I. DOBOSZ*, E. RUDNIK*, L. BURZYŃSKA*

CODEPOSITION OF SiC PARTICLES WITH ELECTROLYTIC NICKEL

WSPÓŁOSADZANIE CZĄSTEK SiC Z NIKLEM W PROCESIE ELEKTROLIZY

Ni/SiC composite coatings were produced by electrodeposition from chloride-sulphate bath. The effect of SiC concentration on the percentage of embedded particles at two current densities (0.75 and 1.50 $A \cdot dm^{-2}$) was determined. SiC content in the nickel matrix was in the range of 13-23 vol%, but lower values were found for higher current density. Increased particles contents in the coatings practically did not change microhardness of deposits (approximately 300 HV), but it increased corrosion resistance. Morphology and particle distribution in the deposits was studied with optical and transmission electron microscopes. Specific surface charge of SiC particles as well as adsorption of Ni^{2+} ions on the powder particles were also determined.

Keywords: electrodeposition; composite; nickel; silicon carbide

Powłoki kompozytowe Ni/SiC otrzymywano na drodze elektrolizy z zastosowaniem kąpieli chlorkowo-siarczanowej. Określono wpływ stężenia SiC na skład osadów katodowych uzyskiwanych przy dwóch gęstościach prądu (0.75 and 1.50 $A \cdot dm^{-2}$). Udział SiC w osnowie niklowej wynosił 13-23 %obj., przy czym niższe zawartości stwierdzono w powłokach otrzymanych przy wyższej gęstości prądu. Wzrost zawartości fazy dyspersyjnej w osadach katodowych nie wpływa na mikrotwardość kompozytów (ok. 300 HV), następuje natomiast wzrost ich odporności korozyjnej. Morfologię powierzchni i rozkład cząstek dyspersyjnych w osnowie niklowej określano na podstawie obserwacji mikroskopowych. Wyznaczono ładunek powierzchniowy cząstek SiC oraz wielkość adsorpcji jonów Ni^{2+}.

1. Introduction

Incorporation of various particles with nickel has been commonly reported in the literature [1, 2]. Among them oxides (e.g.: Al_2O_3, ZrO_2, TiO_2) or carbides (e.g.: SiC, WC, TiC) as hard ceramic particles were used for improvement of hardness or wear resistance as well as thermal stability of the coatings. Moreover, a decrease in the corrosion rate of metal matrix in the presence of the particles was also reported [1, 2]. Such beneficial properties provide a wide application range of nickel composite layers in automotive, aerospace or military industries [3]. Electrodeposited nickel matrix composites with SiC particles seem to be the most often studied systems [1, 2, 4-7]. It is mainly due to feasibility of particle incorporation in a low-cost process. There is no general rule for the composite codeposition with high contents of the particles and each metal-particle system should be considered individually. However, the amount of the incorporated phase is dependent mainly on the particle size and powder concentration in the suspen-

sion, intensity of the bath agitation and current density [1, 2, 4-9]. A significant role in the codeposition process plays also surface properties of the particles. The adsorption of cations on the ceramic particles not only affects the surface charge but also determines the codeposition process. It is commonly accepted that a positive surface charge can enhance codeposition, because the particles are electrostatically attracted to the cathode. Moreover, the reduction of metal ions adsorbed on the particles is required for irreversible incorporation of the particles [1, 2, 5, 9]. The aim of this investigation was to determine the influence and current density and concentration of the particles in the plating bath on the composition and morphology of the Ni/SiC composites. The surface charge as well as adsorption of nickel ions on SiC surface was also studied. Microhardness and corrosion resistance of the obtained coatings was determined.

