

Enhancement of corrosion resistance of electrocodeposited Ni–SiC composites by magnetic field

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Abstract The corrosion behavior and surface morphology of Ni–SiC composite coatings produced by electrodeposition with the aid of magnetic field were studied. The results of the electrochemical analysis including polarization resistance and potentiodynamic polarization curves showed that a magnetic field of 0.1 T could significantly improve the corrosion resistance of the composite. The electrochemical impedance spectra revealed that a passive layer was formed on the surface of the Ni–SiC coating with the magnetic field. The microstructures of electrodeposited Ni–SiC composite coatings were also examined. More SiC particles were found to be incorporated into the coating with the presence of magnetic field, which was considered to be one of the reasons for the enhancement of corrosion resistance as SiC particles were reported to be corrosion inhibitors.

Keywords Corrosion property · Magnetic field · Codeposition · Ni–SiC composites

Introduction

In recent years, nickel-base composite coatings have attracted remarkable research interest because of their ability to provide improved wear, abrasion, and corrosion resistance. Among various research efforts, the electrocodeposition behavior, the corrosion behavior, and the mechanical properties (including microhardness, wear resistance, and refractoriness) of Ni–SiC coatings have been studied extensively [1–4]. It was shown that the corrosion resistance of the composite could be modified by adjusting the electrodeposition parameters. Tang et al. [3] reported that pulse plating could significantly improve the corrosion resistance of nickel coatings, and the improvement was attributed to reduced grain size. Some researchers also examined the effect of microstructure and orientation of the electrodeposits on corrosion behavior of Ni–SiC composite [4]. With the addition of SiC particles, the Ni–SiC composite was reported to have a better corrosion resistance in a 0.6-M NaCl solution than nickel electrodeposits. The corrosion rate of Ni–SiC was decreased by two orders of magnitude with respect to pure nickel. When the particle size is large, the corrosion resistance is relatively independent of the size and the amount of embedded particles. For submicrometric SiC particles, the improved corrosion resistance was believed to be related to the change of grain morphology and texture of the coatings [4]. Periene et al. [5] revealed a promising decrease of the dissolution rate of nickel electrodeposits with reinforced SiC particles in 0.1 M H₂SO₄.

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When an external magnetic field is applied to the Ni–SiC electrodeposition system, the morphology of the coating, the orientation, and the SiC content of the composite were reported to be significantly affected. Devos et al. [6] reported that a uniform magnetic field of about 1 T parallel to the cathode surface changed the morphology of nickel deposited at constant cathodic potentials in a Watts' solution. Chiba et al. [7] observed that the magnetic field effect was pronounced at low current densities. Previous work also illustrated that the SiC content was greatly enhanced with the existence of magnetic field of 0.3 T [8]. However, the effect of magnetic field on corrosion behavior of electrocomposites has less been explored. The aim of this paper is therefore to examine the corrosion behavior of electrodeposited Ni–SiC composite with and without magnetic field and to study its micro-magnetohydrodynamic phenomenon.

Experimental

A two-electrode glass cell for nickel deposition with an electrolyte volume of 100 ml was used. A stainless steel cathode mandrel with dimensions of 30×30×1 mm and a stainless steel anode electrode which was unattractable to magnetic field were used. The composition of the bath solution was nickel sulphamate 330 g/l, nickel chloride 15 g/l, boric acid 30 g/l, and SDS 1 g/l. An amount of 40 g/l of SiC particles (β SiC) about 100 nm in diameter was added. The electrolyte was agitated by a mechanical stirrer, the temperature was kept at 50 °C, and the initial pH of the electrolyte was 4.2 which is a typical value used in electroplating. The strength of the magnetic field used in the plating was 0.1 T, and the magnetic field was perpendicular to the cathode. Details of the experimental setup could be referred to the work of Hu et al. [8].

After electroplating, scanning electron microscopy (Leica Stereoscan 440) and energy dispersive X-ray (spectroscopy) were used to study the surface morphology and composition of the Ni–SiC composite. Their corrosion behavior was studied in a typical corrosion medium, a 0.6-M NaCl solution at room temperature. Potentiodynamic polarization scan tests were carried out in a three-electrode corrosion cell using a PARSTAT 2273 (EG&G) corrosion test system to evaluate the pitting corrosion resistance of the Ni–SiC coatings. The standard Ag/AgCl electrode was used as a reference, and a platinum plate served as a counter electrode.

