

## THE EFFECT OF NANO- $\text{Al}_2\text{O}_3$ DISPERSED PHASE IN NICKEL MATRIX ELECTROCODEPOSITED

Geta CĂRĂC,<sup>a\*</sup> Cătălina ITICESCU,<sup>a</sup> Lidia BENEĂ,<sup>a</sup>  
Thomas LAMPKE<sup>b</sup> and Siegfried STEINHAUSER<sup>b</sup>

<sup>a</sup>University Dunarea de Jos of Galati, Department of Chemistry, Faculty of Sciences,  
Domneasca Street 47, 800008-Galati, Roumania

<sup>b</sup>Chemnitz University of Technology, Institute of Composite Materials and Surface  
Technology, Erfenschalger Straße 73, 09125-Chemnitz, Germany

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Electrocodeposition is a method successfully used to obtain composite coatings. The composite coatings in nickel matrix and nano- $\text{Al}_2\text{O}_3$  particles (20 nm) as dispersed phase were obtained from a Watts electrolytic bath at a current density of  $3\text{A}/\text{dm}^2$ . The concentration of nano- $\text{Al}_2\text{O}_3$  was 5, 10 and respectively 20g/L oxide in the bath. The effect of the embedded of  $\text{Al}_2\text{O}_3$  nanoparticles in nickel matrix was studied. The surface morphology of layers was studied by light and scanning electron microscopy (SEM) and chemical composition by EDAX analysis. The Vickers microhardness on cross section of layers was investigated. The results show that the morphology (structure and roughness) and mechanical characteristics (e.g. microhardness) of the composite coatings differ from nickel deposits without nanoparticles.

### INTRODUCTION

Surface coatings have now a major importance in the successful of technology, effective, and efficient exploitation of materials in engineering practice.<sup>1,2</sup> Coatings may be broadly regarded as improving the properties of materials, such as surface properties optimization, as an integral part of the design process and for synthesis and fabrication technologies. While all new coating methods, requirements and options are being met as challenges by physicists, chemists, and engineers, the existing traditional coating technologies, such as diffusion coating, plating, and vapor deposition, are undergoing their own resurgence.

Electrocodeposition is of increasing interest as an important method to obtain nanocomposite coatings in new technologies.<sup>1-3</sup> Composite coatings consist from a metal matrix with small particles (or fibres) like a dispersed second phase in matrix and they are developed for widely applications. Composite coatings have been primarily developed for their physical and chemical properties because they combine the

properties of the metal matrix and dispersed phases: high temperature strength, good resistance to thermal fatigue, good shock resistance, high thermal conductivity and low coefficients of thermal expansion.

Metal matrix composite coatings have attracted considerable attention because of their relatively low cost and facility to manufacture by co-deposition in an electroplating bath. Composite coatings can be economically realized by co-deposition of different inert particles as a dispersed phase into a metallic matrix from an electrolytic bath.

There are many research data available in scientific forum regarding the composite coatings in nickel matrix.<sup>3-8</sup> The properties of coatings depend on the amount of particles in the electrolyte and also of their inclusion in the metallic matrix.

Composite coatings in nickel matrix with nano- $\text{Al}_2\text{O}_3$  (20 nm) were obtained by electrocodeposition from a typical Watts electrolyte. The paper presents the effect of the dispersed nano- $\text{Al}_2\text{O}_3$  particles on the modification on the structure (roughness) and mechanical characteristics (e.g. microhardness) of the composite coating layers obtained.

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\* Corresponding author: getac@ugal.ro

## RESULTS

Electrodeposition is evolving as an important method in obtaining the composite coatings. To ensure a uniform distribution of the dispersed phases in the metal matrix a good correlation between current density, the particles concentration in the electrolyte and working parameters of the electrocodeposition processes is required. The composite coatings in nickel matrix were obtained by electrochemical codeposition from a Watts electrolyte (section 4: Experimental) with nanoparticles of  $\text{Al}_2\text{O}_3$  (20 nm) into concentration of 5, 10 and 20 g/L oxide like dispersed phase, at the current density of  $3\text{A}/\text{dm}^2$ . The rate of codeposition of nano  $\text{Al}_2\text{O}_3$  particles into a metal layer depends by other on the rate of metal deposition and the flux of the particles to the film surface. The properties of the composite coatings are determined by the interactions of the matrix and the dispersed phase.<sup>9</sup>

The Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings obtained feature good adhesion on the carbon steel substrate and they show a good uniformity of both thickness and particles distribution on the layers.