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, LABORATORY OF THE PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, FACULTY OF NON-FERROUS METALS, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND

2. Experimental

Electrodeposition of Ni/SiC composites was carried out in Watt's-type baths with the composition: 200 g/dm^3 NiCl$_2$·6H$_2$O, 25 g/dm^3 NiSO$_4$·7H$_2$O, 25 g/dm^{3}H$_3$BO$_3$ and 1 g/dm^3 saccharin and pH of 4.4. Technical grade α-SiC powder (with the average particle diameter of 4 μm) with concentrations in the range of 10-50 g/dm^3 was used. Electrolysis was conducted in a vessel containing 2 dm^3 of the suspension. Rectangular stainless steel plates with area of 0.6 dm^2 were used as the cathode substrates. Separated rectangular (5 × 6 cm) nickel rolled plates (99.9%) were used as anodes. A peristaltic pump (7.4 dm^3/h) and a magnetic stirrer (400 rpm) were used for the suspension agitation. The electrolysis was carried out in galvanostatic conditions at two current densities of 0.75 and 1.5 A/dm^2 for 8 hours. Galvanostatic polarization curves were determined in the same conditions as described above. Before registration of the curves, a layer of the deposit was obtained at the current density of 0.75 A·dm^{-2} for 1 h. Cathode potential was registered versus saturated calomel electrode and then calculated according to normal hydrogen electrode (NHE). The as-plated and polished surfaces of the deposits were examined by optical microscope (NEOPHOT-32). Transmission electron microscope (JEM 2010ARP) was used for observations of the composite structure. SiC volume fraction in the nickel matrix was determined by image analysis using the "Aphelion" software. Calculations were done on grey levels images of polished deposit surfaces observed with the optical microscope. Vickers microhardness measurements (100 g load; PTM-3) were carried out on the polished deposits surfaces. Corrosion resistance of the Ni/SiC coatings was determined in 1 M H$_2$SO$_4$ in potentiodynamic polarization studies. A three-electrode cell (100 cm^3) with a composite working electrode (2 cm^2), a platinum counter electrode (1 cm^2) and Ag/AgCl as a reference electrode was used. The scans with the rate of 10 mV/s were realized in the potential range from -1000 mV to 500 mV (vs. Ag/AgCl). Polarization curves were registered in $E-\log i$ mode and corrosion potential as well as corrosion current density were determined from the cross sections of extrapolated linear parts of the curves.

Effective surface charge of the particles was determined by potentiometric titration. It was performed in 0.09 M NaCl solutions (50 cm^3) in the presence of 0.2 g of the SiC powder. 0.05 M HCl was added to the bath until constant final pH (3-5) was achieved. The amount of H$^+$ ions consumed on the particles surface was determined by subtracting of the values obtained for the background electrolyte and suspension. The surface charge of the powder was expressed in C/g, therefore it is

called as "specific charge" in further considerations. Adsorption experiments were also carried out. Adsorption of Ni^{2+} was determined in diluted (10 times) working baths (pH = 4.4). 50 cm^3 of the solutions with 0.2 g of the SiC powder were used in all experiments. Samples of solutions were taken after various time periods and Ni^{2+} concentrations were determined by means of atomic absorption spectroscopy (Perkin Elmer Atomic Absorption Spectrometer 3110). The powder was used as-received, without any cleaning procedure before all experiments.

