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Electrochemical impedance spectroscopy and corrosion behaviour of Al_2O_3–Ni nano composite coatings

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Abstract

In this paper, the results on the electrochemical impedance spectroscopy and corrosion properties of electrodeposited nanostructured Al_2O_3–Ni composite coatings are presented. The nanocomposite coatings were obtained by codeposition of alumina nanoparticles (13 nm) with nickel during plating process. The coating thickness was 50 μm on steel support and an average of nano Al_2O_3 particles inside of coatings at 15 vol.% was present. The structure of the coatings was investigated by scanning electron microscopy (SEM). It has been found that the codeposition of Al_2O_3 particles with nickel disturbs the nickel coating's regular surface structure. The electrochemical behavior of the coatings in the corrosive solutions was investigated by polarization potentiodynamic and electrochemical impedance spectroscopy methods. As electrochemical test solutions 0.5 M sodium chloride and 0.5 M potassium sulphate were used in a three electrode open cell. The corrosion potential is shifted to more negative values for nanostructured coatings in 0.5 M sodium chloride. The polarization resistance in 0.5 M sodium chloride decreases in 24 h, but after that increases slowly. In 0.5 M potassium sulphate solution the polarization resistance decreases after 2 h and after 30 h of immersion the polarization resistance is higher than that of the beginning value. The corrosion rate calculated by polarization potentiodynamic curves obtained after 30 min from immersion in solution is smaller for nanostructured coatings in 0.5 M potassium sulphate (4.74 μm/year) and a little bit bigger in 0.5 M sodium chloride (5.03 μm/year).

Keywords: Al_2O_3–Ni nanostructured composite coatings; Electrochemical impedance spectroscopy; Potentiodynamic polarization; Sodium chloride; Potassium sulphate

1. Introduction

Much attention has been focused on the development of ceramic/metal nanocomposites because such materials offer outstanding mechanical and multifunctional properties [1].

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.

A nano Al_2O_3–Ni composite coating is used primarily to increase the wear resistance of metal surfaces in micro-devices. Although the micro Al_2O_3–Ni composite coating grades have progressed deeply, certain problems persist in its preparation. The volume content of alumina particles in Al_2O_3–Ni composite coatings cannot be controlled quantitatively and the particles are frequently agglomerated together in the composite coatings. The alumina weight content in the composite coatings can be promoted from 3.5% to 14.6% using pulse-reverse electrodeposition. The mechanical properties are also improved. Although the process has been developed for a long time, much recent research effort has been spent on electrodeposition of

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nanostructured coatings. The well-dispersed nanosized inert particles in a metal matrix do not only enhance the mechanical property, but also open up potential applications of the materials in microdevices. Coatings of Al_2O_3–Ni are highly abrasion and heat resistant and have quite good anticorrosion properties. They find application as coatings of engine cylinders, high-pressure valves and dies and in the production of musical instruments, drill fittings, car accessories and small aircraft and electrotechnical parts [7]. Among the processes to produce nanostructured composites, the electrodeposition technique has further demonstrated that a smoother surface, a better bonding between particles and metal and higher microhardness can be achieved. Different types of nanocomposites such as ZrO_2–Ni, SiC–Ni, PZT–Ni, Al_2O_3–Ni, diamond–Ni and Al_2O_3–Cu have been successfully produced by direct, pulse current, pulse reverse current electrodeposition [8,9].

The codeposition of Al_2O_3 was also studied by Kuo et al. [10,11] using pulse current and ultrasonic energy treatment. The corrosion properties of composite coatings obtained were not discussed.

Nanocomposite Al_2O_3–Ni films electrodeposited from a suspension of Al_2O_3 nanoparticles was studied in aqueous nickel sulphamate solution. The volume fraction of particles incorporated increased with electrode rotation rate and decreased with deposition current density. The saturation magnetization showed a weak dependence on particle concentration [12].

Electrochemical responses contain valuable information both on interfacial structures and dynamics of interfacial processes. The established practice of the electrochemical characterisation implies sequential probing of the electrochemical system with various techniques, highly specialised in particular aspects of ac and dc responses. Each of the components of the electrochemical response has a notable potential for interfacial studies: a double electric layer is the thinnest probe, which helps to detect even the slightest changes on the interface by the variation of the double layer capacitance. The losses of opportunities originate from the above-mentioned disintegration of the electrochemical probing between different techniques and the difficulties of components separation in complex responses, which hinder the development of practically feasible integrated probing procedures for the comprehensive characterisation of electrochemical systems [13–15].

