STUDIES AND RESEARCH ON THE CORROSION BEHAVIOR OF Ni-Al₂O₃ COMPOUND COATINGS OBTAINED BY ELECTROCHEMICAL METHODS

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ABSTRACT

The undertaken research which is described in this paper aims at the corrosion behaviour of composite coatings in nickel matrix using as dispersed phase technical alumina with dimensions of 5 µm and their characterization from a microstructural point of view. The corrosion resistance in the saline fog of the coatings is influenced by the microstructure, the stresses developed in the layer and the roughness.

1. Introduction

The field of composite coatings remains a top field in science and technology, currently experiencing great diversification in terms of categories of protected materials (metals, plastics, ceramics, wood or textiles) and the nature / complexity of coatings and technologies used in their application.

The electrochemical deposition of nickel is used as it improves the resistance to corrosion, oxidation and wear at high temperatures, modifies magnetic properties, ensures the reconditioning of worn or dimensionally improper parts, prepares the surface for other types of (organic or enamelled) coatings, constitutes barriers of diffusion in electronic applications.

Electrochemical deposits of nickel and nickel matrix composites are used for decorative purposes in various branches of engineering because the properties of the obtained layers can be varied by controlling the chemical composition of the bath and the deposition parameters.

They are applied in the machine building industry, the chemical industry, the nuclear industry, in telecommunications, for electronic consumables, and in the IT industry.

Over time, several mechanisms for the formation of composite coatings have been proposed. Thus, Guglielmi views the deposition process as a succession of two stages: the solid particles surrounded by the cloud of ions (cations) are transferred, adsorbed on the cathode surface due to Van der Waals forces, and the second stage involves the strong adsorption of these particles at the cathode due to the Coulomb forces developed at the interface with the support.

A frequently accepted model is the one proposed by Kurozaki which involves the transport of particles from the solution to the cathode surface by stirring. The model comprises three steps [1]:

- the uniformly dispersed particles are transported to the double electric layer by mechanical agitation;
- the charged particles are transported to the cathode surface by electrophoresis;
- the solid particles are adsorbed on the cathode surface due to the Coulomb forces developed between the particles and adsorbed anions, followed by their incorporation and growth at the interface with the support.

Another mechanism [2] assumes that a series of complex phenomena take place at the electrode - electrolyte interface. The electrodeposition processes are considered to take place in several stages: mass transport of the electroactive metallic ionic species to the cathode surface; adsorption on the cathode surface; discharge reaction at the cathode surface (charge transfer); surface diffusion of formed atoms and incorporation into the crystal lattice. The nucleation and growth of the crystal can be added to these steps.

Alumina is used as a dispersed phase to obtain composite materials due to its properties: high melting point, hardness, high thermal conductivity and electrical resistivity, high chemical resistance (it

is attacked only by molten hydroxides and alkaline bisulfates and phosphoric acid) [3].

The researches undertaken in this paper aim at the corrosion behaviour of some composite coatings in nickel matrix using as dispersed phase technical alumina with dimensions of approx. 5 µm and their characterization from the microstructural point of view and of the corrosion resistance.

2. Experimental conditions

To obtain nickel coatings and nickel matrix composite coatings, a direct current source, a device provided with a magnetic stirrer and a bath temperature control system as well as an electrolyte container were used. We worked with a solution volume of 300 ml, and the experiments took place at temperatures of 50 ºC.

Watts electrolytes consisting of $NiSO_4 \cdot 6H_2O$ – 300 g/L, $NiCl_2 \cdot 6H_2O$ - 50 g/L and H_3BO_3 – 40 g/L, pH = 4.5, current density of 4 A/dm^2, a concentration of the dispersed phase of 20 g/L, stirring speed of 300 rpm, with deposition times of 60, 90, 120 minutes were used.

The electrodepositions were made by the vertical arrangement of the electrodes at a distance of 14 mm from each other. High purity nickel (99%) was used as an anode, the cathode being made of copper strip, representing the support material for deposits with dimensions of 76x20x1 mm.

The copper strip used was prepared by degreasing (organic solvents - trichlorethylene), pickling (HNO_3 + HCl at room temperature for 1-2 minutes) followed by washing with distilled water.

The metallographic analysis of the samples was performed on a Neophot 2 microscope, with the acquisition of data on the computer and highlighted the appearance of the nickel deposition surface compared to composite coatings, their adhesion, how the electrodeposited crystals grew and the presence of defects such as pores, cracks, and exfoliation.

The qualitative analysis of the surface profile was performed using the Neophot 2 microscope and Image J software.