3. Results and discussion

The cathodic polarization curves were determined in the plating baths with various concentrations of SiC particles (Fig. 1). It was observed that deposition of nickel composite required a considerable overvoltage, but it is characteristic for nickel deposition. The increased powder concentration shifted gradually the polarization curves towards more positive potentials for the currents densities below 0.5 A·dm^{-2}. At higher currents the same tendency was observed, except the curve registered in the bath with the lowest powder content. It seems that SiC particles can decrease the cathode polarization due to ionic clouds created around SiC particles. Watson [5] found that SiC particles can impose a positive displacement of the polarization curve for nickel reduction. It was attributed to the increase in the adsorption of H$^+$ and Ni$^+$ intermediate near the electrode, which can participate in the cathodic reaction.
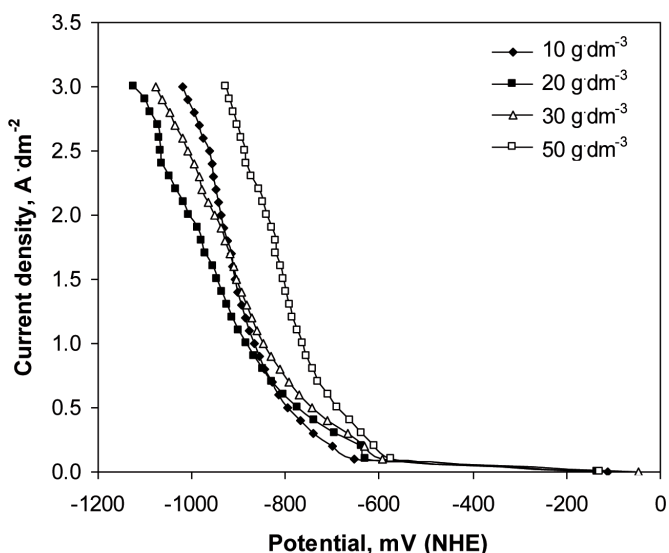

Fig. 1. The influence of SiC concentration on cathodic curves of Ni/SiC codeposition

Fig. 2 shows the dependence of the SiC percentage in the composites on the powder concentration in the suspension for two current densities. It was found

that increased addition of the carbide to the plating bath enhanced the particle incorporation. It led to a change of the SiC fraction in the deposits from approximately 13-15 vol% for 10 g·dm^{-3} SiC to approximately 18-25 vol% for 50 g·dm^{-3} SiC. This tendency was similar to characteristics reported for nickel matrix composites by other authors [2, 4, 6]. Increase in the current density was accompanied by a decrease in the SiC contents by 3-4 vol%. It seems rather obvious, since for the same hydrodynamic conditions in the electrolyser a flux of the particles to the cathode surface remained unchanged, whereas increased current density promoted nickel matrix deposition. It was confirmed by the values of current efficiencies, since higher values for higher current density were obtained (Fig. 3). Current efficiency η was calculated according to the formula:

$$\eta = \frac{m_{Ni}}{k_{Ni}It} \cdot 100\% = \frac{m_{Ni/SiC} - m_{SiC}}{k_{Ni}It} \cdot 100\% \qquad (1)$$

where: $m_{Ni/SiC}$, m_{Ni}, m_{SiC} - mass of the composite, nickel matrix and SiC in the composite, respectively; k_{Ni} – electrochemical equivalent of nickel, I – current intensity, t – electrolysis time. SiC content in the composite was necessary to account in the calculations since only nickel ions could be reduced on the cathode. Mass of the composites was determined gravimetrically, while mass of SiC incorporated was calculated on the volume content of the particles in the deposit, according to the equation:

$$m_{SiC} = \frac{m_{Ni/SiC} \cdot \alpha \cdot d_{SiC}}{\alpha \cdot d_{SiC} + (1 - \alpha) \cdot d_{Ni}} \qquad (2)$$

where: α – volume fraction of SiC in the deposit, d_{SiC}, d_{Ni} – density of SiC and nickel, respectively.
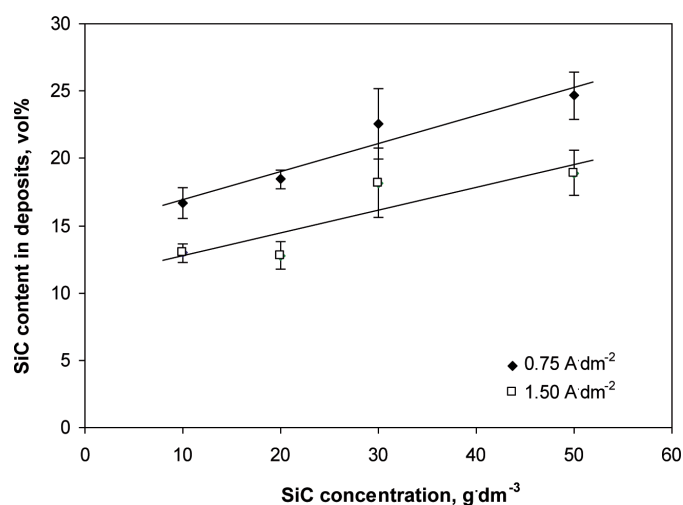

