THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 4 – 2010, ISSN 1453 – 083X

ELECTROCHEMICAL CORROSION PROPERTIES OF SiC/Ni NANO-COMPOSITE COATINGS IN 0.5M NaCl

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ABSTRACT

Nano particles have an influence on nickel electrocrystallisation steps: decreasing charge transfer resistance and activating the nickel reduction. The SEM – EDX surface morphology and TEM structure of the electrodeposited nano-composite were investigated. The dispersed particles perturb the nickel crystal growth resulting in a random rather than in a preferred orientation. The corrosion behaviour of the nano-composite coatings was evaluated in the solution of 0.5M NaCl at room temperature. It was found that the polarization resistances of nano-SiC–nickel composite coatings are higher compared pure nickel coatings. The SiC distribution in the nano-composite coatings at low concentrations of SiC in bath was uniform across the coatings. The incorporation of the SiC nano-particles leads to the changes in the morphology and corrosion resistance of the nano-composite coatings as compared to the pure nickel coatings. The Ni–SiC nano-composite coatings have higher corrosion resistance than the pure nickel coating, which is attributed to the grain-fining and dispersive strengthening effects of the co-deposited SiC nano-particles with nickel.

The silicon carbide nano particles embedded during nickel electroplating have a good effect to corrosion properties of composite coating compared to pure nickel coating.

The polarization resistance increases about two times and the corrosion current density decreases about two times in the case of nano-composite coating.

KEYWORDS: nanocomposite, coatings, electrodeposition, dispersed phase, corrosion

1. Introduction

The goal of composite development is to achieve a combination of properties not achievable by any of the materials acting alone.

The electrochemical deposition of nano size particles in a metallic matrix has led to a new generation of composites, due to the advantages of this technique. Studies by several investigators have proved that the uniform dispersion of the codeposited particles leads to the improvement of the mechanical, tribological, anti-corrosion and anti-oxidation properties of the coatings [1–3]. A large volume fraction of particles is also needed, since they act as load bearing elements.

The ability to produce reinforcing powders with decreasing particle sizes has led to technological interest in the production of new composite materials with improved and well controlled properties. The major challenges in the codeposition of nanoparticles seem to be the codeposition of a sufficient number of particles, and avoiding the agglomeration of particles suspended in the plating solution. SiC/Ni composites in particular have been investigated, due to their improved wear resistance.

This property has led to their commercial use in the protection of friction parts, combustion engines and casting mould [4, 5]. Considerable research has been focused on the impact of the electrodeposition parameters: bath composition, presence of additive, pH, current conditions and type of SiC particles [6 - 12]. Reports on the tribological properties of SiC/Ni deposits containing micron and submicron SiC particles are available [1, 13 - 17].

Composite coatings are produced by codeposition of inert particles into a metal matrix from an electrolytic or electroless bath being considered as metal matrix composite (MMC) coatings. This technique is receiving increased interest because of its ability to produce films with excellent mechanical properties such as wear resistance, corrosion resistance and lubrication [2-6]. These properties depend on the morphology of the inert particles in the composite coatings. Furthermore, metal matrix nanocomposite coatings exhibit unique magnetic, mechanical and optical properties and are promising materials for micro-devices. Nano-composite deposition may be useful in fundamental studies of their nanometric nature. As mentioned above not many reports are available on the corrosion performances of SiC/Ni composite coatings particularly the electrochemical corrosion. It is therefore interesting to study the influence of incorporated nano SiC particles into the coating, which thereby can affect the properties of the coating. To understand the effect of nano SiC (20 nm mean diameter) particles samples with nanostructued SiC/Ni composite coatings were prepared by electrodeposition in a common nickel plating bath by adding 20 g/L SiC (20 nm size) in the electrolyte. A comparison has been made with reference to pure Ni coating obtained from the same electrolyte.

