

Electrodeposition and characterization of Ni-TiO₂ composite coatings

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Electrodeposition of nickel-titania (Ni-TiO₂) composite coatings was carried out from an additive-free Watts solution containing 10 and 20 g/l dispersed TiO₂ particles (size 2 – 3 μm). The influences of current density, bath temperature, TiO₂ concentration in the bath were studied. The corrosion performance, wear behavior and electrocatalytic properties of Ni-TiO₂ composite coatings were investigated. The results indicated that Ni-TiO₂ composite coatings with TiO₂ content 8 –10 wt.% exhibited higher corrosion and wear resistance than Ni coatings. Ni-TiO₂ composites showed electrocatalytic activity for the methanol oxidation.

1. Introduction

Electrodeposition is one of the most important techniques for producing metal matrix composites, owing to many merits, such as low cost, low operating temperature, ease of fabrication and high quality deposits. The metal matrix composites are materials in which the properties of a metallic host material are modified with addition of the second dispersed phase (micro, submicron- or nano-sized particles) by electrodeposition process. Nickel is commonly used as continuous metallic matrix phase of composite coatings because of the high rates of deposition; nickel has excellent mechanical properties and high corrosion resistance; the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and operating parameters of the plating solution [1, 2]. The dispersed phase can be hard oxides (Al₂O₃, TiO₂, SiO₂) [3 – 5], carbides (SiC, WC) [6 – 8], nitrides (BN, AlN) [9, 10] or polymers (PE, PTFE) [11, 12]. Many types of composite coatings have been developed to enhance corrosion

resistance, microhardness, wear resistance, self-lubrication, etc. The percentage and distribution of dispersed particles in metal matrix of composite coatings determine their mechanical and physicochemical properties. Moreover, the rate of particles' incorporation depends on the nature of particles (size, shape, charge) and the deposition conditions (current density, temperature, pH) [1 – 4, 8 – 10, 11].

Nickel based electrodes can be used as catalyst due to its surface oxidation properties. Their electrocatalytic activity depends mainly on the catalytic role of Ni(OH)₂/NiOOH redox couple. Nickel displays potential catalytic properties in a wide number of processes: hydrogen evolution reaction, oxygen evolution reaction, hydrogenation reactions, electrosynthesis of amines, electrooxidation of small organic molecules (alcohols, aldehydes, amino acids, sugars) [13 – 19]. Electrooxidation of small organic molecules gives a promising way for direct converting the chemical energy of a fuel and an oxidant into electric energy in fuel cells. Nickel composite coatings show a higher catalytic activity than pure Ni coatings towards the electrochemical oxidation of methanol due to smaller grain size and larger actual surface area [17 – 19].

Thus, nickel based composite coatings are becoming important for different engineering applications: corrosion protection, hardening of machinery, increasing wear resistance, tool production, electrocatalysis. The aim of this work is to investigate the influence of deposition conditions on the incorporation of micro-sized TiO₂ particles in nickel matrix and to study corrosion and electrocatalytic properties, wear behavior of Ni-TiO₂ composites.

2. Experimental details

Nickel coatings and composite Ni-TiO₂ coatings were electrodeposited from an additive-free Watts solution with a composition (in g/l): NiSO₄·7H₂O 240 – 260; NiCl₂·6H₂O 40 – 60; H₃BO₃ 30 – 40. The deposition conditions were cathode current density, i , 0,8 – 2,5 A/dm², pH 4 – 5, bath temperature, t , 20 and 50 °C, concentration of TiO₂ powder (size 2 – 3 μm) in bath, C_{TiO_2} , 10 and 20 g/l; metallurgical nickel anodes. The electrolyte was stirred by a magnetic stirrer in the electrodeposition process in order to maintain the uniform particles concentration and prevent

sedimentation in solution. Plain carbon steel and tool steel samples were the cathodes. The thickness of coatings was 20 and 30 μm .

Before the electrodeposition, the samples were degreased in alkaline solution, dipped in acid solution (10% HCl with 5 g/l urotropine) and finally washed with distilled water. After electrodeposition, the samples were rinsed by distilled water and dried with air at room temperature. TiO_2 content (wt.%) in the deposits was determined by gravimetric measurements.