Fig. 2. The influence of the powder concentration it the bath and current density on the SiC contents in the composites

Particle incorporation into metal matrix during electrolysis is usually considered to be associated with a pos-itive surface charge of the particles. It originates from the association of hydrogen ions by superficial functional groups and/or from adsorption of the metallic ions. The presence of cations can promote electrophoretic migration of the particles towards negative cathode. However, it seems that this phenomenon is prominent only for nano-sized particles. To clarify the codeposition of micron-sized SiC particles used in this study some adsorption studies were performed.
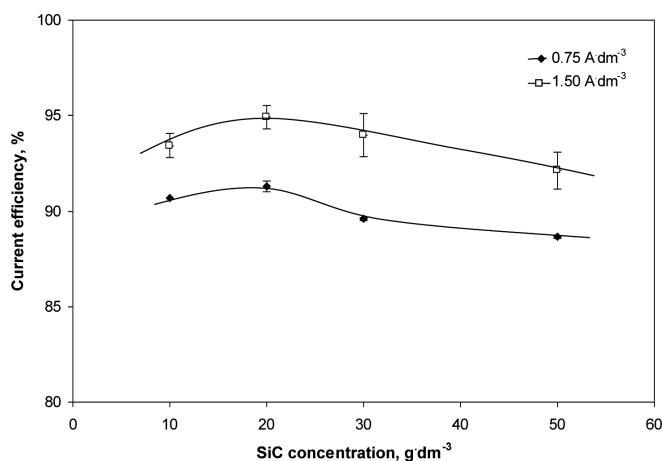

Fig. 3. Dependence of the current efficiency on SiC concentration in the bath

Specific surface charge of SiC particles was determined in NaCl solution. It was assumed that H$^+$ and OH$^-$ ions define the surface charge of carbide particles. Formation of positive or negative charged sites on the SiC surface can be described by the following equations:

$$S - OH + H_2O \leftrightarrow S - OH_2^+ + OH^- \qquad (3)$$

or

$$S - OH + H_2O \leftrightarrow S - O^- + H_3O^+ \qquad (4)$$
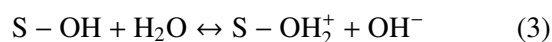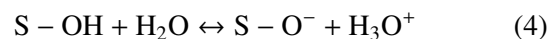
where: S is a particle surface, while -OH represents carboxyl, phenolic and lactonic acidic groups or basic group on the carbide surface [10] created during SiC oxidation [11]. The superficial groups can dissociate or associate an additional proton from the solution causing changes of the pH. The particle surface becomes positively charged by reacting with H$^+$ ions from the solution (Eq. (3)) or negatively charged due to loss of H$^+$ (Eq. (4)). It corresponds to the increase or decrease in the solution pH under powder addition, respectively. It was found that immersion of the SiC powder in the NaCl solution was accompanied by alkalization of the electrolyte, hence determination of the value of the positive SiC surface charge was performed by potentiometric titration with HCl. It was based on the assumption that only OH$^-$ ions (formed according to Eq. (3)) could

participate in this reaction. The specific surface charge σ of SiC was calculated according to the formula:

