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ELECTRODEPOSITION AND CHARACTERIZATION OF Ni-Si NANOCOMPOSITE COATINGS

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ABSTRACT

In this paper is presented morphological aspects and corrosion behaviour of composite coatings having nickel as metal matrix and silicon as dispersed phase obtained during electrodeposition process of nickel. Silicon mean diameter size of particles particles by 50 nm. The Ni-Si composite coatings were electrodeposited from a suspension silicon particles in aqueous nickel sulphate electrolyte by adding 10g/L and 20g/L of silicon particles in the electrolyte solution. The morphological aspects of the coatings and inclusion on particles were investigated using SEM and EDX. As test solution NH_4OH 0.5M (specific coke industry) was used in a three electrode open cell with nickel based nanostructured composite coatings as working electrode (WE), a platinum electrode as counter electrode (CE) and an Ag/AgCl electrode as reference electrode (RE).

KEYWORDS: nanocomposite coatings, silicon, nickel, polarization resistance

1. Introduction

Composite materials have been designed to replace a growing proportion, ferrous and non-traditional materials, which are characterized by some shortcomings on the performance, processes for obtaining and processing, dimensions, weights, geometric complexity, usage and costs.

Applications of composite coating technology can now be found in general consumer products and more applications are on the horizon.

Electrodeposition of ceramic, polymer and metal powders within metal, ceramic or polymer matrix produces composite coatings with attractive properties such as microhardness, polarization resistance, wear-resistance [1]. The production of composite coatings can be achieved through electrochemical deposition of the matrix material from a solution containing suspended particles such as: oxides (TiO_2 [2], Al_2O_3 [3], CeO_2 [4], ZrO_2 [5]), carbides (SiC, WC), nitrides, metal powder (Si [6, 7], P [8], Co [9], W, B [6]).

Nickel matrix composites containing particles like oxides, carbides, nitrides or diamond have been developed for their improved wear resistance and dispersion strengthening.

Among the solid particles used for reinforcement, SiC is the most frequently studied and applied [9-11].

Considerable researches have been mainly focused on the fundamental conditions of the electrolysis such as composition and pH of the electrolyte, the presence of additives, temperature agitation rate, density and type of the current, surface properties of particles, their size and concentration in the bath [12].

The present study aims to codeposit Si into nickel matrix. The effects of Si concentration in the suspension, current density, temperature and pH of the plating bath on silicon inclusion into the deposit were studied. Microhardness and corrosion behaviour of nickel–silicon (Ni–Si) composite in NH_4OH 0.5 M solution have been studied. Microstructure of the composite has also been investigated and reported.

The novelty of the work is the use of nanometer silicon as disperse phase.

2. Experimental procedure

The coating was plated on carbon steel plates (measuring 100x30x2 mm). The nickel matrix was prepared from sulphate electrolyte with the following composition $NiSO_4 \cdot 7H_2O$ 110g/L + Na_2SO_4 x $10H_2O$ 110 g/L + NH_4Cl 25g/L+ H_3BO_3 15g/L, at cathodic current density 2 A/dm^2 and 3 A/dm^2 with electrolyte stirring. The stirring rate in the electrolyte was 500, 750 and 1000 rpm. The electrodeposition was carried out for one hour. Silicon powder (dispersed phases) with a concentration 10 g/L and 20 g/L were introduced into the bath to obtain the composite coatings. The mean diameter size of particles of

silicon powder was 50 nm. The pH of solution was in the range 5-6, the temperature was kept at 293K.

The morphologic aspects of the coatings were investigated by scanning electron microscopy method. The experimental measurements of the Vickers microhardness of composite deposits are described in [13].

Also this paper present the electrochemical corrosion behavior of nanostructured composite coatings using potentiodynamic polarization method.