Polarization methods such as potentiodynamic polarization, potentio-staircase and cyclic voltammetry are often used for laboratory corrosion testing. These techniques can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential [16].

The fact that the second-phase particles affect the nickel composite coating's surface morphology and protective properties in different ways and to different degrees are the reason why the corrosion test results for coatings Al_2O_3–Ni reported in the literature are often inconsistent. The authors Szczygiel and Kolodziej reported in paper [17] the corrosion resistance of Al_2O_3–Ni composite coatings in 0.5 M sodium sulphate solution.

This paper focuses on electrochemical corrosion behaviour of nanostructured Al_2O_3–Ni composite coatings obtained by electrodeposition process. The corrosion behaviour was investigated by electrochemical impedance spectroscopy and polarization potentiodynamic methods in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions.

2. Experimental

Nickel (Ni) and composite (Al_2O_3–Ni) coatings were electrochemically deposited from a Watts bath with the following composition: 1 M $NiSO_4 \cdot 7H_2O$, 0.1 M $NiCl_2 \cdot 6H_2O$, 0.2 M H_3BO_3, 1.2×10^{-3} M sodium dodecyl sulphate (SDS). The pH of the solution was about 4. Suspension was preparated by adding Al_2O_3 nanoparticles (13 nm) to the solution to give a concentration of 20 g/L in the nickel plating electrolyte. Electrodeposition took place in the bath at a temperature of 40 °C and a current density of 2 Ad m^2 for a time sufficient to obtain a 50 μm thick coating. The suspension bath was stirred by a mechanical stirrer at a constant rotational speed of about 300 rpm.

Steel plate with an area of 2 cm^2 was used as the cathode; a pure Ni plate was used as the anode. Prior to electroplating, the substrates were mechanically polished to 0.08–0.12 μm surface roughness and then a sequence of cleanings was performed to remove contamination on the substrate surface. The steel substrate was activated in a mixed acidic bath at room temperature before electroplating.

Before electrochemical corrosion investigations, the surfaces of the Ni coatings and Al_2O_3–Ni composite coatings were examined with scanning electron microscope type AMRAY 1830.

For electrochemical corrosion measurements were used a VOLTAMASTER 4 complete SOFTWARE, a three-electrode open cell with nanostructured Al_2O_3–Ni composite coatings as working electrode (WE), a platinum gauze as counter electrode (CE) and Ag/AgCl as reference electrode (RE) ($E_{RE} = +200$ mV/ENH). As test solutions 0.5 M sodium chloride and 0.5 M potassium sulphate were used at room temperature (20 ± 1 °C).

EIS measurements used initial frequency (I.F.) 100 kHz, final frequency (F.F.) 100 mHz, AC sine wave amplitude of 10 mV; frequency per decade: 10 Hz, delay before integration 1 s. The impedance spectra were recorded on different samples after different times from immersion (30 min, 2 h, 6 h, 24 h and 30 h). All the recorded impedance spectra were analyzed as Nyquist diagrams.

For PD measurements were used initial potential (I.P.) −800 mV (Ag/AgCl), final potential (F.P.) +100 mV (Ag/AgCl) and a scan rate of 1 mV/s. The polarization potentiodynamic curves were recorded after 30 min of immersion. The corrosion current density (i_{corr}) for the particular specimens was determined by extrapolating the anode and cathode Tafel curves.

3. Results and discussions

Figs. 1(A and B) and 2(A and B) compare the surface structure of pure nickel coating and nanostructured Al_2O_3–Ni composite coatings under a scanning microscope. The surface of a nickel is made up of regular pyramidal crystals with a uniform grain size. The Al_2O_3 particles codeposit with nickel radically change the structure of the metal: disorder the regular crystal structure and the structure of the nickel matrix becomes finely crystalline. Al_2O_3 nanoparticles show a distinct tendency to form conglomerates uniformly distributed over the whole surface of the coating. Some of them protrude above the surface of the nickel matrix while other, despite being deeply embedded in it, are not covered by a layer of the metal because of their dielectric properties.

The corrosion investigation of each sample began with monitoring the open circuit potential after immersion into the testing solutions till reaching a relatively stable stationary value (see Fig. 3).