The corrosion behavior in the salt mist of the composite layers was performed according to ISO 9227/2012 for a period of 96 hours. To perform the test, the sodium chloride solution was prepared by dissolving in distilled water, with a conductivity less than or equal to 20 µS/cm^2 at 25 ± 2 ºC, a quantity of sodium chloride, in order to obtain a concentration of 50 ± 5 g/L. The relative density of a solution with this concentration is between 1.00255 and 1.0400. The pH of the saline solution was adjusted so that the pH of the solution collected in the spray chamber was between 6.5 and 7.2. It was measured with a pH meter HI 991001, produced by "Hanna Instruments", also provided with a temperature indicator.

3. Experimental results

Following the microscopic analysis performed on the nickel coatings subject to corrosion in saline fog, it could be found that the best behavior was the P2 sample obtained at a deposition time of 90 minutes. The P3 sample obtained at a deposition time of 120 minutes showed a lower corrosion resistance due to obtaining a higher roughness, as can be seen in Fig. 2. As the deposition time increases, the thickness if the residual stresses in it can either increase, influencing the corrosion resistance or decrease.

The presence of a localized corrosion (points) can be observed, this manifesting itself first in the sections with non-uniformities or imperfections resulting from the bath or from the increase of the coating layer. It then spreads along the paths formed by these defects. A peculiarity of this form of corrosion is the fact that on the metal surface may also appear active points, besides the intact passive areas, without protective film, i.e. areas with very low anodic current densities (wide cathodic areas) and other limited areas with higher values of the current density (anodic areas).

If corrosion products accumulate in the pores or under cover, due to the fact that they have a larger volume in relation to the volume of metal from which they come as a result of the attack, the exfoliation of the coating may occur.

The microscopic analysis performed on electrochemically obtained composite coatings with nickel matrix using as dispersed phase Al_2O_3 particles subject to corrosion in salt mist showed that the best corrosion behavior was presented by the P6 sample obtained at a time of deposition of 120 minutes. This showed a higher passivation compared to the other samples and a low roughness, as can be seen in Fig. 2. The P4 sample obtained at a deposition time of 60 minutes showed a low corrosion resistance, this having a lower thickness and a higher roughness, as can be seen in Fig. 2.

The presence of dispersed phase particles led to changes in the growth mechanism of nickel crystals favoring nucleation. This results in a finer structure than pure nickel coatings with better mechanical properties and good corrosion behavior. Alumina particles act as a barrier against the movement of dislocations through the nickel matrix, and by accumulating at the grain boundary leads to increased hardness and residual stresses.