**1. The thickness of layers.** The thickness of layers depends on the current density applied and the deposition time, and on all the other variables of the electrodeposition process. Additionally, the concentration of the dispersed particles used in electrolyte has an important effect on the thickness of the layers obtained. The deposits of pure Ni and Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings present a variable thickness of layers. Figure 1 shows the thickness of layers depending of the nanoparticles concentration in the Watts electrolyte, kept in uniform dispersion in electrolyte suspension which is magnetically stirred (700 rpm). During the electrodeposition process of 90 minutes, a thickness of composite coatings layers between 40-75  $\mu\text{m}$  was found analyzed by optical microscopy (Fig. 2).

**2. Chemical composition of the composite coatings.** The most important parameter for the incorporated nanoparticles of oxide in a metallic matrix from a suspension bath is current density of the electrodeposition process. There were carried out Ni/ nano- $\text{Al}_2\text{O}_3$  composite coatings at  $4\text{A}/\text{dm}^2$ , using same type of nanoparticles of alumina.<sup>10</sup>

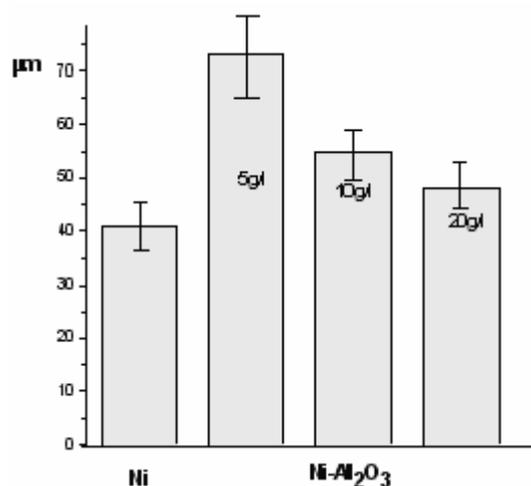


Fig. 1 – Thickness of Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings obtained from a Watts electrolyte, at  $3\text{A}/\text{dm}^2$  and 90 min. electrocodeposition.

In this study a current density of  $3\text{A}/\text{dm}^2$  in the electrodeposition process was experimented, resulting that the incorporation of dispersed particles in nickel matrix is more favorable for lower values of current density.

The typical weight of the codeposited films was of 0.90-1.10 g, determined by weighting the cathode before and after electrodeposition for the samples investigated during the 90 min. electrocodeposition. The chemical composition on

the cross section of composite layers was analyzed by EDAX analysis (Energy Dispersive Analysis X-ray), and the results confirm that the particles are embedded in the nickel matrix. Table 1 shows the correlation between the concentration of the  $\text{Al}_2\text{O}_3$  nanoparticles in the electrolyte, and to their embedded amount in the matrix, presented as weight (wt %) and as volume (vol. %) within the layer.

*Table 1*  
The nano- $\text{Al}_2\text{O}_3$  particles embedded in the nickel matrix compared to their concentration in the electrolyte

Composite coatings	nano- $\text{Al}_2\text{O}_3$		
	in the electrolyte g/L	in the layer (EDAX) wt %	in the layer vol. %
Ni/nano- $\text{Al}_2\text{O}_3$	5.0	1.90	2.30
Ni/nano- $\text{Al}_2\text{O}_3$	10.0	5.22	6.53
Ni/nano- $\text{Al}_2\text{O}_3$	20.0	6.30	6.92

### 3. Microstructure and roughness surface.

The uniformity of the dispersed phase in the Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings was examined by optical microscopy (OM) on the cross section of layers. The microstructure of the deposits shows compact films and a uniform distribution of the

dispersed phase. The particles of nano- $\text{Al}_2\text{O}_3$  appear as agglomerations in the nickel matrix. Figure 2 presents the morphological structure in the cross section for the Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings, compared with pure nickel deposits.