2. Experimental research

2.1. SiC/Ni nano-coatings preparation

The SiC/Ni composite nano-coatings were prepared in a solution containing 260 g/L $NiSO_4$ x $6H_2O$, 30 g/L $NiCl_2$ x 6H2O, 30 g/L H_3BO_3, 20 g/L nano-sized SiC (20 nm mean diameter) and surfactant. The nano sized SiC particles from a TEM image are shown in Figure 1. Electrodeposition was carried out on vertical electrodes, and the bath was agitated during electrodeposition with a magnetic stirrer.

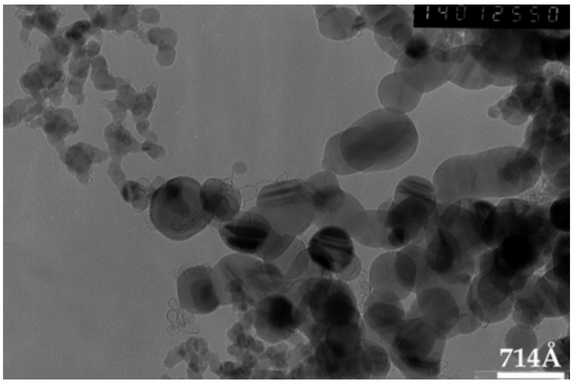

Fig. 1. *TEM image of SiC nano particles (mean diameter of 20nm).*

The temperature of the electrodepositing bath was maintained at 40 ^{0}C and its pH was adjusted to 4.0. A steel plate with dimensions of 50 mm x 80 mm x 1 mm was used as the base plate for the electrodeposition, and the anode was a pure nickel plate. For comparison, pure Ni coatings were also prepared in almost the same solution mentioned above except for SiC particles. In order to standardize the comparison, the thickness of all coatings was controlled at 100 μm.

2.2. Electrochemical corrosion

The solution used for thecomparative study of pure and nanocomposite coatings deposited on steel support was 0.5M NaCl. Corrosion investigations were taken out by electrochemical impedance spectroscopy method in the frequency range from 10^4 Hz to 0.003 Hz with amplitude of 5 mV and potentiodynamic diagrams. After impedance measurements potentiodynamic curves were plotted with a scan rate of 0.5 mVs^{-1} between the potentials: –600 mV and +600 mV (referred to Ag/AgCl electrode). Corrosion current densities, polarization resistance, Tafel slops and corrosion potential were determined in 0.5 M NaCl naturally aerated solution.

3. Results

3.1. SEM – EDX and TEM studies

Surface morphologies of SiC/Ni and pure nickel films deposited are examined using a SEM with EDX system and the presence of SiC dispersed particles inside the composite coatings by TEM. The images are given in Figures 2-3. The surfaces of the films appear to be smooth and densely covered. The crystallites, however, get finer when deposited nano SiC dispersed particles with nickel.

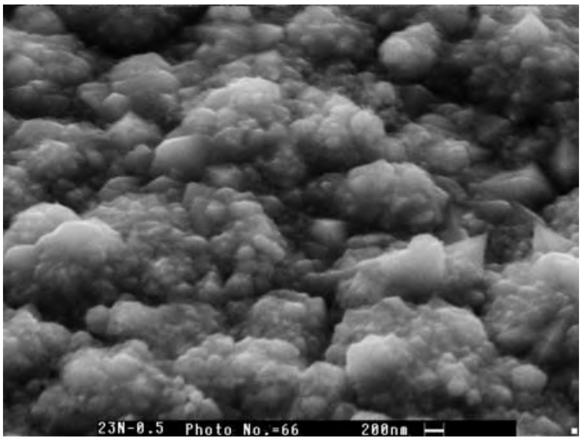

Fig. 2. *SEM image of SiC/Ni nanocomposite coating surface.*

Fig. 2 shows the SEM image of SiC/Ni nanocomposite coatings. The grain size of the composite coated sample was smaller when compared to the pure nickel coating. The presence of SiC provides more nucleation sites and retards the crystal growth and hence the composite coatings samples possess smaller grain size [10]. The nano SiC particles inside o composite coating were visualised by TEM, see Fig. 3.