The Nyquist plot representation of impedance spectra performed in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions at different times of immersion: after 30 min, 2 h, 6 h, 24 h and 30 h are shown in Figs. 4 and 5.

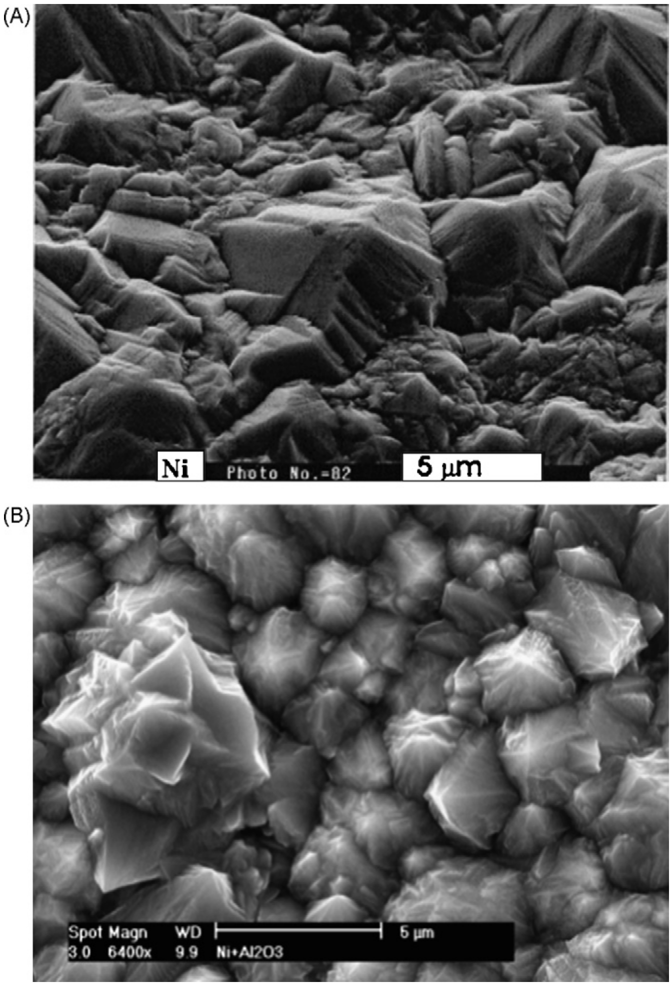

Fig. 1. (A and B) SEM surface morphology of pure nickel electroplating and nanostructured Al_2O_3–Ni composite coatings (5 μm).

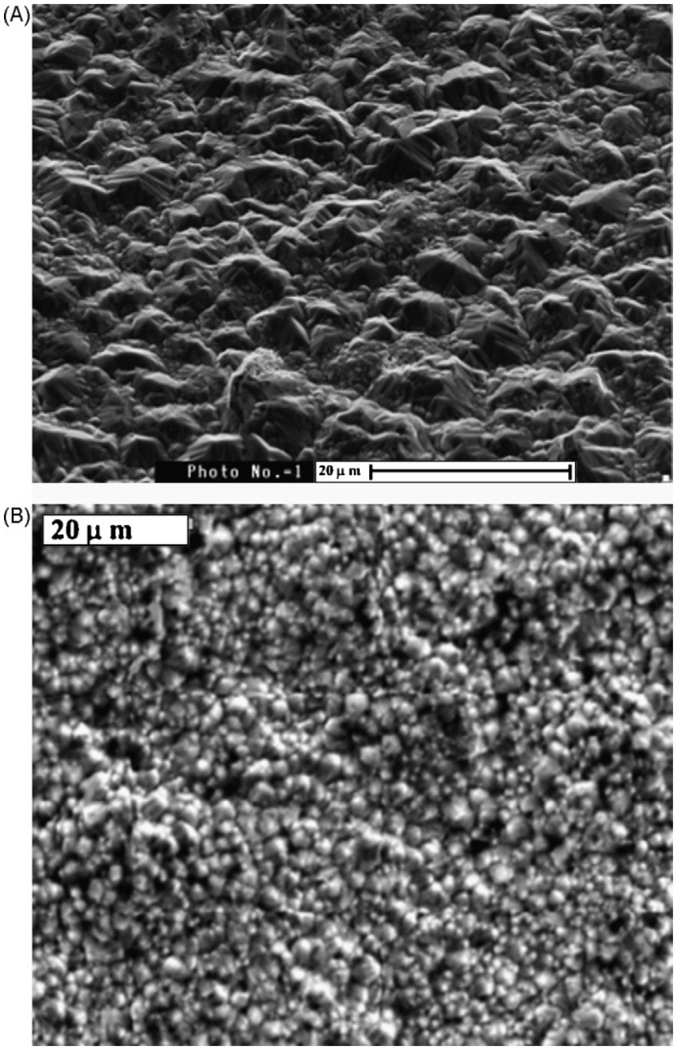

Fig. 2. (A and B) SEM surface morphology of pure nickel electroplating and nanostructured Al_2O_3–Ni composite coatings (20 μm).