Electrochemical studies were carried out in a conventional three-electrode cell powered by potentiostat/ galvanostat PI-50-1.1. An Ag/AgCl-Saturated KCl, a Pt wire and a sample ($S = 1 \text{ cm}^2$) with electrodeposited coating were used, respectively, as the reference, counter and working electrodes,. The corrosion performance of electrodeposited coatings was investigated by potentiodynamic (potential sweep rate, v , was 5 mV/s) and potentiostatic polarization. A model corrosion medium of 5% NaCl solution with pH ~ 6 at temperature 15 – 20 $^\circ\text{C}$ was used. The investigations of methanol oxidation reaction were performed by using cyclic voltammetry at $v = 10$ mV/s. Measurements were carried out at temperature 15 – 20 $^\circ\text{C}$ in 1M NaOH solution in the absence and the presence of 1M of methanol. Prior to performing the polarization measurements, all investigated samples were maintained for a definite period in the solution. Potentials are presented in a standard hydrogen scale. The corrosion potential (E_{cor}) and corrosion current density (i_{cor}) were obtained using the Tafel exploration method. Corrosion rate K (mm/year) was calculated from the following equation

$$K = 8,76 \cdot \frac{i_{\text{cor}} \cdot q_{\text{Ni}}}{\rho_{\text{Ni}}} \quad (1)$$

where i_{cor} is corrosion current density in A/m^2 , q_{Ni} is electrochemical equivalent in $\text{g}/(\text{A}\cdot\text{h})$, ρ_{Ni} is the density in g/cm^3 .

For measuring the wear resistance, dry sliding wear tests were carried out by using a pin on disk type machine on cylindrical samples against a steel wheel. The changes of linear size of sample due to wear of the pin was measured by differential

capacitance sensor. The sliding parameters were rotation speed of the disc 40 m/min, the applied load 60 N, the sliding distance 1000 m.

3. Results and discussion

The effect of deposition conditions on Ni-TiO₂ coatings composition is shown in Table 1. According to the obtained data, the content of TiO₂ particles in the coatings grows considerably due to the increase of concentration of dispersed phase in electrolyte. Apparent influence of current density and bath temperature on incorporation of TiO₂ particles in nickel matrix was observed.

Table 1. Effect of deposition conditions on Ni-TiO₂ coatings composition

i, A/dm ²	C _{TiO₂} , g/l	t, °C	Ni (wt.%)	TiO ₂ (wt.%)
0,8	10	20	95 – 97	3 – 5
1,0	10	20	98 – 99	1 – 2
1,0	10	50	86 – 88	13 – 15
1,5	10	50	90 – 92	8 – 10
1,5	20	50	75 – 78	22 – 25
2,5	10	50	97 – 99	1 – 3
2,5	20	50	82 – 85	15 – 18

These results may be explained by the adsorption mechanism of dispersed particles and metal codeposition [1, 11, 18]. These phenomena play a considerable role in particle codeposition with nickel, due to the high adsorption affinity of nickel for the solid particles. According to this mechanism, the rate of codeposition is determined by initiation of real contact between the metal ions adsorbed on dispersed particles and the cathode surface. Once the particles are absorbed on the cathode surface, they will be imbedded into metal of coatings. With increased amount of TiO₂ dispersed particles in the electrolyte, nickel will be deposited with a higher amount of dispersed particles and a large area of the cathode surface will be covered by them.

It is known, that the increase of current density increases the Coulombic force between Ni²⁺ absorbed on dispersed particles and the cathode. Thus, the rate of

movement of TiO₂ particles from bulk solution to the cathode surface increases, agglomeration of dispersed particles in the solution near the cathode may happen. Big agglomerates were not encapsulated and incorporated in metal matrix. Effect of bath temperature is conditioned on better efficiency of nickel deposition.

Fig. 1a presents potentiodynamic anodic polarization curves of galvanic nickel and Ni-TiO₂ composite coatings deposited at $i = 1,5 \text{ A/dm}^2$ and C_{TiO_2} 10 and 20 g/l. Potentiostatic polarization curves (Fig. 1b) were obtained to evaluate corrosion data. The E_{cor} , i_{cor} and K values were calculated using the Tafel extrapolation method and equation (1) and they are given in Table 2.