$$\sigma = \frac{cF(V_{NaCl+SiC} - V_{NaCl})}{m_{SiC}} \quad (5)$$

where: c – HCl concentration, F – the Faraday constant, m_{SiC} – mass of the powder, $V_{NaCl+SiC}$ and V_{NaCl} – HCl volumes used during titration of suspension and background electrolyte to the appropriate final pH, respectively. It was found that specific surface charge of the SiC was positive, but it decreased from approximately 1.8 C·g^{-1} to approximately 0.5 C·g^{-1} with increased pH from 3 to 5 (Fig. 4). It was consistent with values reported by Grosejan et al. [12], who found a positive surface charge of SiC in NaCl solutions (10^{-3} – 1 M) for pH in the range of 2.5-5.5. It worth also to note that negative values of surface charge in acidic baths were also found for SiC powders [13]. Such discrepancies are understandable, since a sign of SiC surface charge is dependent on the purity of the powder, production method and surface pretreatment.
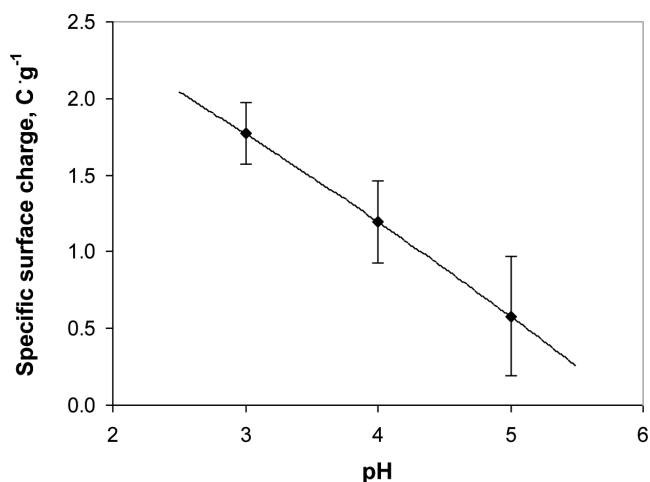

Fig. 4. The influence of pH on SiC specific surface charge in 10^{-3} M NaCl

Fig.5 shows the influence of time on the adsorption of Ni^{2+} ions on SiC powder. It was found that after 15 min of the SiC contact with the solution a characteristic plateau (at approximately 10 mg Ni^{2+}/g SiC) was observed. It shows that adsorption-desorption equilibrium was achieved quite fast. It is beneficial to the codeposition process, since stable plating bath can be achieved in short time after immersion of the powder in the electrolyte.

Obtained results confirm that incorporation of the SiC particles into nickel matrix proceeds trough a few stages. These are:
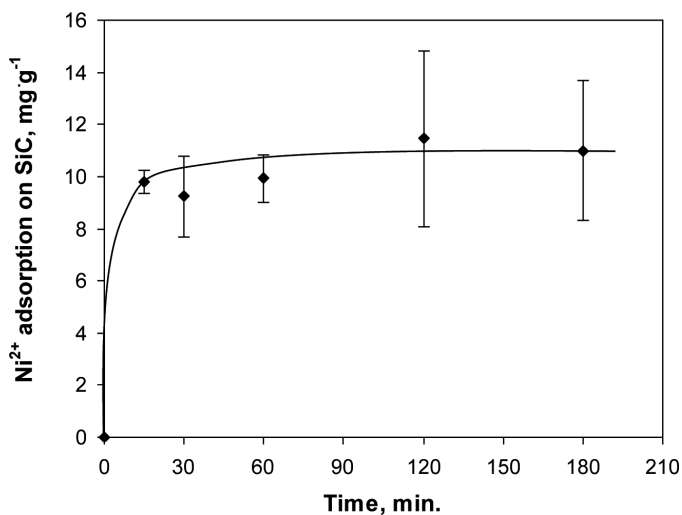

