

PREPARATION AND CHARACTERIZATION OF ELECTROLESS Ni-P-Al₂O₃ NANOCOMPOSITE COATINGS

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The incorporation of Al₂O₃ particles as a disperse phase in a matrix of electroless nickel phosphorous (Ni-P) coatings can influence some characteristics of coating layer such as thickness, surface morphology, structure, chemical composition, hardness, corrosion resistance. Co-deposition of Al₂O₃ particles in electroless Ni-P coating and their influence on the coating layer characteristics depend on their size, concentration in the electrolyte, by the duration of the deposition process and the manner to maintain good dispersion of particles in electroless Ni-P bath. The paper analyzes the influence of nanoparticles (20nm) and micrometer (0,3μm) of Al₂O₃ incorporated in the electrolyte in amounts of 3g/L, 5g/L and 8g/L on the different characteristics of the composite coating layer. By optical microscopy was settled the influence of Al₂O₃ particles on the coating layer thickness and surface morphology. The degree of incorporation and dispersion of Al₂O₃ particles in electroless Ni-P and Ni-P-Al₂O₃ composite coatings were analyzed by scanning electron micrograph (SEM) and energy dispersive spectroscopy (EDS). Influence on the corrosion behavior was analyzed by electrochemical method. Composite and nanocomposite layers were deposited on thin steel band.

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1. Introduction

The composite and nanocomposite coatings in Ni-P matrix can contain as dispersed phase hard particles such as: diamond, SiC, B₄C, Si₃N₄, CeO₂, TiO₂, Al₂O₃, etc., which result in increasing the hardness, wear resistance and corrosion resistance or resistance to soft particles such as PTFE, MoS₂, HBN, graphite etc., which gives the best lubrication, reduces the friction coefficient and improves the corrosion resistance of coated surfaces [1].

Usually, the co-deposition processes of second-phase particles take place in the electroless process, at low temperature when the chemical interaction between particles and metallic matrix is not favored. The particles are attached only physically on the Ni-P matrix, thus, a thermal treatment of these coatings is necessary, in order to promote phase transformations which would influence the adherence but also some properties of the deposited layers [2-6].

The particles co-deposition depends on their size, shape, concentration, density and the realization way of the suspension in a chemical nickel-plating bath. Furthermore, the chemical nickel-plating processes, for composite or nanocomposite layers realization, are very much dependent on the electric charges from the particles [7-9].

The Ni-P-Al₂O₃ composite coatings realized through the electroless method have a wide range of uses due to the increased hardness and a very good corrosion resistance.

The alumina is widely used due to the high elasticity modulus, high capacity of maintaining at high temperatures, as well as to the great wear resistance. Alirezaei et al. [10]

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reported that the deposition rate, particle co-deposition rate, the roughness and hardness of coatings of Ni-P-Al₂O₃ composites were influenced by the concentration of alumina in the bath. The medium roughness and the hardness increase with Al₂O₃ particles content. The resistance towards oxidation of Ni-P alloys at high temperature is significantly higher by Al₂O₃ addition, causing a decrease of oxidation rate for a growing proportion of Al₂O₃ in the composite [11].

The particle incorporation in the Ni-P metallic matrices is a convenient method to prepare composite or nanocomposite coatings and the particles increase the mechanical and physical properties of the coatings. The activation energy of the crystallization is lower due to the presence of co-deposited particles in the composite layer [12, 13].

2. Experimental

The experimental researches aimed to obtain and characterize some composite and nanocomposite coatings by including in the Ni-P matrix some alumina particles with 0.3 μm and 20 nm sizes, for different quantities of alumina from the nickel-plating bath, respectively 3g/L, 5g/L and 8g/L. It was also aimed the verification of some controversial or insufficiently explained aspects, presented in literature, such as Al₂O₃ influence on corrosion resistance or the influence on the Ni and P proportion in the Ni-P-Al₂O₃ composite and nanocomposite layers. The composite and nanocomposite layers were realized on samples with sizes of 30x60 mm, made of 0.4 mm thick steel sheet, with low carbon content and with the chemical composition presented in Table 1.

Table 1. Chemical composition of supporting steel strips

Chemical composition [wt.%]												
C	Si	Mn	P	S	Al	As	Ti	V	Cu	Ni	Cr	Mo
0.025	0.015	0.210	0.013	0.010	0.046	0.004	0.002	0.001	0.005	0.008	0.025	0.001

Before the coating process, the strip surface was prepared as follows:

- chemical degreasing, at 80-90°C, followed by washing in warm (80-90°C) and cold water;
- pickling in hydrochloric acid 20% and washing in warm water, at nickel-plating bath temperature, in order to maintain its temperature at the time of sample immersion in the nickel-plating solution.

The experimental work bench consisted of:

- hot plate with stirrer and temperature sensor;
- 500mL beaker provided with a support for sample attachment, which was immersed in a crystallizer with water for constant temperature maintaining;
- 100°C thermometer;
- pH- meter.

In the conducted laboratory experiments several nickel-plating baths were studied, with different chemical compositions, presented in Table 2.

Table 2. Chemical compositions of the electroless plating bath

Nickel-plating bath components [g/L]	Completed coatings		
	Ni-P	Ni-P-Al ₂ O ₃ composite	Ni-P-Al ₂ O ₃ nanocomposite
Nickel sulphate	24	24	24
Sodium hypophosphite	20	20	20
20 nm sized alumina	-	-	3g/L; 5g/L; 8g/L
0.3μm sized alumina	-	3g/L; 5g/L; 8g/L	-
Sodium acetate	9	11	11
Lead acetate	0.01	0.03	0.03
Acetic acid and sodium hydroxide	For pH correction		

As particles for co-deposition, high purity (99.98%) α alumina was used. Because the insertion of Al_2O_3 powder in the nickel-plating electrolyte caused a rapid destabilization of the bath, an increase of the amount of stabilizer (lead acetate) and sodium acetate was necessary.