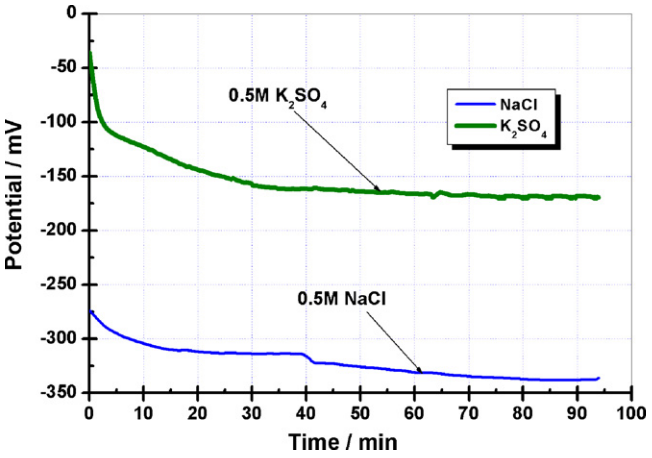

Fig. 3. Variation of the potential of nanostructured Al_2O_3–Ni composite coatings function of time for 0.5 M sodium chloride and 0.5 M potassium sulphate solutions.

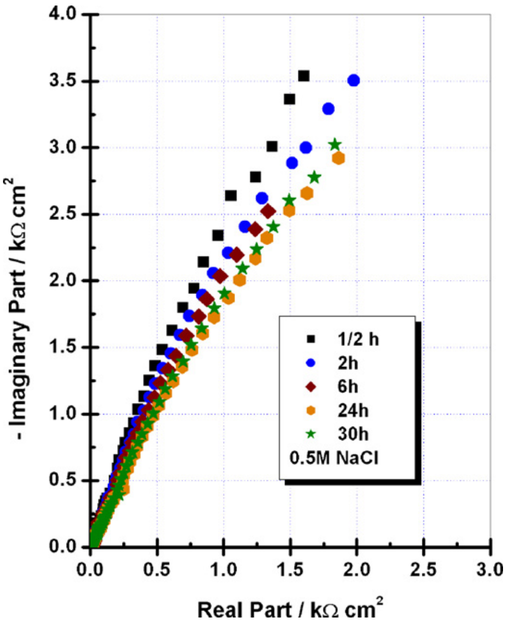

Fig. 4. Nyquist diagrams of impedance spectrum for nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride.

An equivalent electrical circuit was proposed to account for the experimental impedance spectra [18]. In most cases, this circuit, represented in Fig. 7(A) allows to obtain an excellent agreement between experimental and simulated impedance plots. The experimental data of our work was simulated with this equivalent circuit.

The impedance could be described by the following equation:

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

The value of beta (β) accounts for the fact that the centers of the capacitive arcs of circles are under the axis of real part, Fig. 6(B).

The value of β determines the amplitude of the depression and the importance of the discrepancy between the Randles' circuit model with a pure capacitor C_{dl}, and the circuit with the CPE: the borderline case of the Randles' circuit is found if $\beta = 1$.

CPE are a constant phase elements, accounting for the fact that the centres of the capacitive arcs of the 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.