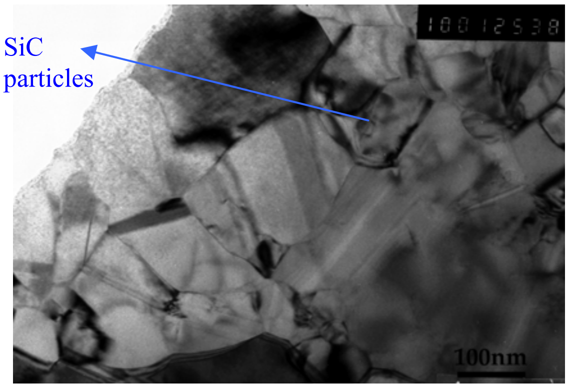

Fig. 3. *TEM image inside of SiC/Ni nanocomposite coating*

From EDX analysis of SEM surfaces silicon content was calculated and transformed after wards in SiC content.

Fig. 4 shows the EDX spectrum of SiC/Ni composite coating surface having 6.29 % of Si layer (A), which represents general analysis on SEM surface. On the layer (B) from Fig 4 a punctual analysis on a SiC particle is shown.

The nano SiC content in the tested nanocomposite coatings was 8.99 as weight % or ~25 as volume %.

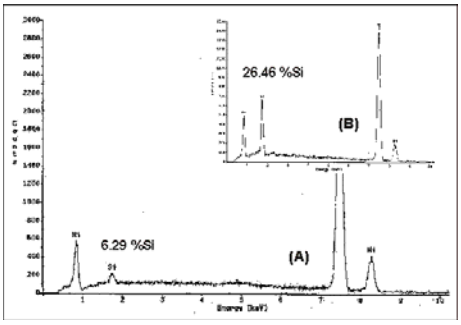

Fig. 4. *SEM-EDX analysis of SiC/Ni nanocomposite surface: Layer (A) – general analysis on entire surface; Layer (B) punctual analysis on SiC particle*

3.2. Electrochemical corrosion studies in 0.5M NaCl

The results of corrosion testing of nano-SiC/Ni composite and pure nickel coatings in aerated 0.5M NaCl solution, pH=7, are presented in Figs. 5 and 6. The test was performed during 24 hours. The polarization resistance of composite coatings, see Fig. 7 is increasing from R_p=600 kΩcm^2 to 1600 kΩcm^2 during the experiment.

Oppositely, the polarization resistance for pure nickel coating (See Fig. 8) is decreasing from about 140 kΩcm^2 after 10 hours and increases slowly at about 160 kΩcm^2 after 24 hours.

It can be observed also that the polarisation resistance of nanocomposite coatings is higher than the one of pure nickel coatings (Figures 5 and 6).

