obtained by Garcia et al. [27], who observed the notably improvement on the susceptibility to localized corrosion of the nickel composite coatings containing sub-micrometric SiC-particles and the dissolution of particle/metallic matrix composite coatings in the interface between the nickel matrix and SiC particles.

As shown in Fig. 6(a), heat-treated NiP coatings presented better tendency to passivation than as-plated NiP. This electrochemical behaviour can be attributed to the formation of Ni_3P, an intermetallic compound with high thermodynamic stability), agreeing with the literature [12] and [30].

Fig. 6. Voltammogram second cycle (−400 to +500 mV (SCE)), in 0.6 M NaCl solution, scan rate 0.5 mV s^{-1}: (a) composite coatings NiP and (b) composite coatings NiP/SiC80 (SiC_{600} 80 g l^{-1}), (1) as deposited and (2) after heat treatment.

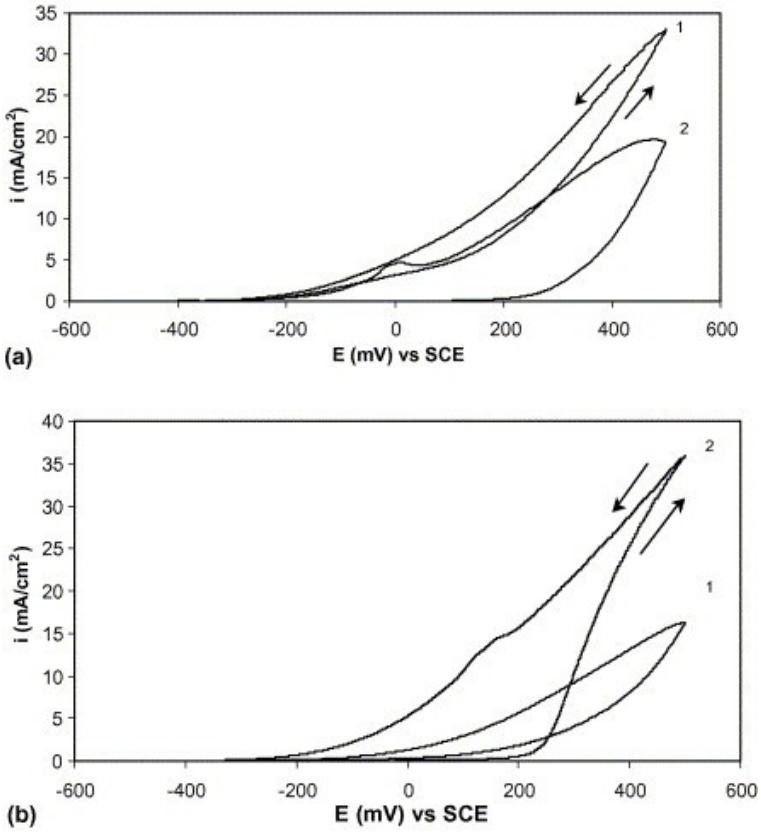
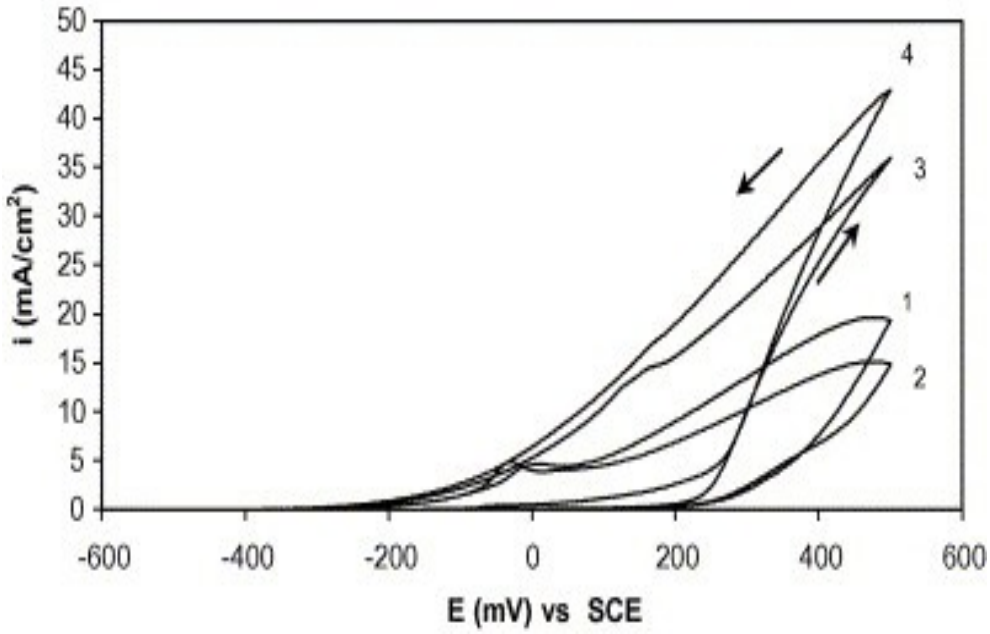