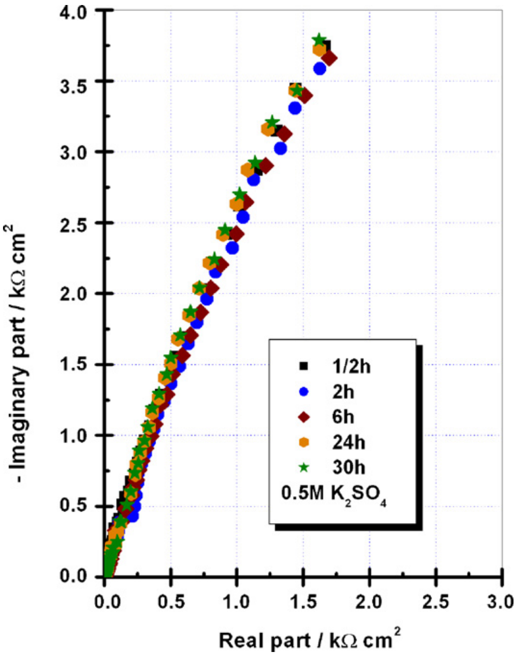

Fig. 5. Nyquist diagrams of impedance spectrum for nanostructured Al_2O_3–Ni composite coatings in 0.5 M potassium sulphate.

In Fig. 7 is represented one experimental diagram together with the simulation curve described by the equivalent circuit from Fig. 6. It could be observed that the experimental impedance data fit very well with the equivalent circuit proposed.

The corresponding calculated polarization resistance and capacitance values from impedance diagrams for nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions using the equivalent circuit from Fig. 7 are presented in Table 1.

It was observed that the polarization resistance of nanocomposite coatings in 0.5 M sodium chloride decreases in 24 h, but after that increases slowly. After 30 min of immersion the polarization resistance is 26.30 kOhms cm^2, after 24 h is 12.00 kOhms cm^2 and after 30 h from immersion is 12.44 kOhms cm^2.

The polarization resistance of nanocomposite coatings in 0.5 M potassium sulphate solution decreases during 2 h (after 30 min is 26.93 kOhms cm^2 and 25.25 kOhms cm^2 after 2 h),

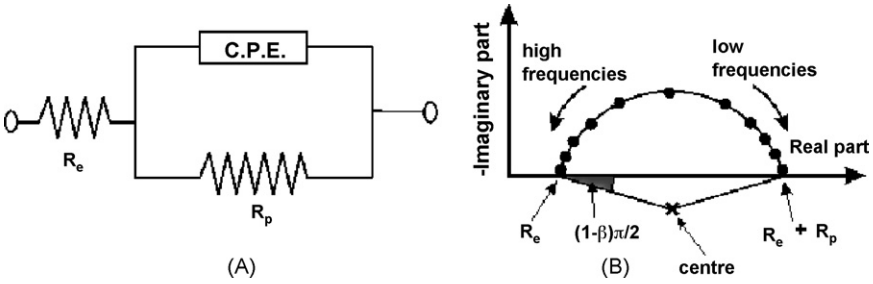

Fig. 6. (A) Equivalent circuit to calculate the polarization resistance from impedance data with a CPE: R_e – electrolyte resistance between the reference electrode and the working electrode; CPE – the double layer capacity in parallel with the polarization resistance R_p; (B) Circuit with a parallel combination of a resistance R and a CPE, and the corresponding Nyquist impedance plot.

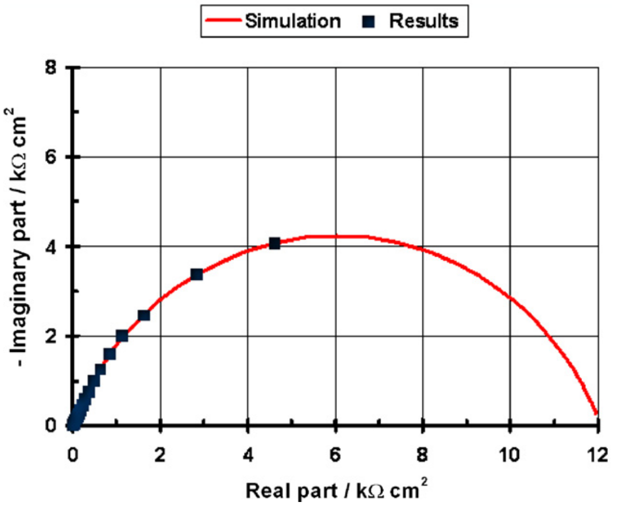

Fig. 7. Nyquist diagrams of impedance spectrum of experimental data (square points) and fitting curve (solid line) for nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride solution after 24 h of immersion.

then the polarization resistance increases. So that after 30 h of immersion the polarization resistance (29.88 kOhms cm^2) is a little bit higher than that the value calculated from Nyquist impedance diagrams after 30 min of immersion, but in the same order of magnitude.

