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BEHAVIOR OF Ni/Al_2O_3 NANOCOMPOSITE THIN LAYERS IN CORRODING ENVIRONMENT

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ABSTRACT

This paper investigates the effects of adding alumina nanoparticles in the electrolyte bath on surface topomorphologies and structure of electrodeposited nickel. The influence on the corrosion process in NaCl solutions having various concentration was investigated by using impedance spectroscopy. The experimental data indicates the beneficial roles of alumina nanoparticles on Ni/Al_2O_3 nanocomposite thin films. The structure of electrocodeposited nanocomposite thin films was investigated by XRD and SEM techniques

KEYWORDS: nanocomposite, structure, corrosion, XRD, SEM.

1. Introduction

This paper investigates the effects of adding alumina nanoparticles in the electrolyte bath on surface topomorphologies and structure of electrodeposited nickel. The influence on the corrosion process in NaCl solutions having various concentrations was investigated by using impedance spectroscopy.

The experimental data indicate the beneficial roles of alumina nanoparticles on Ni/Al_2O_3 nanocomposite thin films.

These results are essential in manufacturing thermal or corrosion barriers by covering of some metallic surfaces with protective layers.

The structure of electrocodeposited nanocomposite thin films was investigated by XRD and SEM techniques and allows doing a correlation with their corrosion behavior in various corroding environments such as: NaCl or Na_2SO_4 having different concentrations.

2. Experimental research

On 5 copper supports, nanocomposite thin layers were deposited consisting of a nickel matrix and Al2O3 particles (20 nm) in concentrations ranging between 3 g/l and 15 g/l.

On 5 copper supports thin layers were deposited consisting of only of nickel matrix in order to compare their behavior with the version with nanoparticles. The copper support specimens have been properly prepared for deposition, using specific solutions for degreasing and in presence of ultrasonic waves.

As nickel plating bath a Watt bath was used having the following features: NiSO4·6H2O-0.90M; NiCl2·6H2O-0.20M; H3BO3-0.28M; sodium dodecylsulphate [CH3(CH2)11OSO3Na]-0.4g/l [1].

The concentration of alumina nanoparticles varied from 3 g/l to 15 g/l, and they were kept in suspension by a magnetic stirrer having a stirring rate of 700 rpm. The pH value of the electroplating solution was maintained at 4.2 – 4.5 and the corrections were made using a typical acidic solution.

Electrocodeposition processes were made at an optimal temperature of 40^{o} C for 60 minutes and a current density of $2A/dm^2$. The cathode consisted of the working specimen, namely copper, and the anode consisted of nickel having the same surface area as the copper specimen.

3. Structural analysis

The obtained electrocodeposited thin films of Ni/Al_2O_3 were studied by SEM at optimal magnifications on order to obtain the best images in which some agglomeration of alumina nanoparticles in the electrocodeposited thin films can be observed.

For this aim a Quanta 200, made of FEI Company instrument was used. In Fig. 1 SEM images of Ni/Al2O3 electrocodeposited for 0g/l and 10g/l alumina are displayed, respectively.

Ni/ Al2O3: 0 g/l   Ni/ Al2O3 :10 g/l

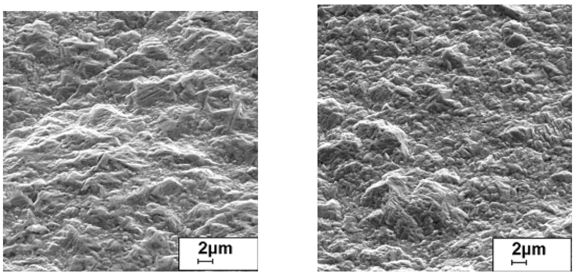

Fig 1. *SEM images of Ni surface without and with Al_2O_3 nanoparticles*

As alumina nanoparticles were added to the electrolyte in increasing concentrations, a general refinement in the grain structure on the surface was observed. With addition of 10 g/l of alumina, the average size of the pyramids on the surface is clearly reduced. These results show that the surface topomorphology is greatly refined by the presence of alumina nanoparticles. The chemical analysis of electrocodeposited thin films of nickel with alumina nanoparticles has been estimated by EDAX method. The typical spectrum showing the chemical construction is presented in Fig. 2.