As test solution NH_4OH 0.5 M (specific coke industry) was used in a three electrode open cell with nickel based nanostructured composite coatings as working electrode (WE), a platinum electrode as counter electrode (CE) and an Ag/AgCl electrode as reference electrode (RE) (E_{RE} = +200 mV/ENH). For potentiodynamic polarization measurements was used initial potential (I. P.) – 1000mV (Ag/AgCl), final potential (F. P.) + 600mV (Ag/AgCl) and a scan rate of 2 mV/s. The polarization potentiodynamic curves were recorded after 60 minutes 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 discussion

In Fig. 1 is presented the thicknesses of composite coatings obtained by electrodeposition at 2A/dm^2 and 3A/dm^2 current density, 60 minutes deposition time and various stirring rate of the electrolyte.

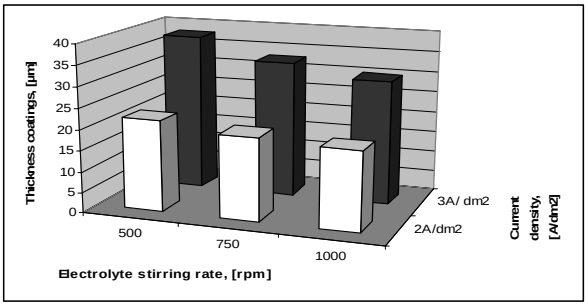

Fig. 1. *The thickness of Ni-Si composite coatings function current density and stirring rate*

From fig. 1 we can observed that deposited layer thickness increases with current density and decreases with increasing electrolyte stirring rate. The higher thickness of the composite coating was observed at these conditions of electrodeposition: current density 3A/dm^2 and 500 rpm electrolyte stirring rate.

Fig. 2 show the minimum variation of the silicon content in the nanocomposite coatings according to the electrolyte stirring rate (current density 2A/dm^2, 60 minutes deposition time).

As it can be observed from figure 2 the content of Si nanoparticles is highest at a stirring rate of 500 rpm and a dispersed phase containing 20 g/L (2.7% wt). It is also noted that at higher agitation rates (750, 1000 rpm) the content of Si included is lower (except composite coating obtained at 750 rpm and a dispersed phase containing 10 g/L).

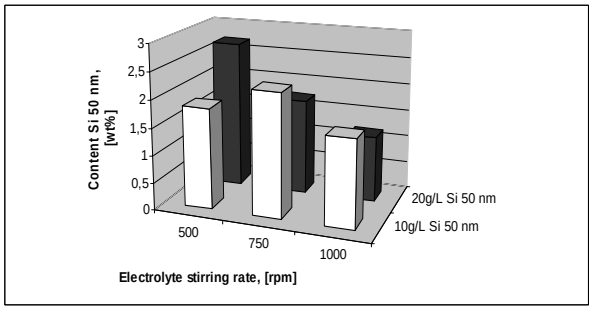

Fig. 2. *Content of silicon wt% in the nickel matrix*

Figs. 3 – 4 compares morphological aspects of Ni-Si composite coatings by scanning electron microscopy method.

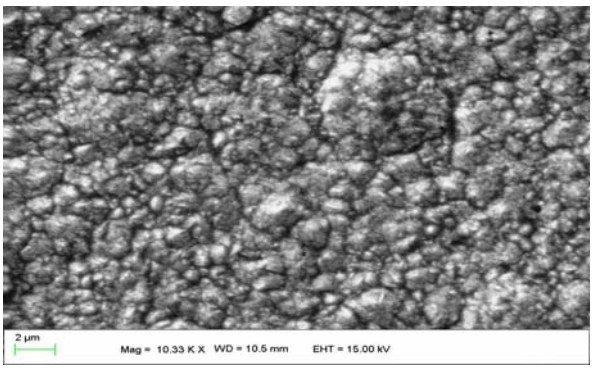

Fig. 3. *SEM surface morphology of Ni-Si composite coatings (20g/L Si, 2A/dm^2, 500 rpm, 60 min.) (x 10000)*