Table 2 show that the corrosion potential of coatings after heat treatment shifted to more positive values; however, the voltammograms (Fig. 6(b)) showed that particle by NiP/SiC coatings. As shown in Fig. 7, the current densities were higher with the increase of the quantity of incorporated particles, even for the heat-treated NiP/SiC coatings, probably due to the voids produced by discontinuous interface around the particle. This effect, however, is more important for heat-treated composite coatings than as-plated ones, because the shrinkage of the metallic matrix due to heat treatment, creates a more discontinuous interface around the particle, causing an increasing in the current density. Verelst [28] and [29] also observed the increase of discontinuous interface between the nickel matrix and alumina particles, after heat treatment.

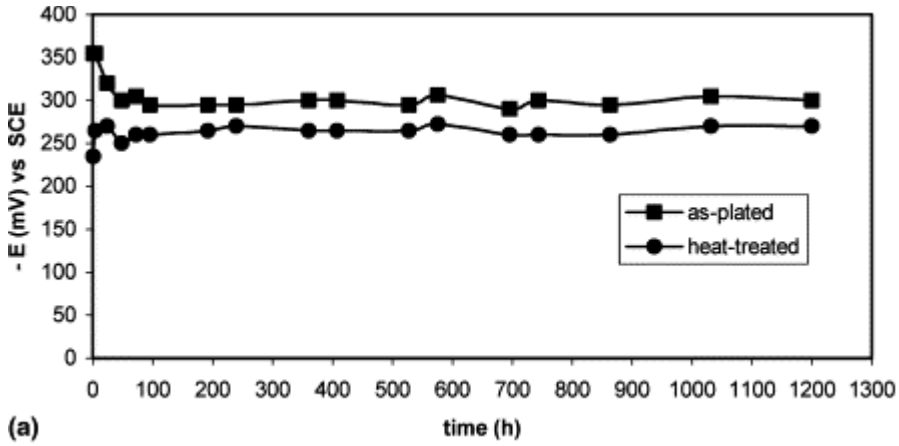
Fig. 7. Voltammogram of composite coatings NiP and NiP/SiC, after heat treatment, second cycle (−400 to +500 mV (SCE)), in 0.6 M NaCl solution, scan rate 0.5 mV s^{-1}. (1) NiP, (2) NiP/SiC40 (SiC_{600} 40 g l^{-1}), (3) NiP/SiC80 (SiC_{600} 80 g l^{-1}) and (4) NiP/SiC200 (SiC_{600} 200 g l^{-1}).



The voltammograms showed that the coatings developed higher current densities when the sweep direction was reversed, what can indicates the occurrence of localized corrosion (f.e. crevice); but minor currents detected for these coatings are not an evidence that the localized attack has occurred or not.

The results obtained in immersion time tests showed that the corrosion potential values measured for all heat-treated samples shifted to more positive values when compared to as-plated coatings (Fig. 8 and Fig. 9). However, NiP/SiC composite coatings (Fig. 8 and Fig. 9) did not show such behaviour; after immersion for 100 h the corrosion potential values remained very close to the as-plated and heat-treated samples. The same behaviour was observed at the end of the immersion tests (1200 h).

Fig. 8. Corrosion potential against immersion time in 0.6 M NaCl solution: (a) NiP and (b) NiP/SiC40 (SiC_{600} 40 g l^{-1}).