Table 2. Corrosion data of Ni and Ni-TiO₂ coatings

Coating	E_{cor} , V	i_{cor} , A/m ²	K, mm/year
Ni	-0,175	0,141	0,15
Ni-TiO ₂ , TiO ₂ content 8 – 10 wt.%	-0,085	0,076	0,08

It was found, that incorporation in nickel matrix of dispersed TiO₂ particles results in shift of corrosion potentials to more positive values, decreases currents of anodic dissolution and corrosion currents in comparison with the pure Ni coatings. One should note here that anodic currents were higher for Ni-TiO₂ coatings deposited at C_{TiO_2} 10 g/l (TiO₂ content 22 – 25 wt.%) at $E > 0,2 \text{ V}$ than for nickel coatings (curve 1, 3 Fig. 1a). It can be attributed to the high content of TiO₂ in deposits which enhances their surface roughness.

The improvement of corrosion behavior of Ni-TiO₂ composite coatings can be connected with screening effect of metal matrix by dispersed particles with low electric conductivity and decrease in pitting at incorporation of dispersed particles. Besides, incorporation of TiO₂ into nickel coatings may reduce the size of Ni grains, due to the distribution of TiO₂ particles on the boundaries of Ni grains in the electrodeposition [18].

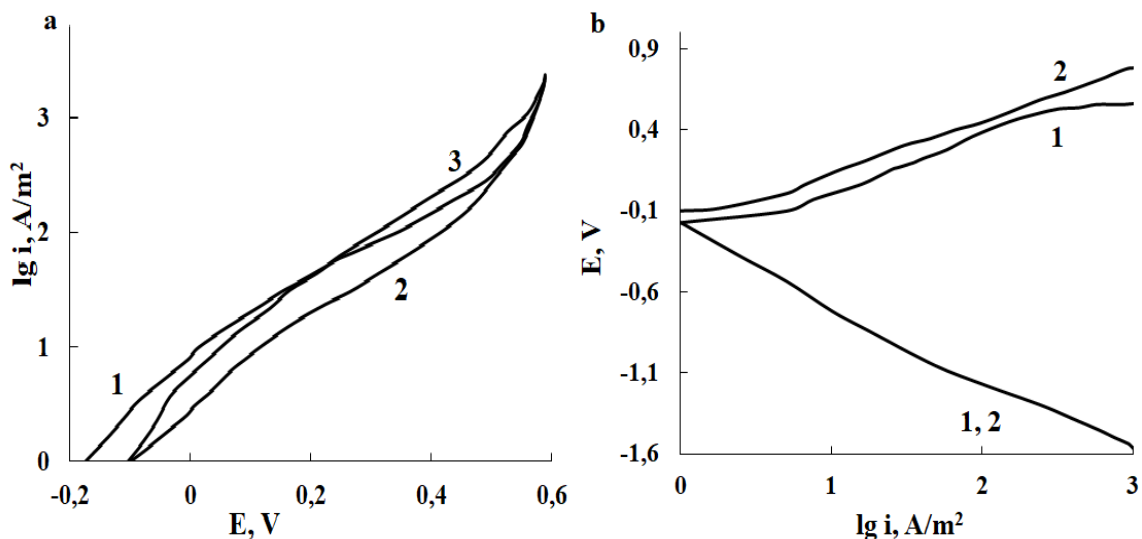


Fig. 1. Potentiodynamic anodic polarization curves, $v = 5 \text{ mV/s}$; (b) potentiostatic polarization curves in 5% NaCl. Ni coatings (1) and Ni-TiO₂ coatings (2, 3) deposited at $i = 1,5 \text{ A/dm}^2$ and C_{TiO_2} : 10 g/l (2) and 20 g/l (3)

The relations between sliding distance and wear of samples with Ni and Ni-TiO₂ coatings is drawn in Fig.2. The results indicate that the wear of the coated surface increases with sliding distance. On the other hand, the wear of some Ni-TiO₂ composite coatings is lower than Ni coatings (curve 3 Fig. 2a; curve 3 Fig. 2b). At sliding distance 1000 m Ni coatings show the wear around 0,150 mm, but the Ni-TiO₂ composite coating deposited at $t = 20 \text{ }^\circ\text{C}$ and current density 1 A/dm^2 (TiO₂ content 1 – 2 wt.%) show the wear 0,058 – 0,060 mm and Ni-TiO₂ composite coating deposited at $t = 50 \text{ }^\circ\text{C}$ and $i = 1,5 \text{ A/dm}^2$ (TiO₂ content 8 – 10 wt.%) show the wear 0,065 – 0,070 mm. By comparison, wear of uncoated samples was 0,450 – 0,495 mm.