The corrosion rates resulting from the salt mist test on pure nickel coatings and nickel matrix composite coatings using Al_2O_3 particles as the dispersed phase can be seen in Fig. 3.
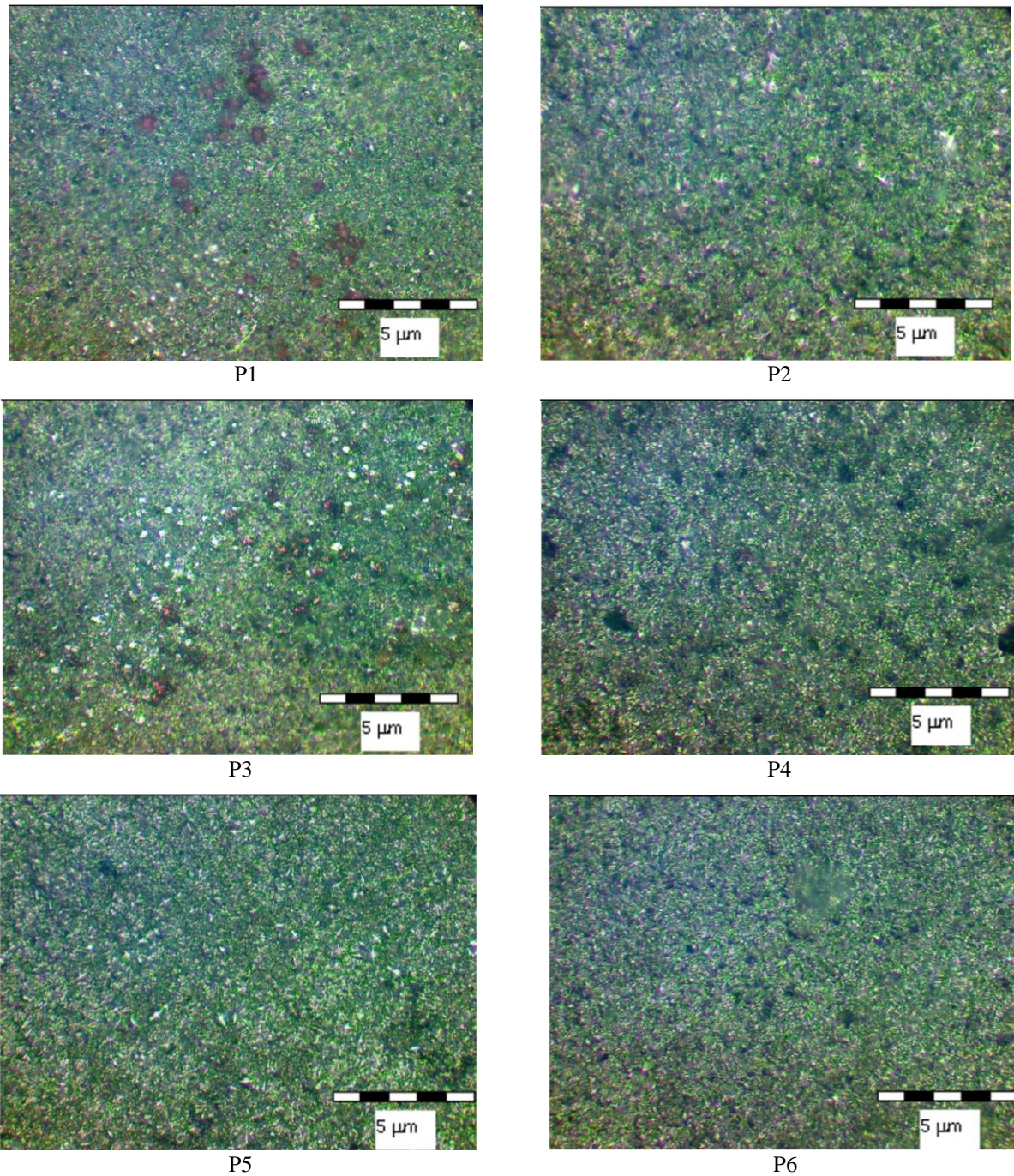
Fig. 1. *Microstructure of pure nickel coatings P1 - 60 minutes, P2 - 90 minutes, P3 - 120 minutes and of composite coatings P4 - 60 minutes, P5 - 90 minutes and P6 - 120 minutes*