Polarization curves were obtained by sweeping the potential from -0.05 V (vs open-circuit potential) to 1.6 V, with a rate of 2 mV/s after stabilizing the open-circuit potential. In the tests, the specimens had an area of 1 cm² exposed to the electrolyte, and the rest of the surface was preserved by anticorrosion plastic. The impedance

measurements were performed at the corrosion potential, E_{corr} , with a perturbation amplitude of 10 mV and a frequency range from 6.5 KHz to 16.5 MHz. The impedance at the low frequency range was usually interpreted as the polarization resistance. All measured spectra were presented as Nyquist and Bode diagrams.

Results and discussion

Potentiostatic polarization behavior

To compare the corrosion resistance of nickel and nickel matrix composite coatings, potentiostatic tests, at a constant applied voltage of 0.01 V vs open-circuit potential, were performed in the 0.6-M NaCl solution. The resulting current densities (i.e., dissolution rates) as a function of time up to 20 s are shown in Fig. 1. The nickel dissolution rate reaches a steady state very quickly for all the coatings. A maximum current density of 0.4672 μA is observed for the pure nickel coating, and a minimum of 0.0042 μA is measured for the M.F.-plated Ni–SiC coating. The dissolution rate is reduced by about 100 times compared to pure nickel and by 50 times compared to conventional Ni–SiC composites, suggesting that the M.F.-plated Ni–SiC coating exhibits excellent corrosion resistance. From the potentiostatic polarization curves, the short charging times also illustrate the formation of protective film on the coating surface.

The polarization results

The polarization curves for pure nickel, Ni–SiC composite, and M.F.-plated Ni–SiC composite coatings in a 0.6-M NaCl electrolyte are given in Fig. 2. The corrosion current density (i_{corr}) calculated from the intercept of the Tafel

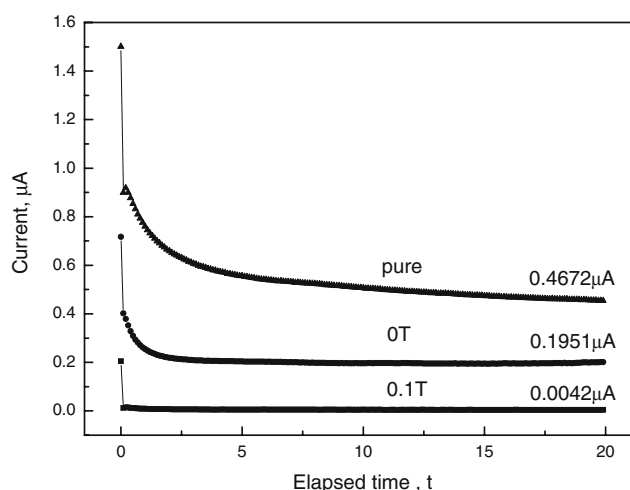


Fig. 1 Potentiostatic polarization behavior of the pure nickel, Ni–SiC composite, and M.F.-plated Ni–SiC composite coatings

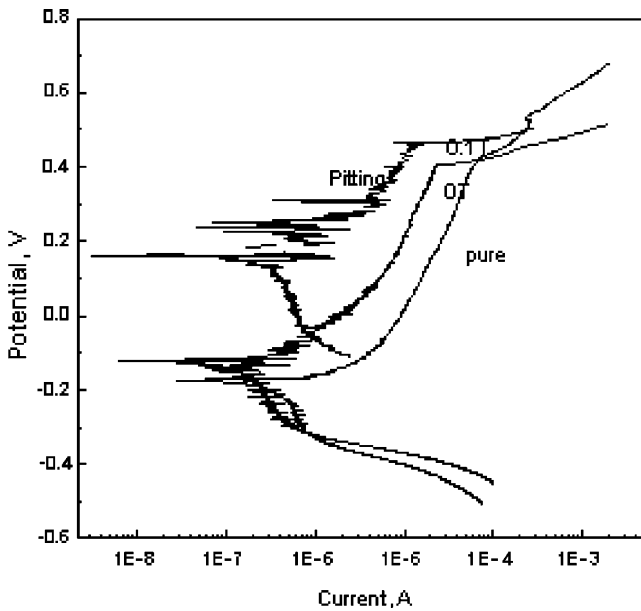


Fig. 2 Polarization curves obtained by pure nickel, Ni-SiC composite, and M.F.-plated Ni-SiC composite coatings