Fig. 5. The influence of time on adsorption of Ni^{2+} ions on SiC particles

(i) adsorption of ionic species (H^{+}, Ni^{2+}) on SiC surface resulting in a positive surface charge of the particles;
(ii) movement of the particles by forced convection to the cathode surface;
(iii) adsorption of the particles on the cathode surface provided by a positive surface charge of the particles;
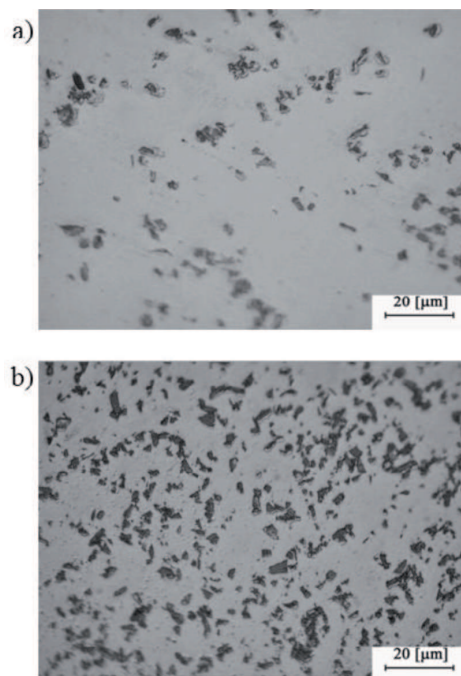(iv) reduction of adsorbed nickel ions by which the SiC particles are irreversibly incorporated in the metal matrix.

Fig. 6. Micrographs of polished surfaces of Ni/SiC composites deposited at 0.75 A·dm^{-2}: a) 10 g·dm^{-3} SiC, b) 50 g·dm^{-3} SiC

Microscopic observations of the polished surface of the composites showed allocation of the particles within the matrix. Fig. 6 shows exemplary micrographs of

the composites. It was found that the SiC particles were uniformly distributed within the matrix. TEM microphotograph of the composites showed that all SiC particles were strictly surrounded with the metallic matrix (Fig.7a). There were no micropores or holes. Ni matrix characterized with a very fine grain structure. The average diameter of the metallic grains was about 10 nm (Fig.7b).
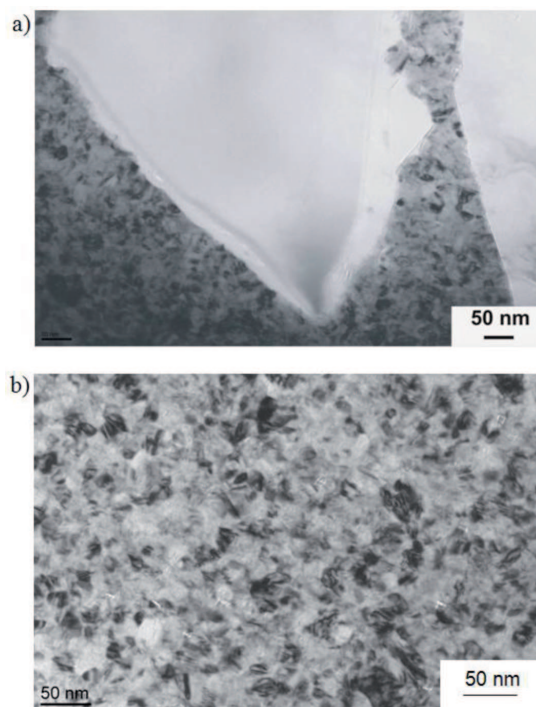

Fig. 7. TEM micrographs of Ni/SiC composite (50 g·dm^{-3} SiC, 1.50 A·dm^{-2}): a) SiC particles in the deposit, b) nickel matrix

The microhardness of the composites was determined (Fig. 8). Practically no influence of SiC content in the deposits or current density was found and the Vickers microhardness of coatings reached approximately 300 HV. It suggests that a fine grained nickel matrix was responsible mainly for hardness of the deposits.
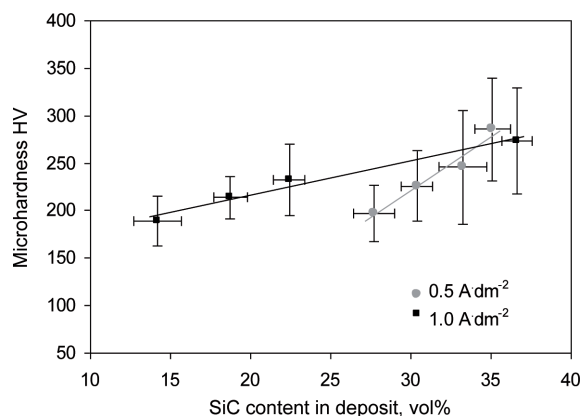