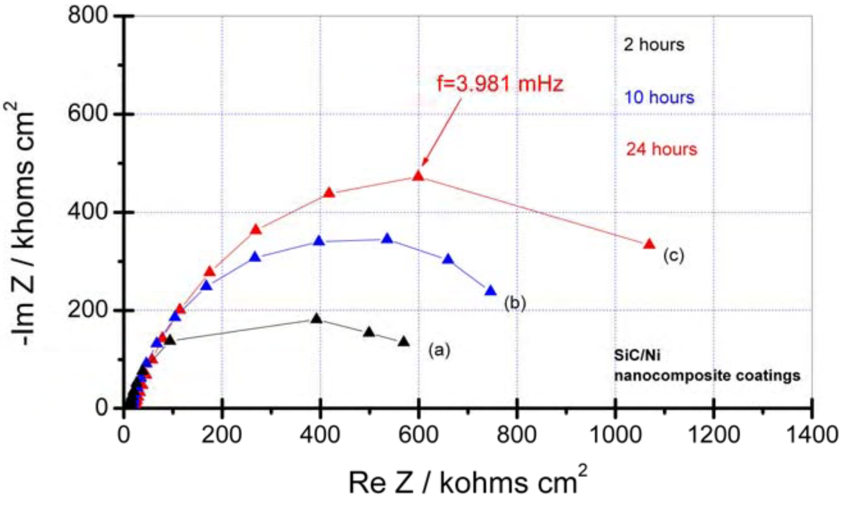

Fig. 5. *Nyquist plot of impedance data of SiC/Ni nanocomposite coatings in aerated 0.5 M NaCl: (a) after 2 hours of immersion; (b) after 10 hours; (c) after 24 hours. The line connecting the points represents the simulation diagram.*

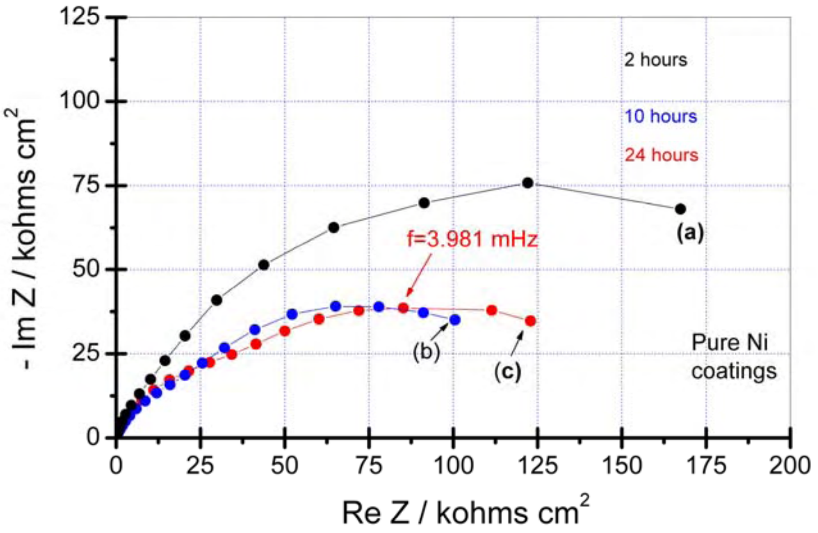

Fig. 6. *Nyquist plots of impedance data of pure nickel coatings in aerated 0.5 M NaCl (a) after 2 hours of immersion; (b) after 10 hours; (c) after 24 hours The line connecting the points represent the simulation diagram.*

One equivalent circuit was proposed to fit the experimental impedance data [18]. In the composite coatings corrosion experiments this circuit, represented in the Fig. 7, allow obtaining an excellent agreement between experimental data and simulated impedance plots.

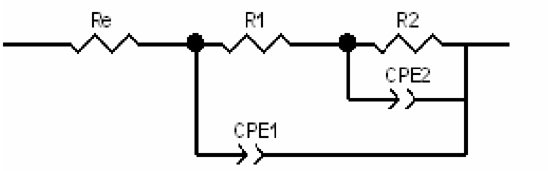

Fig. 7. *Equivalent circuit proposed to fit the experimental impedance data of SiC/Ni nanocomposite and pure Ni coatings immersed in 0.5 M NaCl solution*

The experimental data was simulated with this equivalent circuit, where:

R_e – electrolyte resistance between the reference electrode and the working electrode;

CPE_1 – the double layer capacitance depending on frequency of nickel coating or nanocomposite coating;

CPE_2 - double layer capacitance depending on frequency of pores (in the case of nickel coating, or double layer capacitance depending on frequency of insulating SiC nano-particles).

R_1 – the polarization resistance of nickel or nanocomposite coatings.

R_2 - resistance of pores (in the case of pure nickel coating) or resistance of insulating nanoparticles in the case of nanocomposite coatings.