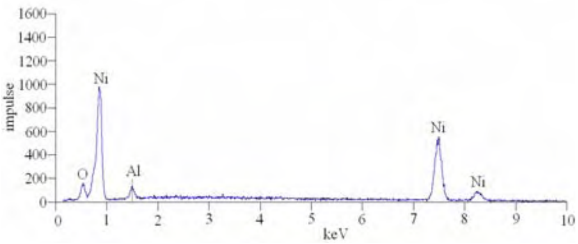

Fig. 2. *EDAX spectrum of electrodeposited film with 10% alumina*

X-ray pattern obtained on DRON-3 equipment from electrocodeposited thin films of nickel having a concentration of 10 % alumina nanoparticles is presented in Fig. 3 [2, 3]. Although EDAX spectra pointed out aluminum, only the characteristic peaks of nickel can be observed.

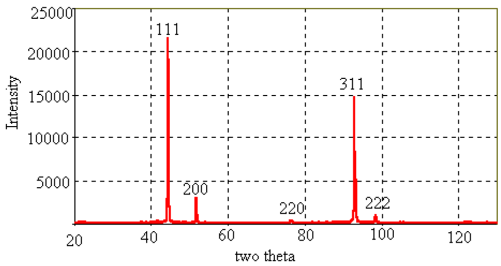

Fig.3. *XRD pattern of electrocodeposited nickel thin film with 10 % alumina*

4. Corrosion tests

Corrosion tests have been performed for nanocomposite thin films on specimens of Ni/Al_2O_3 in three different types of solvents: NaCl 3%, 5% and 7%. The results were compared with depositions of metallurgical nickel [4, 5]. Previously, the surface not subjected to electrochemical tests was isolated with polytetrafluoroethylene. Out of the eletrocodeposited thin films (Ni/Al_2O_3) of area of 4 cm^2, an area of 0.5–1cm^2 was kept for the electrochemical experiments consisting in drawing polarization curves [6-9]. The electrochemical tests were performed in an electrochemical cell consisted of a glass recipient with a lid having a series of apertures through which were inserted the corrosion solution, the working electrode [electrocodeposition thin films as specimen obtained on the copper support], the auxiliary electrode [helical platinum (Pt) wire] and the referential electrode [horn mercury electrode $Hg/HgCl_2$sat. (ε = 0.234 V)].

The solution was stirred by introducing a small magnet covered by glass layer, which was then moved by magnetic stirrer. Nickel specimens with aluminium oxide particles have been studied against pure nickel specimens. Initially, polarization curves were achieved in the electrolyte solutions of NaCl. The working circuit consisted of: referential electrode: horn mercury, auxiliary electrode: platinum and working electrode: deposition in nickel matrix.

This circuit was connected to a computer which recorded the experimental data. The polarization curves i = i (E) were obtained in the following conditions: voltage 1: - 500 mV; voltage 2: +500 mV; voltage 3: +1000 mV; sweeping rate v = 150 mV/min; number of cycles: 1, minimum current: -50 mA and maximum current: +50 mA. Figs. 4 and 5 contain the obtained polarization curves in NaCl 3% solution, while Figs. 6 and 7 display the polarization curves obtained in Na_2SO_4 having a concentration of 0.1 M.