The capacitance values are smaller in 0.5 M potassium sulphate solution (between 4.13 and 5.25 μF/cm^2) than in 0.5 M sodium chloride solution (between 8.09 and 15.32 μF/cm^2).

The performed potentiodynamic diagrams for nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions after 30 min of immersion are presented in Fig. 8.

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation, as follows [19]:

$$i_{\mathrm{corr}} = \frac{1}{2.303 R_{\mathrm{p}}} \left(\frac{\beta_{\mathrm{a}} \times \beta_{\mathrm{c}}}{\beta_{\mathrm{a}} + \beta_{\mathrm{c}}} \right) \qquad (2)$$

- i_{corr} is the corrosion current density in Amps/cm^2;
- R_{p} is the corrosion resistance in ohms cm^2;
- β_{a} is the anodic Tafel slope in Volts/decade or mV/decade of current density;
- β_{c} is the cathodic Tafel slope in Volts/decade or mV/decade of current density;

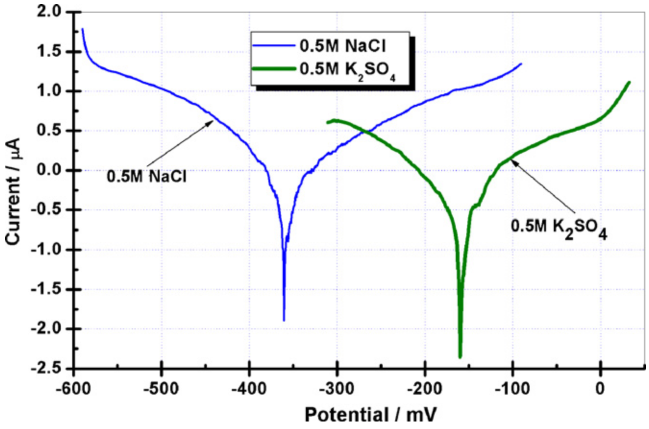

Fig. 8. Comparative polarization potentiodynamic curves for nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions obtained after 30 min from immersion time (log scale).

- the quantity, $(\beta_{\mathrm{a}} \cdot \beta_{\mathrm{c}})/(\beta_{\mathrm{a}} + \beta_{\mathrm{c}})$, is referred to as the Tafel constant.

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_{p}), which were obtained from the potentiodynamic polarization curves are summarized in Table 2.

The corrosion potential is shifted to more negative values for nanostructured coatings in 0.5 M sodium chloride (−359.2 mV) and to positive values for same coatings in 0.5 M potassium sulphate (−158.8 mV).

The polarization resistance values calculated with Stern-Geary formula from potentiodynamic diagrams were in good agreement with those obtained from impedance measurements. From potentiodynamic polarization curves the polarization resistance is 25.03 kOhms cm^2 in 0.5 M sodium chloride and in 0.5 M potassium sulphate the polarization resistance is 32.17 kOhms cm^2.From impedance diagrams the polarization resistance is between 26.30 kOhms cm^2 (after 30 min of immersion) and 12.44 kOhms cm^2 (after 30 h of immersion) in 0.5 M sodium chloride and between 26.93 kOhms cm^2 (after 30 min of immersion) and 39.88 kOhms cm^2 (after 30 h of immersion) in 0.5 M potassium sulphate.

From experimental data it was observed that corrosion rate (corrosion current) is 0.50 μA/cm^2 for Al_2O_3–Ni nanocomposite coatings in 0.5 M potassium sulphate. In 0.5 M sodium chloride solution was obtained a little smaller value by 0.43 μA/cm^2 for same nanocomposite coatings. VOLTAMAS-

Table 1

Polarization resistance and capacitance values of nanostructured Al_2O_3–Ni composite coatings in 0.5 M sodium chloride and 0.5 M potassium sulphate solutions after different time of immersion calculated with equivalent circuit from Fig. 7

Solution	Data from impedance spectra	Time (h)				
		0.5	2	6	24	30
0.5 M sodium chloride	R_{p} (kOhms cm^2)	26.30	19.39	19.07	12.00	12.44
	C (μF/cm^2)	8.83	15.32	11.11	11.77	8.09
0.5 M potassium sulphate	R_{p} (kOhms cm^2)	26.93	25.25	25.37	26.56	29.88
	C (μF/cm^2)	4.90	5.25	4.13	4.95	4.79

Table 2
Polarization resistance values of nanostructured Al_2O_3–Ni composite coatings calculated from polarization potentiodynamic curves obtained after 30 min from immersion in solutions