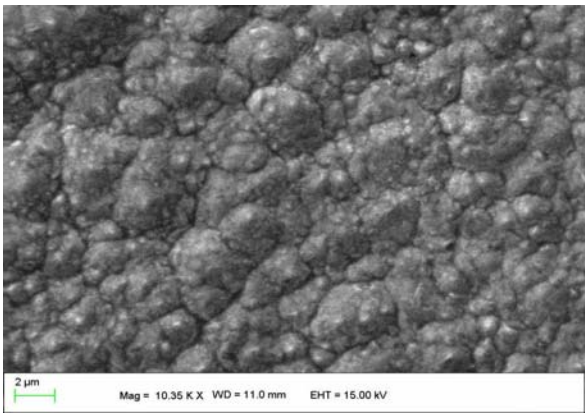

Fig. 4. *SEM surface morphology of Ni-Si composite coatings (20g/L Si, 3A/dm^2, 500 rpm, 60 min.) (x 10000)*

It has been found by SEM that with increasing current density, nodular structure is more pronounced, crystal size becomes larger. At a current density of 2A/dm^2 finer structure indicates a greater number of nucleation centers and thus a more homogeneous coating. The electrochemical investigation of each sample began with monitoring the open circuit potential (OCP). OCP changes immediately after the immersion into the testing solutions till reaching relatively stable stationary values.

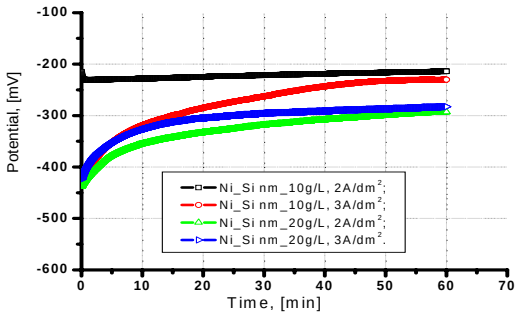

Fig. 5. *Open circuit potential Ni-Si composite coatings in NH_4OH 0.5 M*

Fig. 5 show that potential value of composite coating Ni-Si obtained at 3 A/dm^2 with 20 g/L silicon nano in electrolyte is more positive suggesting a more noble the deposit. This may be associated with an inhibition of the anodic reaction and therefore a higher resistance to corrosion

The typical anodic potentiodynamic polarization curves of various nanocrystalline Ni-Si coatings measured in NH_4OH 0.5 M solutions are shown in Fig. 6.

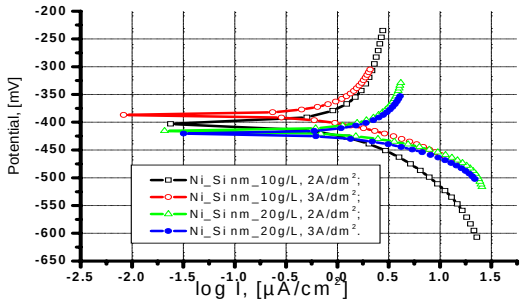

Fig. 6. *Polarization curves of Ni-Si composite coatings in NH_4OH 0.5 M*

Corrosion rates of the coatings were derived from the Stern–Geary equation:

$$i_{corr} = \frac{1}{2.303 R_p}\left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c}\right) \quad (1)$$

- 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;

- the quantity, $(\beta_a \cdot \beta_c)/(\beta_a + \beta_c)$, is referred to as the Tafel constant.

The polarization resistance, Rp, was determined from the slopes of the potential-current plots measured by the linear polarization curve (LSV) at a scanning rate of 2 mV/s.

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarisation resistance (R_p), which were obtained from the potentiodynamic polarisation curves are summarized in Table 1.