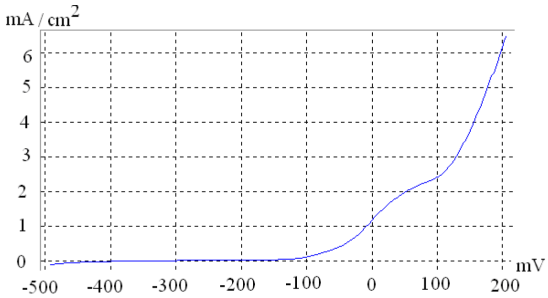

Fig.4. *Polarization curve of Ni in NaCl 3% solution*

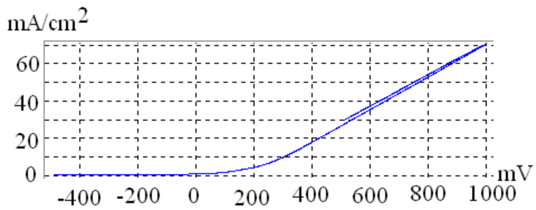

Fig.5. *Polarization curve of Ni/ Al_2O_3 in NaCl 3% solution*

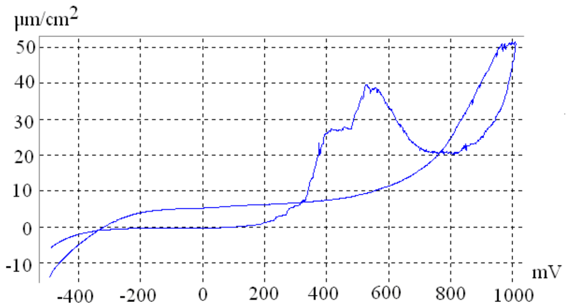

Fig.6. *Polarization curve of Ni in Na_2SO_4 having a concentration of 0.1 M.*

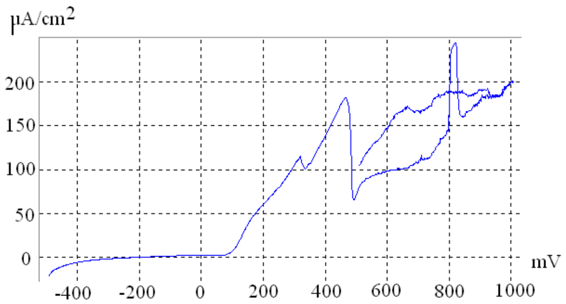

Fig.7. *Polarization curve of Ni/ Al_2O_3 in Na_2SO_4 having a concentration of 0.1 M.*

Analyzing the above polarization curves obtained for pure nickel and for nanocomposite of type Ni/Al_2O_3, it result a major difference in behavior of the two materials in corroding solutions of NaCl and Na_2SO_4. These results show the versatility of nanocomposite based on nickel matrix reported to various corroding solutions having certain compositions and/or concentrations [10].

The corrosion protection can be accredited to the presence of Al_2O_3 nanoparticles in nickel matrix, because their presence on the metal surface creates a barrier for oxygen reduction. In solutions, the composites are not stable. It is possible to selectively dissolve the metallic matrix or the disperse phase or both (matrix-disperse phase).

Corrosion process is essentially electrochemical; voltage and current parameters can be precisely measured with modern equipment. For the corrosion study, polarization resistances can be estimated from spectro-electrochemical impedance data (EIS) in a large frequency range (105 – 10-3 Hz). A voltage change indicates a corresponding change of intermediate species concentration.

Figures. 8 and 9 show the representation of impedance spectroscopy diagrams for the experimental system of Ni/ Al_2O_3 in Na_2SO_4 0.1 M solution at, 1h, and 46 h.

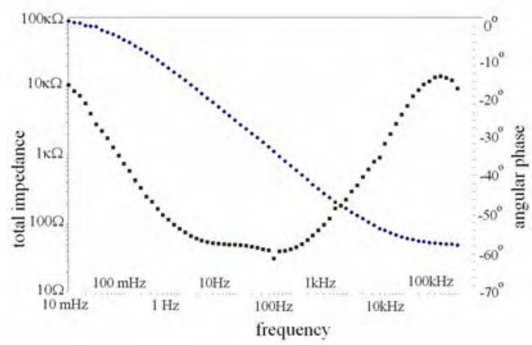

Fig. 8. *EIS diagram at 1h.*

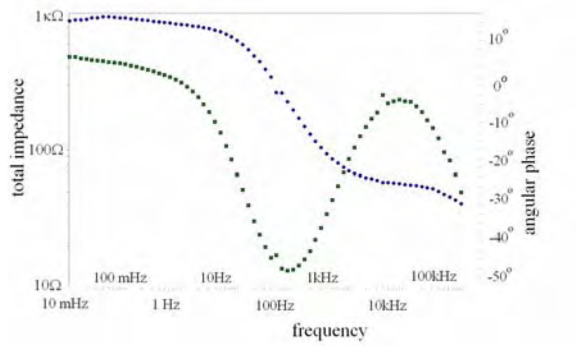

Fig. 9*. EIS diagram at 46 h*

5. Conclusions

This paper reveals some experimental data concerning the preparation by electrocodeposition of a nanocomposite of type Ni/Al_2O_3 on a copper substrate as well as its behavior in a corroding environment as NaCl.

It has been determined that the most relevant factors for the success of nanocomposite coatings with directed composition are the nature of constituents, and electrolyte and electrolysis conditions.

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