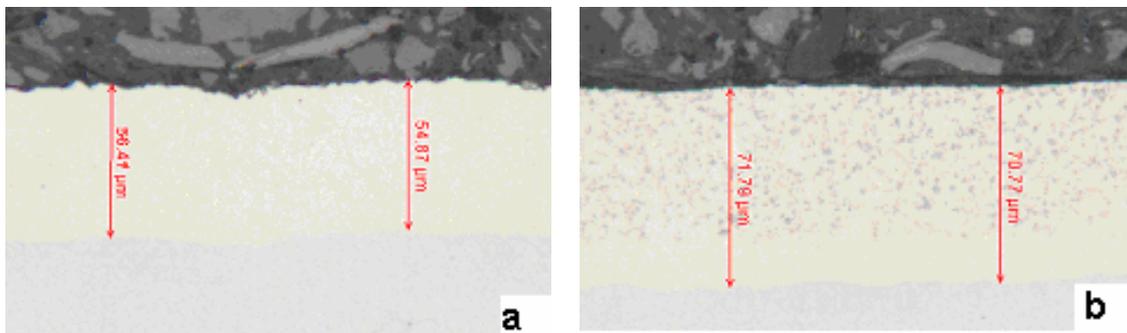


Fig. 2 – Optical micrographs on the cross section of Ni/nano- $\text{Al}_2\text{O}_3$  composite electrodeposited from a Watts electrolyte: a) 5 g/L oxide; b) 10g/L oxide.

The scanning electron microscopy (SEM) studies reveal the morphological surfaces of coatings deposited with and without dispersive nanoparticles in the composite deposits. SEM micrographs of the composite coatings were compared with those of pure Ni deposits (Fig. 3). The deposits reveal smooth uniform and compact

films of fine grains without any pores or fissures on the surface. The alumina nanoparticles codeposited of alumina cannot be separated from the electrodeposition process of nickel ions reduction. Table 2 shows that  $\text{Al}_2\text{O}_3$  nanoparticles change the roughness of the surface of layers obtained.

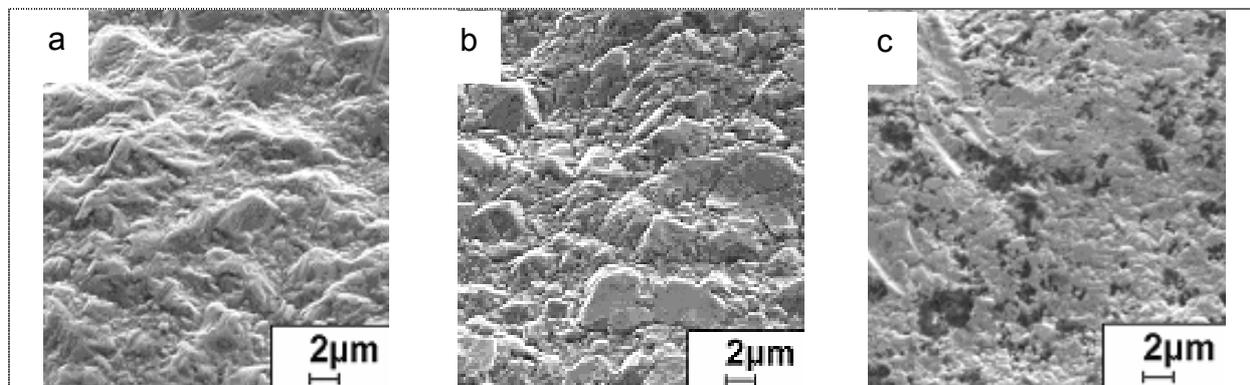


Fig. 3 – SEM micrographs of Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings on the surface: pure Ni (a), 5 g/L nano- $\text{Al}_2\text{O}_3$  (b) and 10 g/L nano- $\text{Al}_2\text{O}_3$  in the electrolyte.