Solution	E_{corr} (mV), Ag/AgCl	i_{corr} (μA/cm^2)	β_a (mV/decade)	β_c (mV/decade)	R_p from Tafel (kΩ cm^2)	Corrosion (μm/year)
0.5 M sodium chloride	−359.2	0.43	77.1	61.8	25.03	5.03
0.5 M potassium sulphate	−158.8	0.50	126.5	128.5	32.17	4.74

TER 4 calculates and displays the corrosion rate Corr. in mm/year: this rate is calculated from the i_{corr}: corrosion current density found, the *D* density, the *M* atomic mass and *V* valence entered in the Tafel dialogue box. The calculation is performed as follows:

$$\text{Corr} = \frac{i_{corr}(\text{A/cm}^2) \times M(g)}{D(\text{g/cm}^3) \times V} \times 3270 \quad (3)$$

with 3270 = 0.01 × [1 year (in seconds)/96497.8] and 96497.8 = 1 Faraday in Coulombs.

Comparing these values with the value reported for the polarization resistance and corrosion rate of nickel pure coating [20] at $R_p = 8.20$ ohms cm^2 and $i_{corr} = 4.1\ \mu$A/cm^2 obtained in 0.5 M sodium sulphate (similar to potassium sulphate) the conclusion is that Al_2O_3–Ni nanocomposite coatings have a better corrosion resistance and a smaller corrosion rate. Also it was reported that the corrosion rate for the Ni coating and composite coating Al_2O_3–Ni in a 0.5 M sodium sulphate solution decreases during the first day of exposure. With time the corrosion current for the Ni coating increases markedly, reaching 360 nA/cm^2. After 14 days the rate of corrosion of Al_2O_3–Ni composite coating is three times lower than that of the Ni coating [17].

This improvement of corrosion resistance could be due to the fine surface structure of composite coating compared with pure nickel coating as well as to the incorporation of Al_2O_3 nanoparticles into composite coatings.

4. Conclusions

The surface morphology of nanostructured Al_2O_3–Ni composite layers is different compared with pure nickel coatings: the regular crystal structure characteristic of electroplated nickel coatings was disturbed. The Al_2O_3 particles embedded in the nickel matrix perturb the nickel growth during electrodeposition.

Electrochemical impedance spectroscopy and polarization potentiodynamic methods are powerful techniques to investigate the corrosion protection of nanostructured Al_2O_3–Ni composite coatings. The polarization resistance values obtained from both methods are in good agreement.

The corrosion potential of nanostructured Al_2O_3–Ni is shifted to more negative values in 0.5 M sodium chloride (−359.2 mV) and to more positive values for same coatings in 0.5 M potassium sulphate (−158.8 mV).

From experimental data it was observed that the corrosion rate (corrosion current) is higher for nanostructured Al_2O_3–Ni composite coatings in 0.5 M potassium sulphate and a little bit smaller in 0.5 M sodium chloride. Thus the corrosion rate is smaller for nanocoatings in 0.5 M potassium sulphate (calculated value from corrosion current density is 4.74 μm/year) and for 0.5 M sodium chloride the rate of corrosion is a little bit higher (calculated value from corrosion current density is 5.03 μm/year).

The polarization resistance of nanocomposite coatings in 0.5 M sodium chloride decreases during 24 h of immersion, but after that increases slowly. Thus after 30 min of immersion the polarization resistance is 26.30 kOhms cm^2, decreasing after 24 h at 12.00 kOhms cm^2. The polarization resistance of nanocomposite coatings in 0.5 M potassium sulphate solution decreases during 2 h (after 30 min having the value of 26.93 kOhms cm^2 and 25.25 kOhms cm^2 after 2 h), after that the polarization resistance increases. So that after 30 h of immersion, the polarization resistance (29.88 kOhms cm^2) is a little bit higher than the value calculated from Nyquist impedance diagrams after 30 min of immersion, but in the same order of magnitude.

The nanostructured Al_2O_3–Ni composite coatings have a better corrosion resistance than pure nickel coating in agreement with others publication data.

The better corrosion resistance behaviour of Al_2O_3–Ni composite coatings could be due to the fine surface structure of composite coating compared with pure nickel coating as well as to the incorporation of Al_2O_3 nanoparticles into composite coatings acting as insulators on composite surface.

Acknowledgments

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