STUDIES AND RESEARCH ON THE INFLUENCE OF DEPOSIT PARAMETERS ON THE CHARACTERISTICS OF COMPOSITE COATINGS Ni-Al₂O₃ OBTAINED BY ELECTROCHEMICAL METHODS

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ABSTRACT

The paper presents the characterization of composite coatings with nickel matrix using as dispersed phases Al_2O_3 particles, both from the microstructural point of view and from the point of view of the layer thickness, micro-hardness and corrosion behavior in saline fog. The presence of dispersed phase particles led to the finishing of the structure because they acted as nucleus centres, reducing the size of nickel crystallites. The parameters of the deposits influence the structure and properties of the obtained layers.

KEYWORDS: Ni composite coatings, electro-depositing, Al_2O_3, corrosion in saline fog

1. Introduction

Electrodeposition of a metal in a solution containing dispersed particles (Al_2O_3, ZrO_2, TiO_2, SiO_2 SiC, Si_3N_4, WC) leads to their incorporation in the metal matrix with the formation of composite coatings that sum up both the properties of the metal and those of the dispersed particles.

The composite layers thus obtained have special properties such as improved corrosion resistance, increased hardness, wear resistance, good adhesion of subsequent paint layers and longer life [1, 2].

The superior properties are due to the dispersed phase which is an obstacle to the displacement. It must have optimal shapes, sizes, distributions and quantities, correlated with the electrodeposition parameters, it must also have low solubility in the matrix material and it should not lead to chemical reactions with the matrix.

The co-deposition of the dispersed particles in the metal matrix, simultaneously with the electrodeposition of the metal is performed in the following stages:

- After the introduction of the dispersed phase particles in the electrolyte, a diffuse electric double layer of adsorbed ionic species (ionic cloud) is formed around them;

- The particles are transported to the limit of the hydrodynamic layer due to the agitation of the electrolyte;

- Under the influence of the electric field the positively charged particles diffuse towards the cathode surface, and those that have not been adsorbed on the surface, predominantly negative ions, will be rejected towards the solution volume;

- At the cathode there is a reduction of free or adsorbed electroactive ion species on particles;

- As a result of the reduction of ionic species adsorbed on particles, the incorporation of particles in the metal matrix takes place [3].

The properties of alumina are: high thermal conductivity, hardness, high melting point, high chemical resistance (it is attacked only by molten hydroxides and alkaline bisulphates and phosphoric acid) and electrical resistivity [4].

In this paper, the metallographic analysis and the corrosion resistance on composite coatings in nickel matrix using as dispersed phase technical alumina with dimensions of around 5 µm, have been achieved.

2. Experimental conditions

To obtain nickel and nickel matrix composite coatings, an electrochemical cell with a volume of 300 mL was used.

Watts electrolytes have been also used [5], temperature 50 ºC, pH = 4, current density of 3 and 6 A/dm², dispersed phase concentration of 10 and 30

g/L, stirring speed of 500 rpm, deposition time of 60 minutes.

The anode (99% nickel) was positioned at a distance of 14 mm from the cathode (being made of copper strip, with dimensions 20 x 40 x 10 mm).

The copper cathode was prepared by organic degreasing (trichloroethylene), stripping (HNO_3 + HCl) followed by washing with distilled water.

The microstructural characterization of the samples was performed on a Neophot 2 microscope.

To determine the micro-hardness, the PMT-3 micro-hardness hardness tester was used with a load of 50 g.

The corrosion behavior in the salt mist of the composite layers was performed according to SR EN ISO 9227:2017 for a period of 96 hours.