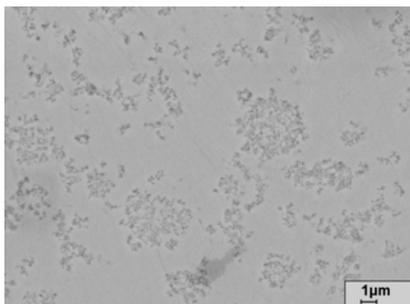


Fig. 4 – SEM image on the cross section of Ni/ nano- $\text{Al}_2\text{O}_3$  composite coating; 20g/L oxide in electrolyte.

Table 2

The surface roughness of Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings

Coatings	$\text{Al}_2\text{O}_3$ (g/L) in the electrolyte	Ra	Rz	$R_{\max}$
Ni	-	1.05	8.13	18.97
Ni/nano- $\text{Al}_2\text{O}_3$	5	0.88	5.29	6.35
Ni/nano- $\text{Al}_2\text{O}_3$	10	0.78	5.34	7.89
Ni/nano- $\text{Al}_2\text{O}_3$	20	0.88	5.03	5.64

**4. Microhardness.** The most frequently used tests to estimate the properties of electrodeposits may be on the strength and ductility, which is also an indicator in the same case of the hardness. It can be also useful as an indication of wear resistance. The microhardness is controlled by the amount of dispersed particles embedded in the layer. There are different effects by other characteristics on the

hardening mechanism, e.g. grain specimen, dispersion hardening etc. The microhardness of Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings was carried out on the cross section of layers by means of the Vickers test. The presence of the dispersed nanoparticles of  $\text{Al}_2\text{O}_3$  in the composite coatings increases the microhardness of the layers obtained. The results are presented in Figure 5.

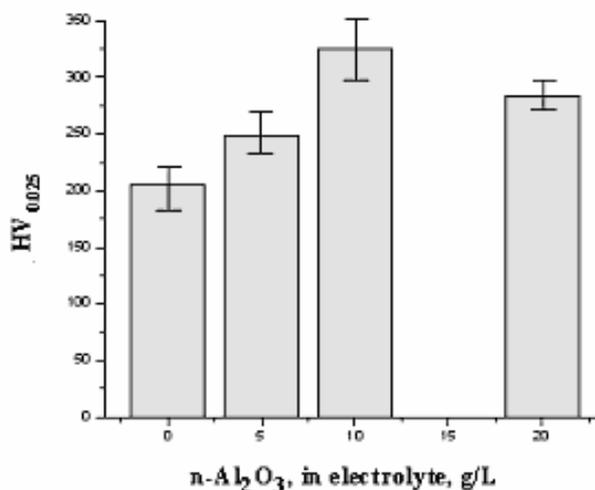


Fig. 5 – Microhardness of Ni/nano- $\text{Al}_2\text{O}_3$  composite coatings obtained at 3  $\text{A}/\text{dm}^2$  and 90 min. electrodeposition.

## DISCUSSION

The purpose of the present study is to explain the effect of nano- $\text{Al}_2\text{O}_3$  particles as dispersed phase in the nickel matrix on the morphological surface and to correlate this with the mechanical characteristics (microhardness) of the obtained composite coatings.

**1. Thickness.** The thickness of layers obtained (Fig. 1) at low nano- $\text{Al}_2\text{O}_3$  concentration (5 g/L oxide) in the electrolyte is about 80 % bigger than in the case of pure nickel deposition, keeping constantly all electrolyse parameters (electrolyte composition, pH electrolyte, deposition time, current density). This effect can be attributed to the effect of the surface area on the nanoparticles

embedded in the matrix. This means that the nickel ions deposit on the carbon steel substrate, as well as on the available surface of the particles which will in the following step be incorporated in the growing layer. In case of Ni/nano-Al<sub>2</sub>O<sub>3</sub> composite coatings using bigger nanoparticles concentrations (10 and 20 g/L oxide in electrolyte), the layers' thickness decreases with about 20 % than for the layers obtained with 5g/L oxide. This fact can be explained by the growth of the agglomerating nanoparticles in the layers in case of using 20g/L oxide particles in the electrodeposition bath (Fig. 4).<sup>11-12</sup>