Table 1. *Corrosion parameter values determined from polarization curves*

Composite coatings [500 rpm, 60 min]	**E_{cor}, mV Ag/AgCl**	**β_a mV/dec**	**β_c mV/dec**	**i_{cor}, µA/cm²**	**R_p kΩ·cm²**
Ni-Si, 2A/dm^2, 10g/L Si nm	-384.0	139.8	123.4	0.8864	32.10
Ni-Si, 2A/dm^2, 20g/L Si nm	-406.0	145.0	67.8	1.5464	12.97
Ni-Si, 3A/dm^2, 10g/L Si nm	-383.3	154.5	73.5	0.9429	22.93
Ni-Si, 3A/dm^2, 20g/L Si nm	-414.8	194.1	75.0	2.0888	11.24

From the data presented it can be seen that the corrosion potential tends to negative values for composite coating Ni-Si obtained with 20 g/L silicon nano in electrolyte solution.

From potentiodynamic polarization curves the polarization resistance for composite coating Ni-Si obtained at 3 A/dm^2 with 20 g/L silicon nano in electrolyte was 11.24 kΩ·cm^2. For composite coating Ni-Si obtained at 2A/dm^2 with 10 g/L silicon nano in electrolyte the polarization resistance was 32.10 kΩ·cm^2.

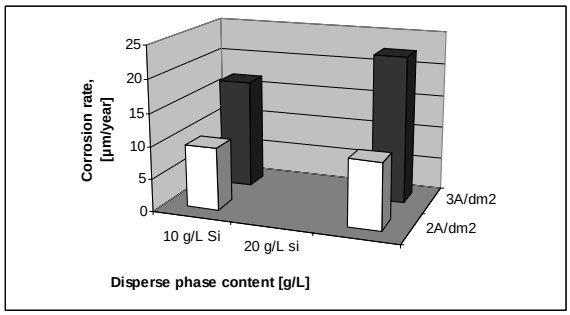

Fig. 7. *The variation of corrosion rate with the content of the disperse phase and current density*

The better corrosion resistance coating Ni-Si obtained at 2A/dm^2 could be due to the fine surface structure of composite coating compared with coating Ni-Si obtained at 3A/dm^2. Microhardness measurements were carried out using a Vickers microhardness tester, applying 20 g load for 10 s time [11].

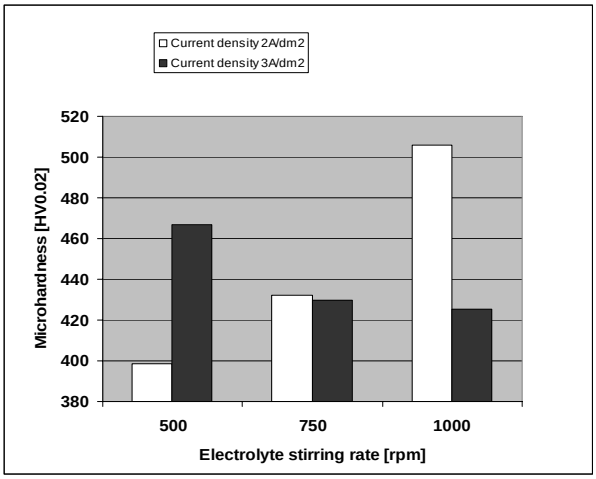

Fig. 8. *Microhardness as a function of electrolyte stirring rate (10 g/L Si) [13]*

The mean value of Vickers microhardness of pure nickel coatings has been found of about 300 $HV_{0.02}$ while composite coatings Ni-Si obtained at 2A/dm^2 with 10 g/L silicon nano in electrolyte is about 505 $HV_{0.02}$. This result shows that the codeposition of Si nanoparticles ameliorates the mechanical properties by 70% microhardness increase.

4. Conclusions

Nano-sized Si particles were successfully co-deposited in the nickel matrix by electrodeposition technique with a current density of 2 A/dm^{2}and 3 A/dm^2. Deposited layer thickness increases with current density and decreases with increasing electrolyte stirring rate. It is also observed that the Ni–Si nanocomposite sample deposited from electrolyte with a current density 2A/dm^2 and with 20 g/L silicon nano in electrolyte solution has the highest corrosion resistance. This is due to the fact that it has the smallest crystallite.

Highest microhardness value was obtained for composite coating Ni-Si at 2A/dm^2 with 10 g/L silicon nano in electrolyte.

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