slopes is shown in Table 1. The i_{corr} value for both Ni-SiC composite and M.F.-plated Ni-SiC composite coating is about $3 \times 10^{-7} \text{ A cm}^{-2}$, which illustrates that it is not affected by the magnetic field. As compared to the pure nickel coating (9×10^{-7}), the corrosion current density is reduced by almost a factor of 3, and the passive current densities, i_p , of the composite coatings ($1 \sim 2 \times 10^{-5} \text{ A cm}^{-2}$) are reduced also by about one order of magnitude. Table 1 also shows that the M.F.-plated Ni-SiC coating has the highest corrosion potential (E_{corr}); in addition, the pitting potential (E_{pit}) is about the same for both Ni-SiC coatings with or without magnetic field, which suggests that the pitting corrosion of the two composite coatings are about the same. For the pure nickel coating, the crevice corrosion instead of pitting corrosion is observed. One of the possible reasons for the enhanced corrosion resistance of the composite coatings is the formation of protective film, which is not observed in the pure nickel coating.

Electrochemical impedance spectra

Although the corrosion resistance of electrodeposited Ni and nickel matrix composites can be examined and compared based on the polarization curves, electrochemical

Table 1 The corrosion parameters obtained by the polarization curves

	i_{corr}	E_{corr}	i_p	E_{pit}
Pure	9.18E-7	-0.18	9.30E-5	0.44
0 T	2.96E-7	-0.12	2.27E-5	0.41
0.1T	2.99E-7	0.16	1.36E-5	0.47

impedance spectroscopy (EIS) is further applied in this paper to assess the corrosion resistance of different deposits and to determine the mechanism pathway by which the deposits are corroded. Figures 3 and 4 show the Bode and Nyquist plots of the three coatings at their respective open-circuit potentials. All the curves appear to be similar with respect to their shapes at high frequencies. They consist of a big semicircle in the Nyquist plot, which corresponds to an arc in the Bode plot. However, at low frequencies, a line instead of an arc is observed for M.F.-plated Ni-SiC coatings. The difference in the impedance values indicates that their corrosion resistance is different. The pure nickel coating has poorest corrosion resistance, while the M.F.-plated Ni-SiC coatings have the best resistance.

The impedance spectra can also be used to illustrate the fundamental corrosion processes. From the Bode plot, it can be seen that the corrosion processes for the pure nickel and Ni-SiC composite coatings involve two time constants, while the corrosion process of the M.F.-plated Ni-SiC composite coating has one time constant. Figure 2 shows that the corrosion of the substrate is not obvious at 0.4 to -0.2 V from the polarization curve. It could be attributed to the high resistibility of the passivation film. By taking the film into consideration, the equivalent circuit models as shown in Fig. 5 are used to simulate the metal/solution interface. In the model, the corrosion resistance of the passive layer is illustrated by R_f , and the charge transfer resistance R_{ct} and the double-layer capacitance C_{dl} are utilized to illustrate the corrosion process of the substrate. Similar circuit [9] was also applied for studying the corrosion behavior of Ni-P coatings.

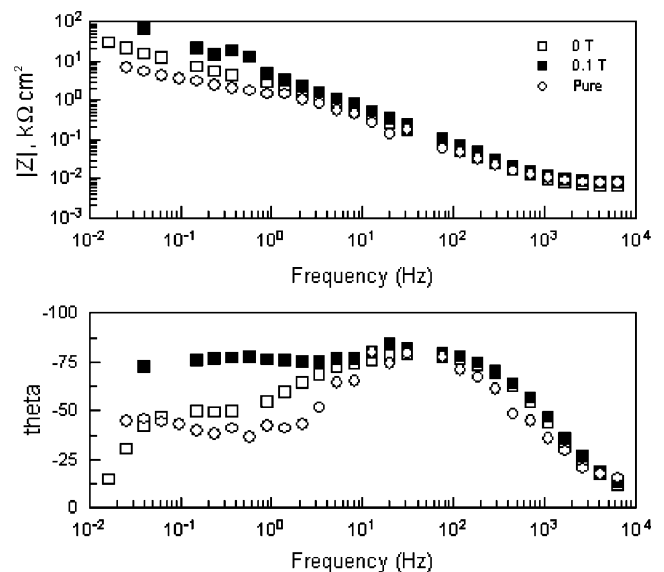


Fig. 3 The Bode plots of the pure nickel, Ni-SiC, and M.F.-plated Ni-SiC composite coatings