400
350
300
250
200
150
100
50
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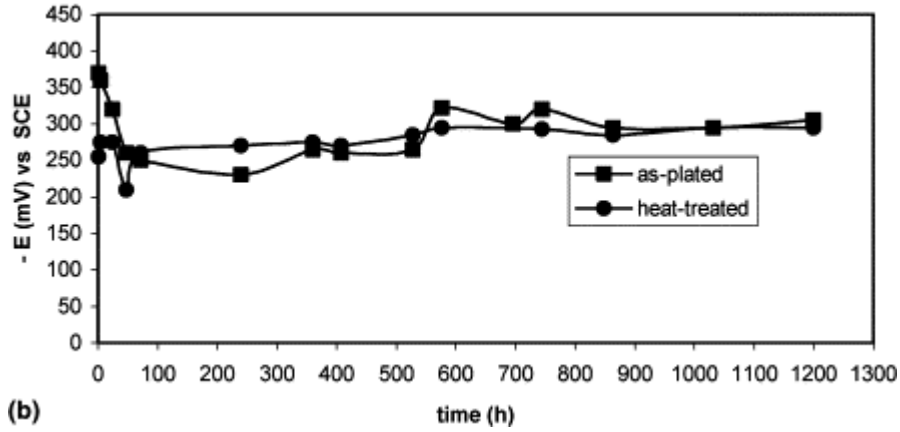
- E (mV) vs SCE
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
time (h)
as-plated
heat-treated

(a)


450
400
350
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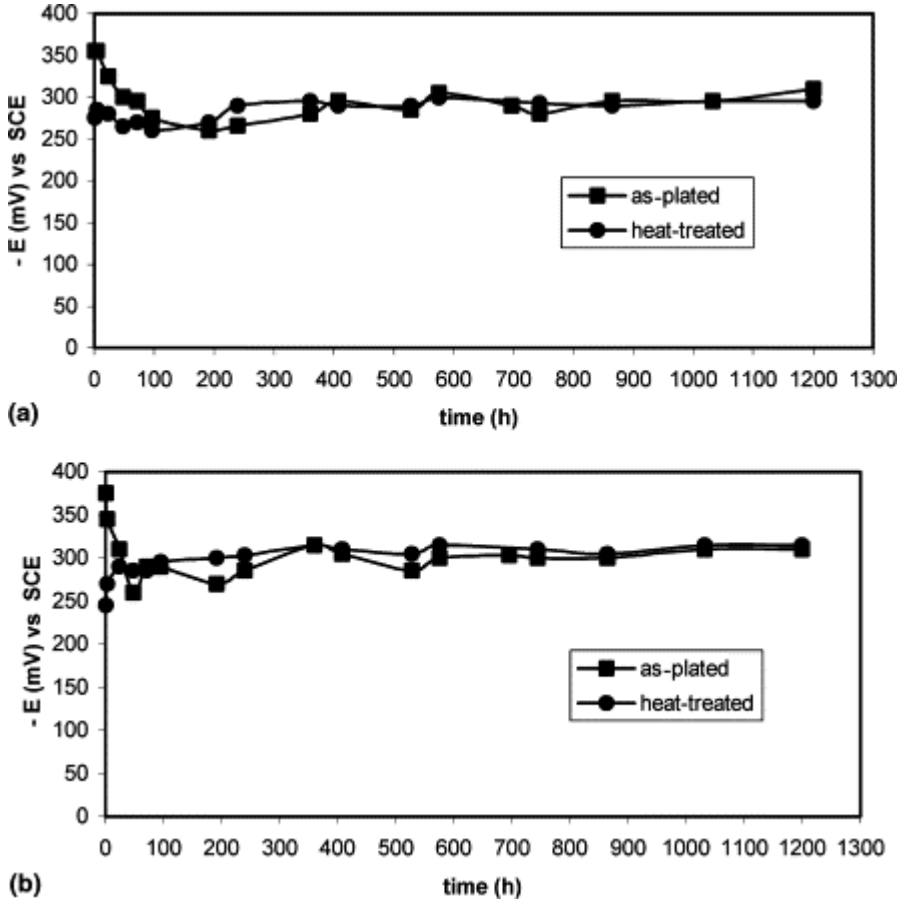
250
200
150
100
50
0
- E (mV) vs SCE
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300
time (h)
as-plated
heat-treated

(b)

Fig. 9. Corrosion potential against immersion time in 0.6 M NaCl solution: (a) NiP/SiC80 (SiC_{600} 80 g l^{-1}) and (b) NiP/SiC200 (SiC_{600} 200 g l^{-1}).