Fig. 8. The influence of SiC content in the deposits on the microhardness of the composites

However, results for every tested coating were characterized by quite wide scatter of data (up to ± 100 HV). This effect can be related to locally varied distribution of hard SiC particles in the microareas and positioning of the microindenter on the material surface.

Corrosion resistance of Ni/SiC coatings was also tested. Fig. 9 shows exemplary polarization curves registered in H$_2$SO$_4$ solution. Detailed data on the corrosion current densities and corrosion potentials are summarized in Table 1. It was found that the increased SiC content in the composites improved corrosion resistance of the deposits, but it was better for the coatings obtained at lower current density. It suggests that decrease in the corrosion currents at higher amounts of particles embedded in the matrix was probably due to non-conducting properties of silicon carbide and, hence, less receptivity for formation of galvanic cells in uniform nickel matrix.
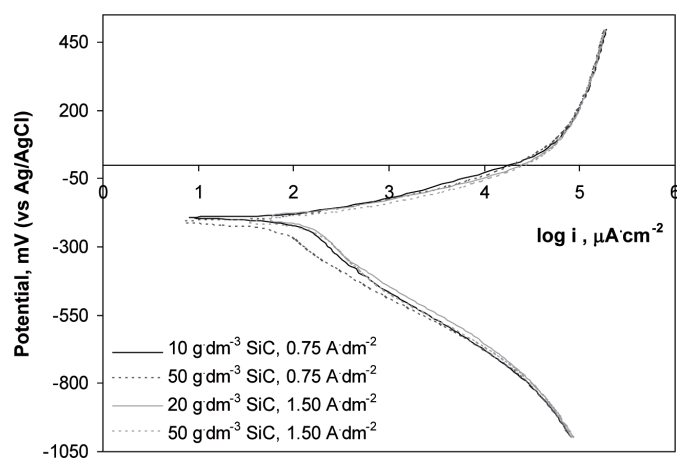

Fig. 9. Polarization curves of Ni/SiC composites in 1 M H$_2$SO$_4$ (scan rate: 10 mV·s^{-1})

TABLE 1

Corrosion resistance of Ni/SiC deposits

SiC concentration, g.dm^{-3}	SiC content in deposit, vol%	Corrosion current density, μA·cm^{-2}	Corrosion potential, mV (vs Ag/AgCl)
0.75 A·dm^{-2}			
10	16.6	60.3	-230
20	18.4	52.5	-200
30	22.6	39.8	-240
50	24.7	39.8	-210
1.50 A·dm^{-2}			
20	12.8	89.1	-200
30	18.2	66.1	-250
50	18.9	63.1	-230

4. Conclusions

Ni/SiC composite layers of were produced by the electrodeposition from the Watt's-type bath. SiC incorporation increased under powder addition to the bath, but increase in the current density promoted nickel matrix deposition. The last one resulted in smaller particles contents in the coatings accompanied by an increase in the current efficiencies. Codeposition of SiC in relation to the surface features of the particles was also discussed. Microscopic observations of the coatings revealed uniform distribution of the particles within nickel as well as a very fine grained structure of the matrix. Microhardness of the composites was approximately 300 HV, however, a wide scatter of data related to locally varied distribution of SiC particles in the microareas was observed. Corrosion resistance of the coatings was improved by increased SiC content in the composites due probably to less receptivity for formation of galvanic cells in uniform nickel matrix in the presence of non-conducting ceramic inclusions.

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