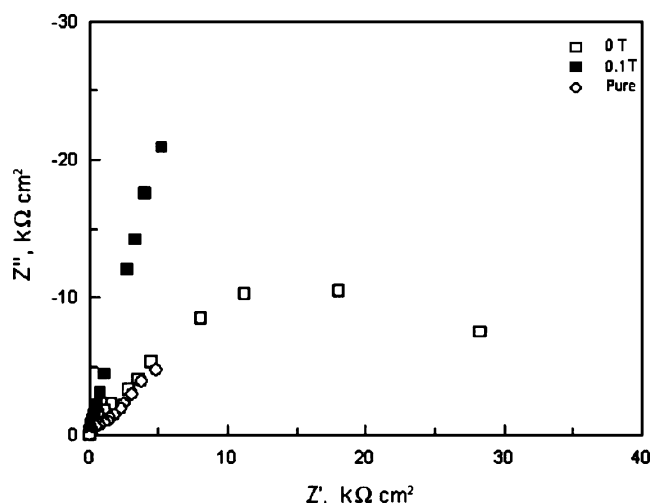


Fig. 4 The Nyquist plots of the pure nickel, Ni-SiC, and M.F.-plated Ni-SiC

Table 2 summarizes the electrochemical parameters obtained from EIS data for the three coatings. A maximum R_f value of $5.36 \times 10^5 \Omega$ is obtained for the M.F.-plated Ni-SiC coatings, and a minimum value of 21.52Ω is observed for the pure nickel coating. It suggests that a better corrosion protective film is formed when a magnetic field is applied on the electrodeposition process, which is consistent with the results revealed by the Bode plots. It is worth mentioning that the corrosion resistance of the coatings can be significantly improved by using only a simple magnetic field. The reaction resistance for the substrate obtained for the three coatings is also shown in Table 2. The substrate with the composite coating has a reaction resistance of $9.52 \times 10^4 \Omega$, which is much larger than that of the pure nickel coatings ($6,588 \Omega$). It is worth to note that the reaction resistance for the conventional Ni-SiC composite coatings is much greater than that of the pure nickel because the pure nickel is subject to crevice corrosion.

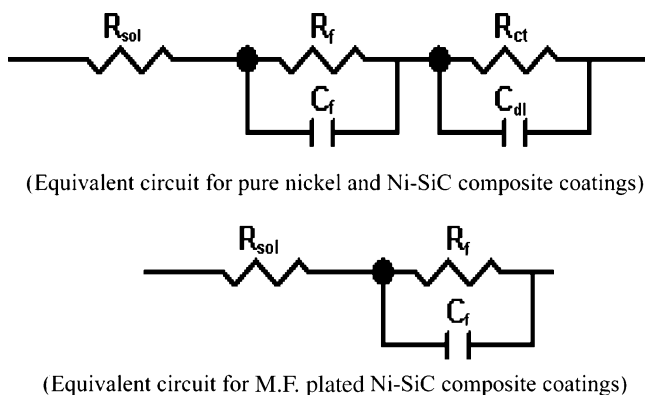


Fig. 5 The equivalent circuit of the electrodeposition systems. R_f the resistance of the passive layer, R_{ct} the reaction resistance for deposited film. Equivalent circuit for pure nickel and Ni-SiC composite coatings. Equivalent circuit for M.F.-plated Ni-SiC composite coatings

Morphology

The microstructure of the pure nickel and Ni-SiC composite coatings electrodeposited at 4 A dm^{-2} are shown in Fig. 6. The pure nickel coatings consist of pyramidal crystals with pronounced crystallographic polyhedral forms and with equigranular texture. The surface morphology of Ni with SiC particles has similar crystallographic forms as pure nickel crystals. For the M.F.-plated Ni-SiC composite coatings, the amount of incorporated SiC particles is the largest, and the surface morphology is disordered and different from other coatings.