**2. Chemical composition.** With an increase of dispersed nanoparticles concentration in the electrolyte, the embedded particle amount in the composite layers increases as well. From Table 1 it can be seen that the nano-Al<sub>2</sub>O<sub>3</sub> amount embedded

in composite layers is more than double (approx. 50%) when the particle concentration was of 10g/L oxide, instead of 5 g/L in the electrolyte (Fig. 5). When the particles concentration in the electrolyte increased from 10 to 20 g/L, the amount of incorporated nanoparticles was about 20 % bigger. As already mentioned, the thickness of the composite layers decreases by increasing the concentration of the particle in the electrolyte. The above phenomena corresponds to the agglomeration of particles in the electrolytic bath, especially at larger concentrations. For agglomerations of nanoparticles, the phenomena can be observed in Fig. 4. The EDAX analysis for the Ni/ nano-Al<sub>2</sub>O<sub>3</sub> composite coatings shows the presence of nanoparticles of alumina (Fig. 6). Consequently, the oxide particles are embedded in the deposit layers.

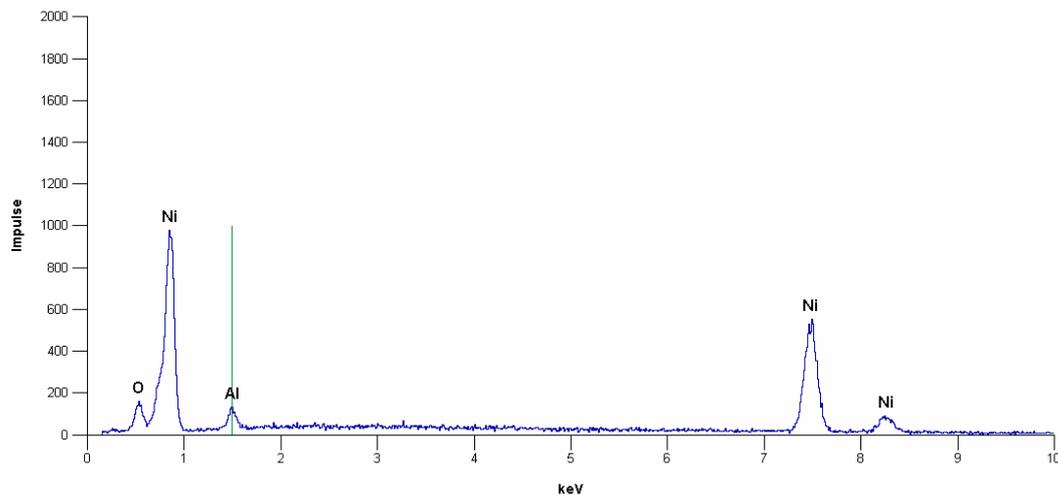


Fig. 6 – EDAX analysis on the cross section of Ni/ nano-Al<sub>2</sub>O<sub>3</sub> composite coatings deposited with 10 g/L nano-Al<sub>2</sub>O<sub>3</sub> in electrolyte.

### 3. Microstructure and roughness surface.

The microstructure of the Ni/ nano-Al<sub>2</sub>O<sub>3</sub> composite coatings present a different morphology compared to the pure nickel layer (Fig. 3). This depends on the nanoparticles which are in the electrolyte, as well as those embedded in the layer. The mechanism of electrocodeposition with inert particles is not fully understood. The dispersed phase embedded in the coatings is, predominantly by means of mechanical agitation in the electrolyte, incorporated into the metal coatings that develop through electro-crystallization. The changes in the grain size of pure nickel, compared with the grains from composite coating with incorporated nanoparticles from the same electrolyte, give information on the effect of the

dispersed phase in the electrocodeposition process. The structure of Ni/nano-Al<sub>2</sub>O<sub>3</sub> obtained from an electrolyte with 5g/L oxide differs from the composite obtained from an electrolyte with 10 g/L oxide in the electrolyte and pure nickel.