3. Experimental results

Metallographic analysis of pure nickel deposits, Fig. 1 showed that the deposited layers are homogeneous, uniform, adherent to the substrate and do not show cracks. It was found that, as the current density increases from 3 A/dm^2 for sample P1 to 6 A/dm^2, for sample P2, the thickness of the deposited layer increases from 0.0331 mm to 0.06 mm. The increase of the current density determines the formation of finer grains due to the additional activation of the inactive areas on the cathode.
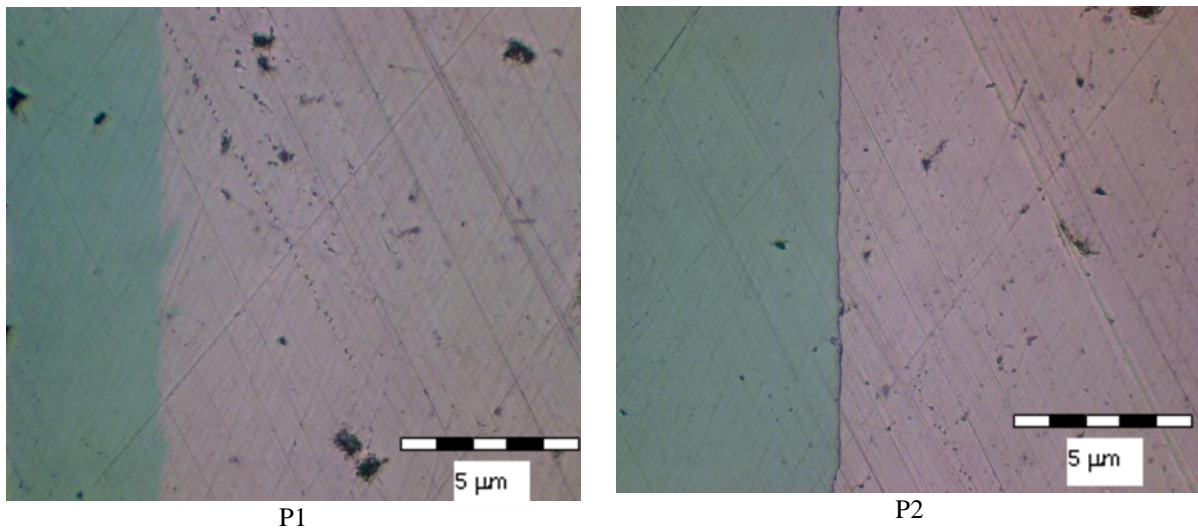

| P1 | P2 |

Fig. 1. *Microstructure of pure nickel layers obtained at current densities of 3 A/dm^2 - P1 and 6 A/mm^2 - P2*
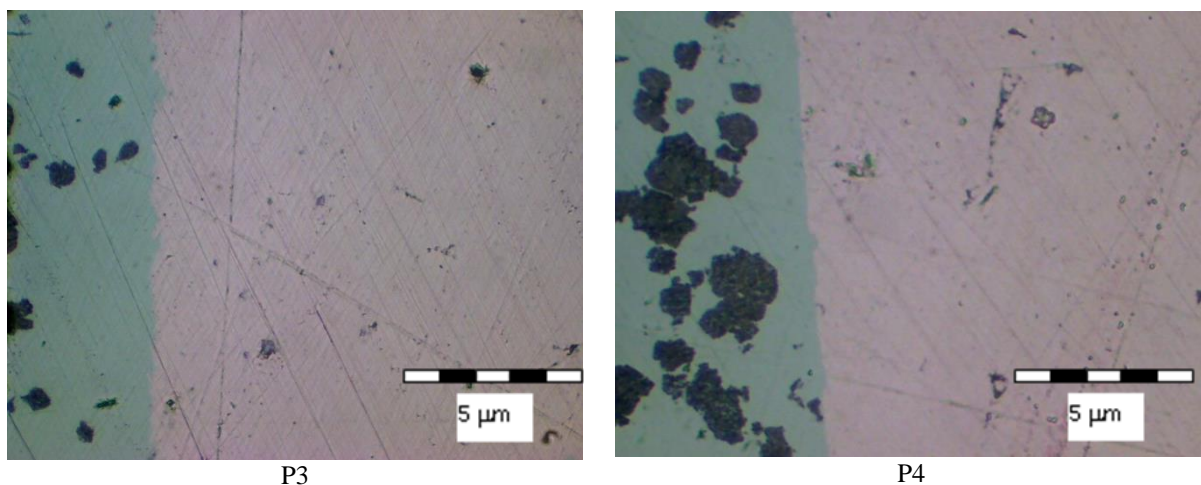

| P3 | P4 |

Fig. 2. *Microstructure of composite coatings obtained at a current density of 3 A/dm^2 and dispersed phase concentrations of 10 g/L - P3 and 30 g/L - P4*

As for the microhardness of the deposited nickel layers, it increases from 257.2 daN/mm² for sample P1 to 360 daN/mm² for sample P2, being greater than the microhardness of the substrate which was 104.4 daN/mm².

Metallographic analysis of composite coatings performed at current density of 3A/dm², Fig. 2 highlighted the fact that with the increase of the dispersed phase concentration in the electrolyte from 10 g/L to 30 g/L there is an increase of the percentage of phase included in the deposited layer. There is also