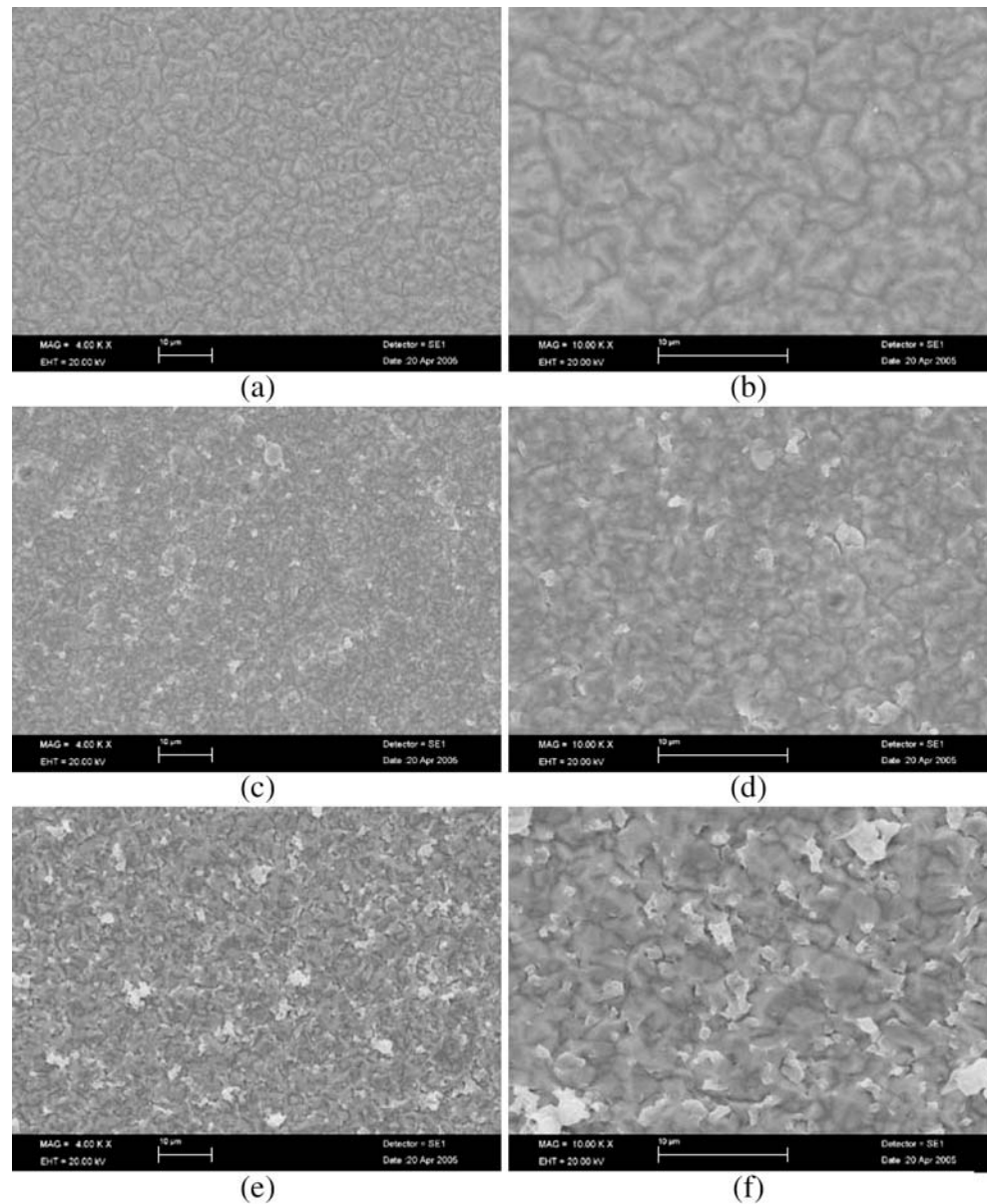
The nonmetallic inclusions, such as SiC particles, in the metal can change its electron structure and break up the crystal lattice, and affect their physical and mechanical properties. It is reported that SiC particles act as a corrosion inhibitor because the SiC will block the metallic surface and because also of its corrosion properties [10]. Garcia et al. [4] also stated that the inert material in the coatings surface would diminish the exposed metallic area. With the increasing amount of incorporation of SiC particles, the surface coverage of nickel is decreased, and the corrosion resistance is enhanced. Garcia et al. [4] have also explained that the corrosion process proceeds along the grain boundaries, and the corrosion path will be hindered when SiC particles are embedded in the nickel matrix.

In the previous studies of electrodeposition of Ni-SiC composite [11], the effect of magnetic field on the amount of incorporated SiC particles was examined, and the increased amount is considered to be attributed to the improvements of convection process and the charge transfer process due to the presence of magnetic field. Moreover, the nickel electrodeposition is accompanied by the hydrogen reduction [11]. Yeh and Wan [12] observed that hydrophobic SiC particles promote a greater area for the adsorption of Ni_{ads}^+ intermediate in the form of $\text{SiONi}_{\text{ads}}$ on the SiC surface. SiC particles are also found to be a medium for H^+ transfer and can enhance hydrogen evolution. Therefore, the codeposition of inert particles with metal mainly depends on the hydrophilic-hydrophobic balance of the particle surface and on the interaction forces between the cathode and the particles. Compared with the electrodeposition process of Ni-SiC and M.F.-plated Ni-SiC, the magnetic field will enhance the ionic mass transfer near the cathode surface, and the SiC particles will be attached to nickel ions and moved to