For NiP coatings (Fig. 8(a)), the corrosion potential after heat treatment, shifted to more positive values. It indicates that the heat treatment was beneficial regarding NiP coatings. These results are in agreement with those obtained by cyclic voltammetry (Fig. 6(a)), which showed that heat-treated NiP coatings had better electrochemical behaviour than as-plated NiP coatings.

In general, all samples exhibited oscillations in the corrosion potential values before 100 h of immersion time, and this effect was more remarkable for the as-plated samples. This can indicate the formation of a film in the coatings surface during the first moments of immersion tests (time < 100 h), but not necessarily a typical passive film. After 100 h, the potential corrosion values for as-plated coatings were more positive when compared to immersion times shorter than 100 h; this potential corrosion became stable right at the end of immersion time tests (1200 h).

Published data present controversial information concerning corrosion characteristics of NiP alloys, especially about the nature of its anodic dissolution, ability to passivate and susceptibility to pitting [10], [13], [31], [32] and [33].

Heinz et al. [11] reported results of a detailed study on microstructure and corrosion behaviour and demonstrated that resistance to pitting corrosion of amorphous coatings in certain environments is limited. However, pitting sensitivity to can be reduced or even eliminated by suitable heat treatment. Ni_3P proved to be fully resistant to pitting; only the few nickel islands adjacent to the

surface were dissolved.

The results of immersion time tests showed that under the corrosion potential conditions the electrochemical behaviour of both NiP and NiP/SiC composites are quite similar. When the systems are polarized to more positive potentials, the amount and size of incorporated particles, and the heat treatment affect the electrochemical behaviour of NiP/SiC composite coatings; in such case, the occurrence of localized corrosion can be assisted by anodic polarization.

In this work the results were obtained by cyclic voltammetry and immersion time. In future works, impedance spectroscopy tests will be performed for a better understanding of the corrosion mechanisms of NiP/SiC composite coatings.

4. Conclusions

The NiP coating without heat treatment developed higher current densities than NiP/SiC composite coatings. The presence of SiC particles in NiP metallic matrix caused an improvement in the coatings electrochemical behaviour, because of the reduction of the NiP metallic matrix exposed area.

Nevertheless, the current densities developed by NiP/SiC composite coating increased with the amount of incorporated particles; this is probably due to the reduction in size of the incorporated particles, and consequent increase of metallic matrix/particle interfacial area. This effect indicates that this composite coating tends to have a unfavorable resistance against localized corrosion at the discontinuous interface around the particles, and it is more effective when smaller particles are co-deposited.

Heat treatment increases corrosion resistance on the NiP coatings, probably due to the formation of high thermodynamic stable intermetallic compounds (such as Ni_3P).

The heat-treated NiP/SiC composite coatings developed higher current density than as-plated NiP/SiC. The increase in current densities is higher after heat treatment because of the shrinkage effect on the metallic matrix after treatment.

The electrochemical behaviour of NiP/SiC depends on the structural state of NiP metallic matrix and on the quantity and size of incorporated particles (SiC).

The results of immersion time tests showed that under the corrosion potential conditions the electrochemical behaviour of NiP coatings is similar to the NiP/SiC composite coatings. However, when the systems are polarized to more positive potentials, both the quantity and size of incorporated particles and heat treatment affect the electrochemical behaviour of NiP/SiC composite coatings. In this case, the localized corrosion on the interface metallic matrix/particle can be assisted by anodic polarization.

Main conclusions of this work show the importance of take into account not only the volume of co-deposited particles ($*_v$) but also the number of particles per area unit ($*_{pn/A}$) when determining the composite properties. It is also shown that is risky to interpret the electrochemical behaviour of NiP/SiC composite coatings only as a function of the incorporated particle volumetric fraction, disregarding the amount and size of the particles.

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