The impedance could be described by the following equation:

$$Z = R_e + \frac{R_p}{1+(j\omega\tau)^{\beta}} \quad (\text{with } 0 < \beta \ \le 1) \qquad (1)$$

The value of β determines the amplitude of the depressed impedance semi-circle and the importance of the discrepancy between the Randles' circuit model with a pure capacitor C_{dl} and the equivalent circuit with the CPE insteade of C_{dl}. The borderline case of the Randles' circuit is found if $\beta = 1$. CPEs are constant phase elements, accounting for the fact that the centres of the capacitive arcs of the impedance circle are under the axis of real part. This feature of capacitive arcs is encountered in all electrochemical impedance studies performed on inhomogeneous surfaces and has given rise to extensive studies. CPE are not pure capacitors but components depending on frequency.

The proposed equivalent circuit fitted better the experimental data as it is shown in Figs 5 and 6 as lines connecting the experimental points of the impedance measurements.

Evolution of the polarisation resistance (R_1) of pure nickel coatings and nanocomposite coatings during the experiment is presented in Figure 8 and evolution of the CPE_1 in Figure 9.

The continuous increases of capacitance (CPE) for pure nickel coatings can be explained by the increases in the permittivity of the coating and/or increases in porosity due to the pitting corrosion installed in chloride solution.

The decreases of capacitance for nanocomposite coating can be explained by improving the passivity film protection on the composite surface due to the presence of insulating SiC nanoparticles.

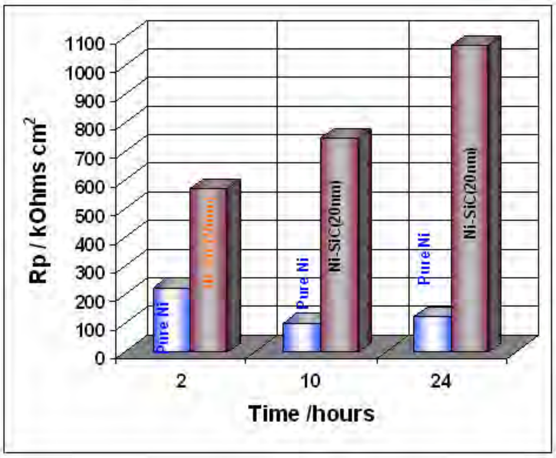

Fig. 8. *Evolution of polarisation resistance during immersion time in 0.5M NaCl solution.*

From the evolution of polarisation resistance diagrams during immersion time it is shown the same differences between nanocomposite and pure nickel coatings, increase in the polarization resistance for nanocomposite coating and decreasing the polarization resistance for pure nickel coatings.

The corrosion current densities of both type of coatings were calculated from potentiodynamic diagrams plotted in 0.5 M NaCl solution with a scan rate 0.5 mVs^{-1}.

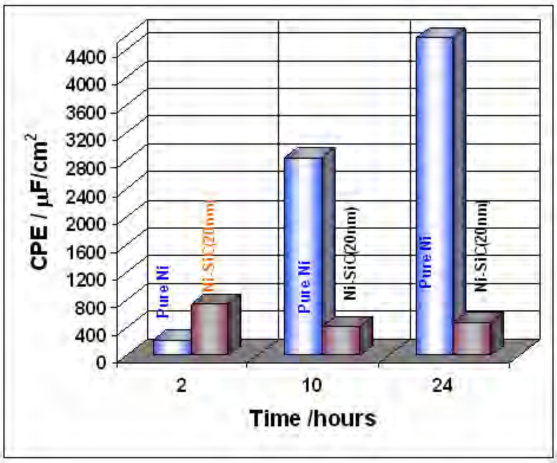

Fig 9. *Evolution of CPE$_1$ during the immersion time in 0.5M NaCl solution.*

From the potentiodynamic diagram of nanocomposite coating, curve [b] in Fig. 10, the calculated corrosion current density has a value of i_{corr}=65.06nAcm^{-2} and a corrosion potential situated at E_{corr}= –169mV (Ag/AgCl).