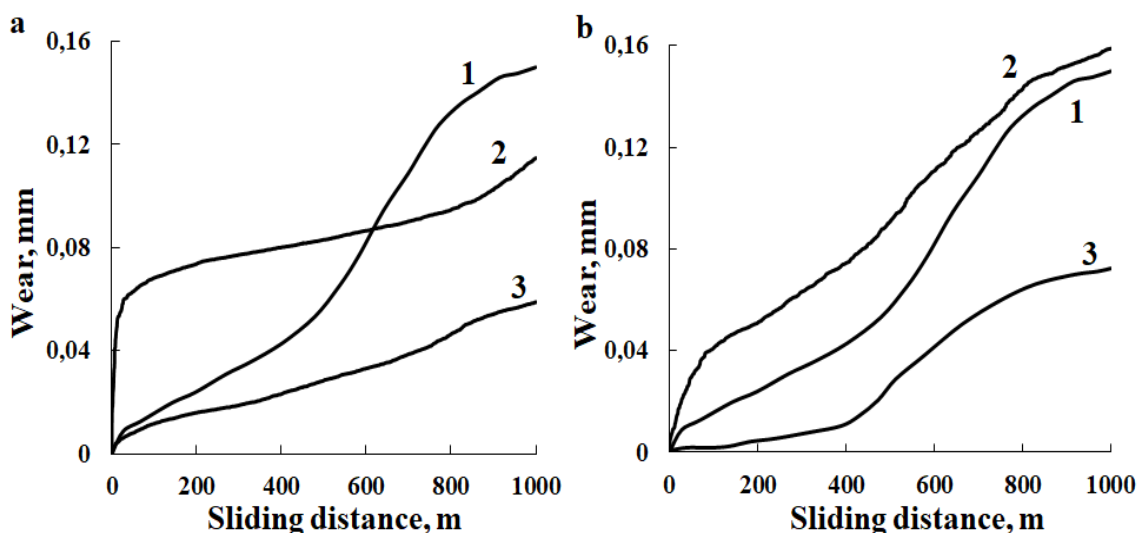


Fig. 2. Relations between sliding distance and wear of samples with Ni coating (1) and with Ni-TiO₂ coating (2,3). (a) Ni-TiO₂ coating deposited at $t = 20$ °C and $i: 0,8$ A/dm² (2), 1 A/dm² (3); (b) Ni-TiO₂ composite coating deposited at $t = 50$ °C and $i: 1$ A/dm² (2), 1,5 A/dm² (3)

It was established, that wear behavior of Ni-TiO₂ composites depends on deposition conditions which determinate TiO₂ content into deposits and size of Ni grains [1, 2]. The improvement of wear behavior for some Ni-TiO₂ composites with TiO₂ content 1 – 10 wt.% may result from optimum number and distribution of dispersed particles in Ni matrix. TiO₂ particles with high hardness are barriers for shift of coating microlayers that lead to changing the friction conditions in sliding couple.

Fig. 3 shows cyclic voltammograms of Ni and Ni-TiO₂ coatings in 1M NaOH in the absence and presence of methanol. Two small peaks are observed in the voltammograms of Ni and Ni-TiO₂ coatings in 1M NaOH in anodic direction. One – at about 0,10 – 0,12 V due to formation of NiO and Ni(OH)₂ and the other – at about 0,65 – 0,7 V due to conversion of Ni(OH)₂ to NiOOH and enrichment of Ni³⁺ species on the electrode surface.