Analyzing Fig. 3, it the composite coatings can be seen to have a higher passivation, and thus, a better corrosion resistance, compared to pure nickel coatings. Among the pure nickel coatings, the best corrosion compote was presented by sample P2, and in the case of composite coatings, sample P6.
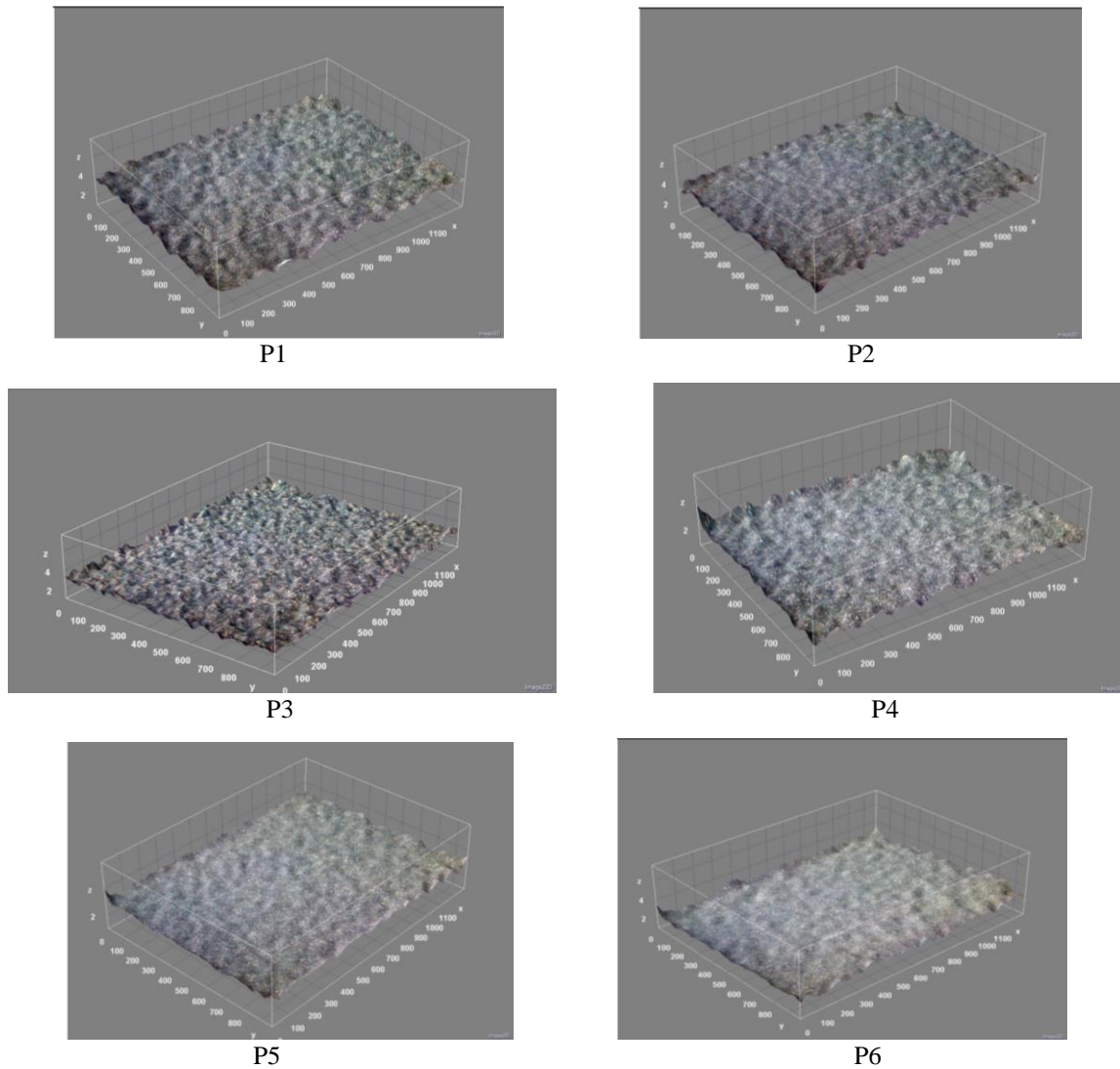
Fig. 2. *Images of the surface profile for pure nickel coatings subjected to corrosion P1 - 60 minutes, P2 - 90 minutes, P3 - 120 minutes and of composite coatings P4 - 60 minutes, P5 - 90 minutes and P6 - 120 minutes*
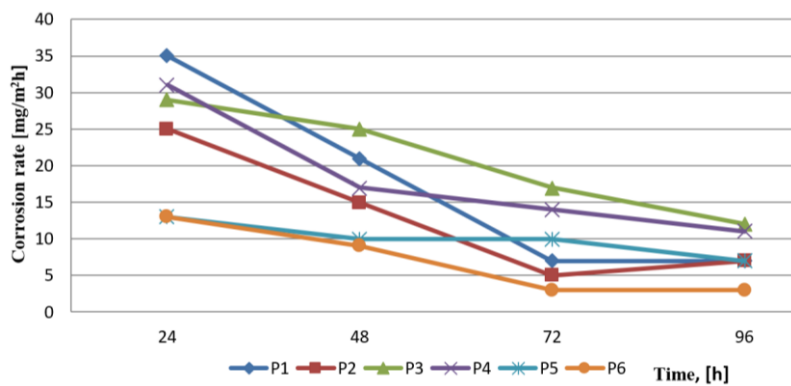

Fig. 3. *Corrosion behavior of pure nickel coatings P1 - 60 minutes, P2 - 90 minutes, P3 - 120 minutes and of nickel matrix composite coatings using Al_2O_3 particles as dispersed phase P4 - 60 minutes, P5 - 90 minutes and P6 - 120 minutes*

4. Conclusions

Further to the experimental research, the following conclusions can be drawn:

- The corrosion resistance in salt mist of pure nickel coatings and nickel matrix composite coatings using Al_2O_3 particles as dispersed phase is influenced by microstructure, the stresses developed in the layer and roughness.

- As the deposition time increases, the thickness of the pure nickel coatings increases, the value of the residual stresses develops in the layer and the roughness. These aspects can have the effect of reducing corrosion resistance.

- As the roughness increases, the corrosion resistance decreases.

- Compared to pure nickel deposits, the presence of complementary phase particles led to changes in the mechanism of growth of crystals in the nickel matrix, and to a decrease in crystallites, respectively, favoring nucleation, which led to finer structures and reduced roughness. These changes resulted in the improvement of the composite coatings, which showed a higher passivation.

- The presence of Al_2O_3 particles acts as a barrier against the movement of dislocations through grains, and the accumulation at the grain limit determines the increase of residual stresses, respectively the increase of resistance to deformation. As the residual stresses in the layer increase, the susceptibility to corrosion increases.

The corrosion observed in pure nickel and electrochemically deposited composite layers is a localized one (in points), that usually is caused by chlorine ions, which manifests itself around such defects as pores, bath inclusions or micro-cracks caused by internal stresses.

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