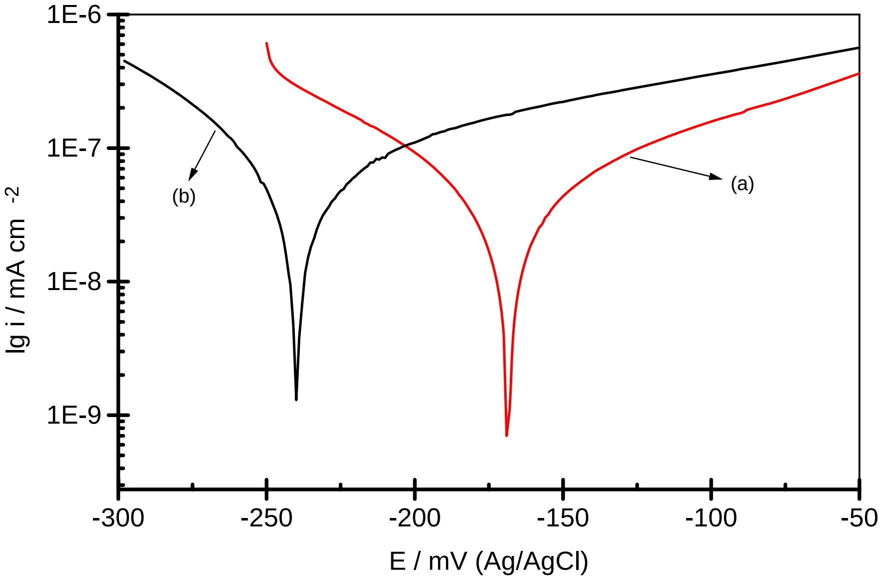

Fig. 10. *Potentiodynamic diagrams of: (a) nickel SiC composite coating and (b) pure nickel plating in aerated 0.5M NaCl; scan rate 0.5 mV/s.*

The corresponding Tafel slopes were the following: B_a=161.5 mV/decade and B_c=101.9 mV/decade for anodic and cathodic reactions, respectively.

From the potentiodynamic diagram performed on pure nickel coating, curve [b] in Fig. 10, the calculated corrosion current value is i_{corr}=178nAcm^{-2} with a corrosion potential situated at E_{corr}= –236mV (Ag/AgCl). The corrosion potential is shifted with about 66 mV to more negative values that in the case of nanocomposite coating.

The corresponding Tafel slopes were the following: B_a=380mV/decade and B_c=133 mV/decade for anodic and cathodic reactions respectively.

We can conclude that the silicon carbide nano particles embedded during nickel electroplating process have a good effect to corrosion properties of nanocomposite coatings compared with pure nickel coatings. The polarization resistance increases about two times and the corrosion current density decreases about two times in the case of nanocomposite coating.

4. Conclusions

SiC nano-particulates can be successfully co-deposited with nickel by electrodeposition process from a nickel plating bath.

The benefit of presenting codeposition results was demonstrated for the codeposition of SiC/Ni with particle sizes having a mean diameter of 20 nm. For this system, it was found a better corrosion resistance.

The incorporation of the SiC nano-particulates leads to the changes in the surface morphology, grain sizes and corrosion resistance of the nano-composite coatings as compared to the pure nickel coatings.

The SiC/Ni nano-composite coatings have higher polarization resistance and better corrosion resistance than the one pure nickel coating in chloride containing solution, which is attributed to the grain-fining and dispersive strengthening effects of the deposited hard SiC nano-particulates.

The values of polarization resistances of pure nickel and SiC/Ni nanocomposite coatings determined by two electrochemical methods, electrochemical impedance spectroscopy and potentiodynamic polarization respectively are in good agreement.

The improved properties of SiC/Ni nano-composite coatings must be tested also to other applications, on the better resistance to bacterial adhesion and biofilm formation compare to pure nickel coatings.

Acknowledgments

The authors gratefully acknowledge the European Project **COST D33 - Electrochemical and biotribocorrosion studies of interfaces between materials (composites, metallic, polymeric, ceramic) and microorganisms**.

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