an increase in the micro-hardness of the layers deposited from 435.3 daN/mm² for a dispersed electrolyte phase concentration of 10 g/L for sample P3 at 495.3 daN/mm² for a concentration of 30 g/L, to sample P4. The increase in hardness is due to the combined effect of particle dispersion, finer grain size compared to pure nickel deposits and increased deformation resistance due to limited displacement (by dispersed particles), reduced mobility and accumulation at the grain boundary.
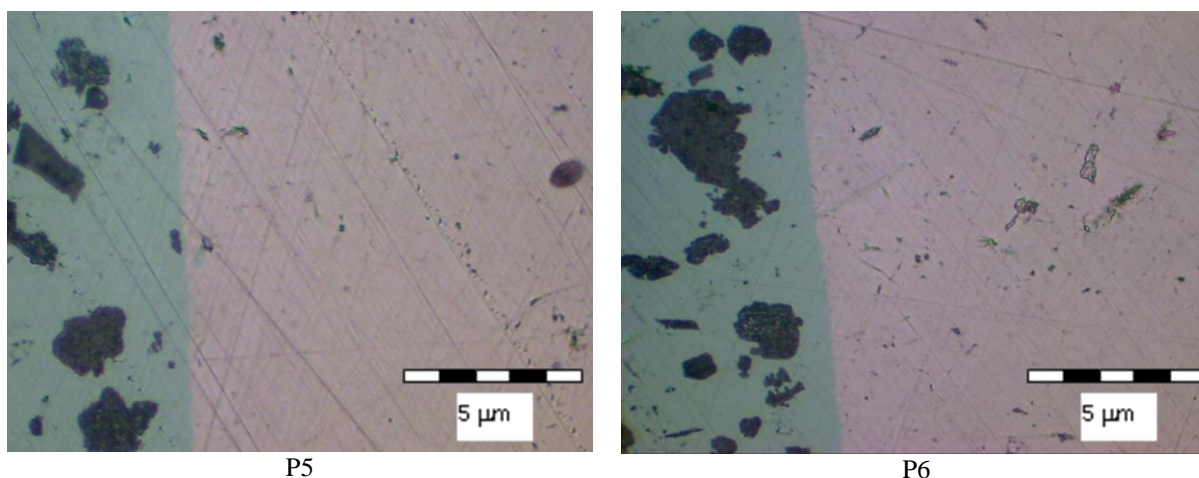

P5   P6

Fig. 3. *Microstructure of composite coatings obtained at a current density of 6 A/dm² and dispersed phase concentrations of 10 g/L - P5 and 30 g/L - P6*
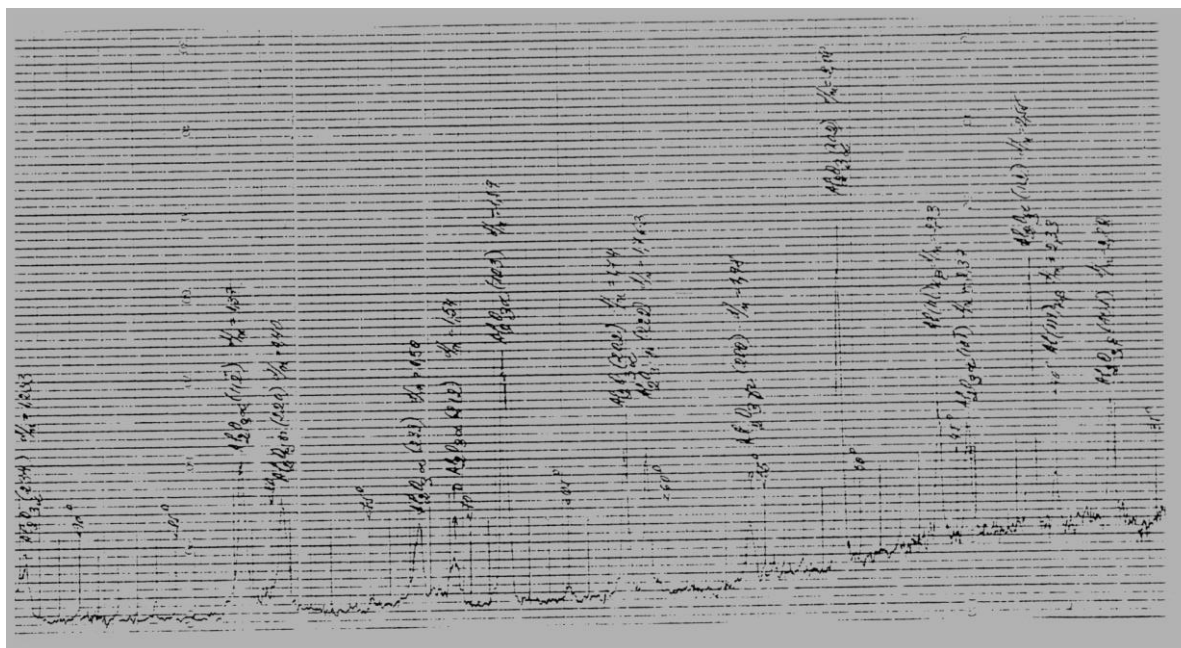

Fig. 4. *The diffractometric analysis of the dispersed phase particles*

There is also an increase in layer thickness from 0.0417 mm to 0.0531 mm.