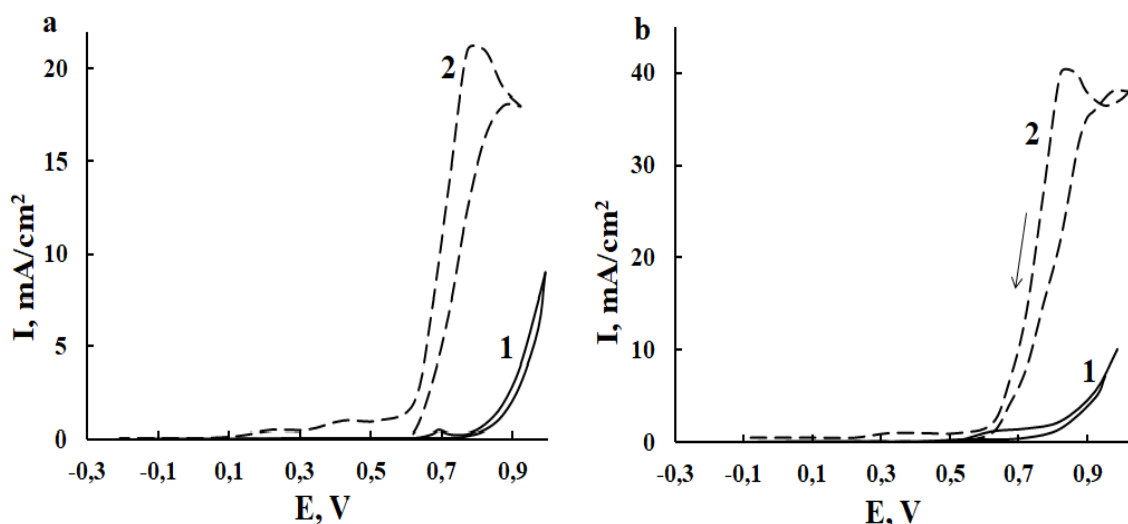


Fig. 3. Cyclic voltammograms in the absence (1) and the presence of 1M of methanol (2). (a) Ni coating; (b) Ni-TiO₂ coating; deposition conditions were $i = 1,5 \text{ A/dm}^2$, $t = 50 \text{ }^\circ\text{C}$, $C_{\text{TiO}_2} = 10 \text{ g/l}$, $v = 10 \text{ mV/s}$

The electro-oxidation of methanol on pure Ni and Ni-TiO₂ coatings starts at about 0,65 V when the electrode surface is covered with formed NiOOH species, then the current density reaches its maximum values at around 0,87 – 0,9 V in anodic direction. The response of methanol electro-oxidation at Ni-TiO₂ composite coatings is larger than the response obtained for pure electrodeposited nickel. Thus the oxidation current density of CH₃OH at 0,87 V was 18 mA/cm² on Ni coating and 35 mA/cm² on Ni-TiO₂ coatings (curve 2 Fig. 3a and 3b).

It is seen from Fig.3 that another reoxidation peak appeared in the reverse scan at about 0,8 V. This peak was, probably, due to the reoxidation of CH₃OH or the intermediate products generated during methanol oxidation. Formate and CO₂ were identified as the main reaction products in alkaline solutions [18], but it is possible that formation of absorbed CO may occur. Absorbed CO causes deactivation and blocking of the active sites of electrode surface during oxidation process. In the reversible half cycle absorbed intermediates and products are removed and the oxidation of CH₃OH continues at the initial stage of the cathodic half cycle. The rate of methanol oxidation in the reverse scan drops as the unfavorable potentials ($E < 0,5 \text{ V}$) are reached.

It was suggested that methanol is oxidized on Ni and Ni-TiO₂ coatings through the reaction with NiOOH to form Ni(OH)₂, that is NiOOH acts as electron transfer mediator for the oxidation process [16 – 18]



The enhancement of the catalytic activity of Ni-TiO₂ composite coatings was probably attributed to the presence of the mixed oxides (the nickel oxides and titanium oxides) which can be good electron transfer mediators for the oxidation process of organic molecules [18, 19]. In addition, the presence of TiO₂ dispersed particles can reduce the grain size of Ni and increase the actual surface area of electrodes that lead to formation of the great amount of active sites.

4. Conclusions

Composite coatings consisting of nickel matrix and TiO₂ particles were obtained by means of electrodeposition. The content of TiO₂ particles in the coatings depends on current density, bath temperature, TiO₂ concentration in the bath. From results of electrochemical studies and wear tests, a conclusion can be drawn that Ni-TiO₂ composite coatings with TiO₂ content of 8 – 10 wt.% have improved corrosion and wear behavior. These composite coatings were deposited at current density of 1,5 A/dm², bath temperature of 50 °C and concentration of dispersed particles of 10 g/l.

Ni-TiO₂ composite coatings showed a higher catalytic activity than pure Ni coatings towards the electro-oxidation of methanol. The process of methanol oxidation occurs at E = 0,65 – 0,9 V in anodic direction and continues in the initial stage of the cathodic half cycle of voltammograms.

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