The surface roughness measured by parameters Ra (arithmetic mean deviation), Rz (maximum height of profile) and R<sub>max</sub>(maximum height for largest profile peak) depends on the amount of Al<sub>2</sub>O<sub>3</sub> embedded in the nickel matrix (Table 2). In general, it can be seen that the roughness of the layers measured by Ra decreases when there is an increase of nanoparticles in the electrolyte. In contrast to the clear data in Table 2 and Fig. 3, the smoothing effect is not due to the embedded particles. The coating surfaces are smooth and dense, but they also present roughness.

**4. Microhardness.** An increase of layers' microhardness of about 100 HV<sub>0.025</sub> (50% more) was investigated for the Ni/nano-Al<sub>2</sub>O<sub>3</sub> composite coatings, obtained by using of 10 g/L oxide in electrolyte (Fig. 5). This concentration of oxide can be seen as a certain limit in the electrolyte for the improvement of the layers microhardness. Exceeding concentration of oxide will lead to a lower hardness. The results of microhardness carried out at layer without additive (sodium dodecylauryl) prove the necessity of using it in the electrodeposition processes.

## EXPERIMENTAL

The Ni / nano-Al<sub>2</sub>O<sub>3</sub> composite coatings were obtained by electrodeposition from a suspension of Al<sub>2</sub>O<sub>3</sub> nanoparticles (20 nm, Degussa) into Watts electrolyte. The composition of nickel bath used in experiments was 0.90 M nickel sulfate (NiSO<sub>4</sub>·6H<sub>2</sub>O), 0.20 M nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O), 0.28 M H<sub>3</sub>BO<sub>3</sub> and 0.4 g/L sodium dodecylauryl [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSONa] as additive. Particles of nano-Al<sub>2</sub>O<sub>3</sub> were added in concentration of 5 to 20 g/L in the bath. To preserve the uniformity of the suspension, the electrolyte was magnetically stirred at 700 rpm. The electrochemical cell used in this study was a 500 mL glass cylinder. The pure nickel used as anode was placed 50 mm away from the cathode surface, the carbon-steel substrate having an active area of 25 cm<sup>2</sup>. Before the electrodeposition the samples were polished using alumina powder, degreased, electrochemically cleaned, and washed.

All composite coatings experiments were obtained at a temperature of 50-54°C using a potentiostat Univat -Lab. The current density was of 3 A/dm<sup>2</sup>. The pH value of the electrolyte was kept between 4.20-4.50, by carefully controlling the electrocodeposition processes. Due to the number of variables which affect the resulting deposits, five separate experiments were carried out for each working parameter preserved. The thickness of the composite layers obtained varies depending on the electrolyse parameters, and were measured in the cross section with a Fischerscope equipment and by means of a light microscope (Olympus PME 3). The morphological surface and composition of composite coatings were studied by scanning electron microscopy (SEM), with an X-ray analyzer (EDAX) and using a JEOL 6400F equipment. The Vickers microhardness was measured on the cross section of layers using a microhardness analyzer of Buehler (micromat 1). Additionally, the surface roughness of layers was measured by applying a Hammel tester.

The results are compared to pure nickel coatings without particles, so as to understand the effect of the Al<sub>2</sub>O<sub>3</sub> nanoparticles on the microstructure and mechanical characteristics of composite coatings during the electrocodeposition processes.

## CONCLUSIONS

Electrocodeposition of nano-Al<sub>2</sub>O<sub>3</sub> particles in a nickel matrix was investigated with the main goal to evaluate the effect of nanoparticles in electrolyte suspension during of the nickel reduction. The particles embedded in the layer depend on the concentration of Al<sub>2</sub>O<sub>3</sub> particles in the Watts bath. However, the nanoparticles of alumina appear agglomerated in the layers of a nickel matrix when the concentration of oxide is of 20g/L in electrolyte. The microstructure of Ni/nano-Al<sub>2</sub>O<sub>3</sub> composite coatings changes as compared to pure nickel deposits. The microhardness of the composite layers was improved with more than 50%.

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