When increasing the current density at 6 A/mm² it is found that the percentage of phase included in the

metal matrix decreases. This is due to the activation phenomenon of the reduction of unabsorbed metal ions on the particles caused by the increase of the current density. The flux of metal ions in the diffusion layer towards the cathode surface increases with increasing current density, and that of oxide particles with adsorbed ionic species decreases, due to their lower mobility.

Regarding the evolution of the micro-hardness of the composite coatings obtained at current densities of 6 A/dm² it can be mentioned that values

of 398.4 daN/mm² for a dispersed phase concentration of 10 g/L and of 414.5 daN/mm² for concentrations of 30 g/L have been obtained / have been achieved.

Layer thicknesses have values of 0.0741 mm for the layers obtained with a concentration of 10 g/L of the desperate phase and of 0.0798 mm for a concentration of the dispersed phase of 30 g/L.

Figure 4 presents the diffractometric analysis of the dispersed phase particles.
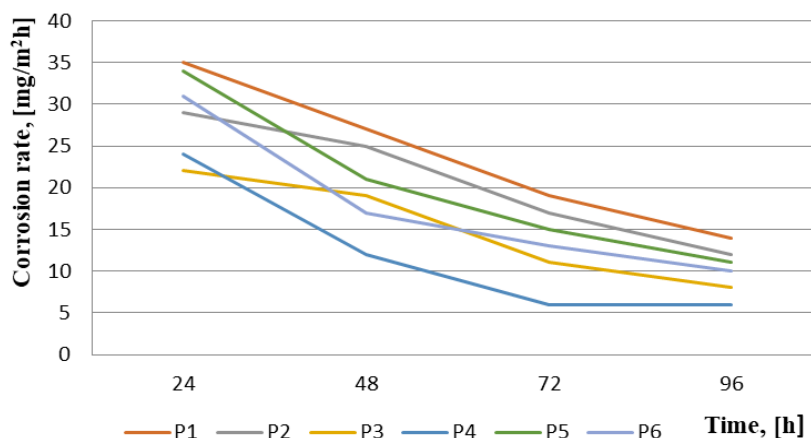

Fig. 5. *Corrosion behavior of nickel coatings and composite coatings obtained*

It was found that the composite coatings show a better corrosion behavior in accelerated corrosion test performed in saline fog compared to the pure nickel coatings, as it can be seen in Fig. 5. Dispersed phase particles of Al₂O₃ act as a barrier against the initiation and development of corrosion. A spot corrosion was observed around the imperfections from the growth of the film, or around the inclusions from the electrolyte bath, or around the pores. It is found that the corrosion resistance of composite coatings obtained at current densities of 3 A/dm² is superior to the corrosion resistance of coatings obtained at 6 A/dm².

4. Conclusions

Following the experimental research performed, the following conclusions can be mentioned:

- Nickel coatings obtained at different current densities do not have cracks, they are homogeneous and they have a good adhesion to copper supports;

- As the current density increases, the thickness of the deposited nickel layers increases from 0.0331 mm to 0.06 mm;

- The micro-hardness of the deposited nickel layers, increases from 257.2 daN/mm² for sample P1 to 360 daN/mm² for sample P2, being greater than the micro-hardness of the substrate which was 104.4 daN/mm²;

- Electrochemically obtained composite coatings in nickel matrix using as dispersed phases particles of Al₂O₃ are homogeneous and they have no cracks; the increase in current density causes the formation of finer structures due to the multiplication of crystallization germs on the cathode compared to pure nickel deposits;

- At a current density of 3 A/dm² there is an increase in the micro-hardness of the deposited composite layers from 435.3 daN/mm² for a dispersed phase concentration of the electrolyte 10 g/L for sample P3 to 495.3 daN/mm² for a concentration of 30 g/L in the sample P4; there is also an increase in layer thickness from 0.0417 mm to 0.0531 mm;

- When increasing the current density at 6 A/mm² it is found that the percentage of phase included in the metal matrix decreases.

- Micro-hardness of composite coatings obtained at current densities of 6 A/dm² is of 398.4 daN/mm² for a dispersed phase concentration of 10 g/L and of 414.5 daN/mm² for concentrations of 30 g/L.

- The layer thicknesses have values of 0.0741 mm for the layers obtained with a concentration of 10 g/L dispersed phase and of 0.0798 mm for a concentration of the dispersed phase of 30 g/L.

- Composite coatings have a better corrosion behavior compared to pure nickel coatings, due to their passivation.

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