Table 2 The equivalent circuit parameters obtained from the pure nickel, Ni-SiC, and M.F.-plated Ni-SiC composite coatings

	$R_{\text{sol}} (\Omega)$	$R_f (\Omega)$	$C_f (\text{F})$	$R_{\text{ct}} (\Omega)$	$C_{\text{dl}} (\text{F})$	Chi square
Pure	32.02	21.52	1.73E-5	6,588	1.22E-5	0.03317
0 T	25.66	9,646	8.74E-6	9.51E4	4.22E-5	0.03225
0.1 T	32.51	5.36E5	5.81E-6	–	–	0.1328

Fig. 6 The SEM morphology of pure nickel (a, b), Ni–SiC (c, d), and M.F.-plated Ni–SiC (e, f) composite coatings. Magnification: a, c, e 4,000 \times ; b, d, f 10,000 \times



the cathode surface. It will offer higher chance for the SiC particles to contact with the cathode electrode. Due to the increase of hydrophobic interaction forces under the magnetic field, the adhesion of particles to the cathode also increases [12]. As a result, the magnetic field will lead to a larger quantity of SiC particles to be contacted and be codeposited with metal. Furthermore, it appears to be possible to achieve an excellent anticorrosion deposit by controlling the hydrophobic–hydrophilic balance of the particle surface using an external magnetic field.

Conclusions

The corrosion resistance of pure nickel coating differs from the Ni–SiC composite coatings produced with or without the

aid of magnetic field. A protective film was formed on the surface of Ni–SiC composite coatings, and pitting corrosion was observed for the composites, whereas crevice corrosion was observed on the surface of pure nickel coatings leading to their poor corrosion resistance. With an external magnetic field, a higher amount of SiC incorporation was obtained and hence a highly protective film was believed to form on the composite's surface. It is possible to obtain excellent anticorrosive coatings and achieve a tailored level of corrosion protection by adjusting the process parameters and magnetic fields. The findings have both environmental as well as economic advantages.

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References

1. Hou KH, Ger MD, Wang LM, Ke ST (2002) The wear behaviour of electro-codeposited Ni–SiC composites. *Wear* 253:994
2. Grosjean A, Rezrazi M, Takadoum J, Bercot P (2001) Hardness, friction and wear characteristics of nickel–SiC electroless composite deposits. *Surf Coat Technol* 137:92
3. Tang PT, Watanabe T, Andersen JET, Bech-Nielsen G (1995) Improved corrosion resistance of pulse plated nickel through crystallization control. *J Appl Electrochem* 25:347
4. Garcia I, Conde A, Langelaan G, Fransae J, Celis JP (2003) Improved corrosion resistance through microstructural modifications induced by codepositing SiC-particles with electrolytic nickel. *Corros Sci* 45:1173
5. Periene N, Cesuniene A, Taicas L (1993) Corrosion resistance of Ni/Al₂O₃ coatings in NaCl solution. *Plating Surf Finish* 80:73
6. Devos O, Azboubi O, Chopart JP, Meienne E, Olivier A, Amblard J (1998) Magnetic field effects on nickel electrodeposition. *J Electrochem Soc* 145:4135
7. Chiba A, Ogawa T, Yamashita T (1988) Magnetic field effects on the electrodeposition of copper from copper sulphate in sulphuric acid. *Surf Coat Technol* 34:455
8. Hu F, Chan KC, Qu NS (2006) Effect of magnetic field on electro-codeposition behaviour of Ni–SiC composites. *J Solid State Electrochem* DOI 10.1007/s10008-006-0103-5
9. Balaraju JN, Sankara Narayanan TSN, Seshadri SK (2001) Evaluation of the corrosion resistance of electroless Ni–P and Ni–P composite coatings by electrochemical impedance spectroscopy. *J Solid State Electrochem* 5:334
10. Medeliene V (2002) The influence of B₄C and SiC additions on the morphological, physical, chemical and corrosion properties of Ni coatings. *Surf Coat Technol* 154:104
11. Hu F, Chan KC (2004) Deposition behaviour and morphology of Ni–SiC electrocomposites under triangular waveform. *Appl Surf Sci* 243:251
12. Yeh SH, Wan CC (1994) Codeposition of SiC powders with nickel in a Watts bath. *J Appl Electrochem* 24:993