It was found that an amount of 0.03 g/L of lead acetate and 11g/L of sodium acetate is necessary to stabilize the electrolyte in the presence of Al_2O_3 , regardless of size and amount of particles added.

Prior to introduction into the nickel-plating bath, the alumina particles were placed in 100mL of electrolyte and agitated at 600 rpm for 120 minutes, for optimal dispersion and wetting of these particles.

The parameters tested in the deposition process for composite layers obtaining are presented in Table 3.

Table 3. The working parameters provided for coatings obtaining

pH	T [°C]	Process duration [min]	Stirring rate [rpm]
4.8-5	85±1	15; 20; 30; 60	200 for Ni-P 600 for Ni-P- Al_2O_3

The realization in an acid (4.8-5 pH) electrolyte was opted, for several reasons:

- a better adhesion on coatings on steel substrate is ensured;
- a greater stability of the bath is ensured, which is important in the case of destabilization effect of alumina particles.

The pH correction from the fresh solution (pH 6.67) to the working level was done using acetic acid. Maintaining the pH at low values during the process was done by using 10% solution of sodium hydroxide. The pH correction presents the risk of salt precipitation in the electrolyte, for a certain amount of added sodium hydroxide, by sodium sulfite forming.

Macroscopically, the electrolyte goes from clear green liquid to an opaque green liquid with white flocks. For this reason the correction was done after each nickel-plated sample with very small quantities of sodium hydroxide solution.

While in the case of obtaining Ni-P coatings the stirring has the role of removing the hydrogen resulted from the process, in the case of obtaining composite coatings it has a supplementary role of maintaining the alumina powder in a uniformly dispersed suspension. Maintaining the stability of particle dispersion (especially for the nano-sized ones) throughout the nickel-plating bath required the application of a high speed stirring of 600 rpm (three times higher than the one for Ni-P deposition).

Research has shown that low-rate stirring allows the settling of alumina particles. Stirring rates higher than 600 rpm (for the particular conditions of the experiment) creates vortex currents leading to non-uniform deposition on both sides and preferential ones on the side of the holder. Even at 600 rpm a different deposition is observed on the both sides of the sample and a deficiency of particle incorporation in the layer, especially for the micro-sized ones. To compensate this effect a periodically rotation (every 5-10 minutes) of the sample was applied during the plating process.

The temperature was maintained at values lower than 90°C to avoid the bath destabilization. Different immersion durations were tested to observe the effect of alumina particle presence on the film thickness.

3. Results and discussion

3.1. EDS analysis

The chemical composition of the layers was obtained by EDS analysis on a Quanta 200 type scanning electron microscope produced by FEI (China). The analysis was performed on the

section of the layer. The experimental results revealed a low Ni and P content in the composite coatings compared to the ones obtained using the same working conditions but without Al_2O_3 , respectively 12.42% P. This fact is universally revealed by the literature [14-18]. The results regarding the influence of alumina particles quantity and size in the electrolyte towards nickel and phosphorus content in the layer is however differently characterized in the literature. Thus, when alumina content in the electrolyte increases from 0.25 g/L to 2 g/L the decreasing of both phosphorus and nickel content is supported while in [16] and [17] is mentioned that nickel content decreases and the phosphorus content increases for 3; 5; 10 g/L of alumina. For high alumina contents (20-100 g/L) the Ni and P content decreases in the coating for increasing alumina contents as shown in [16] and [18]. In [14] is mentioned that the Ni content increases in the composite compared to the Ni-P coating and the P content decreases when the alumina size is higher, for the same content in the nickel-plating bath, respectively 6 g/L.

In this study was observed a constant decrease of nickel content and an increase of P in the coating when 0.3 μm sized Al_2O_3 content was increased, as shown for similar alumina contents in the electrolyte [16] and [17]. For nanocomposite coatings the chemical composition variation with nano-sized alumina from electrolyte was not significant.

The decreasing of Ni content in the matrix when alumina particles content increases in the plating bath is explained by the fact that alumina does not have an auto-catalytic effect towards nickel thus, hinders its coating on the surface and occupies areas that would have been occupied by nickel [16]. This phenomenon was observed during the metallographic analysis of the layer, (Figure 1).

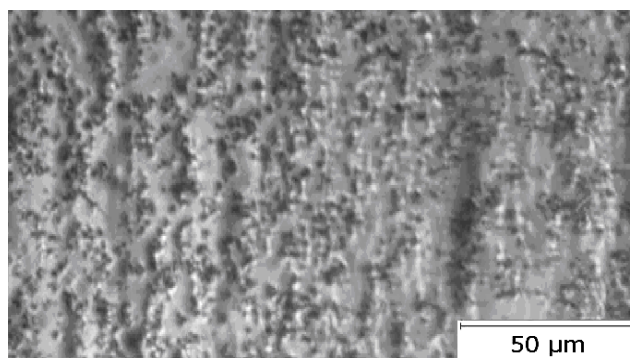


Fig. 1. Surface of Ni-P- Al_2O_3 composite coating plated in the bath with 8 g/L Al_2O_3 - 0.3 μm

The increasing phosphorus content when the alumina content in the electrolyte is increased may be explained by its driving by the alumina particles towards the sample surface. The results from [16] shows that this mechanism is possible for certain alumina contents when alumina presence starts to limit the phosphorus deposition.

The results of EDS analysis for the composite samples with 0.3 μm sized alumina are shown and Figure 2. The amount of alumina incorporated, reflected by the Al content, is relatively close for the three alumina contents in the bath.

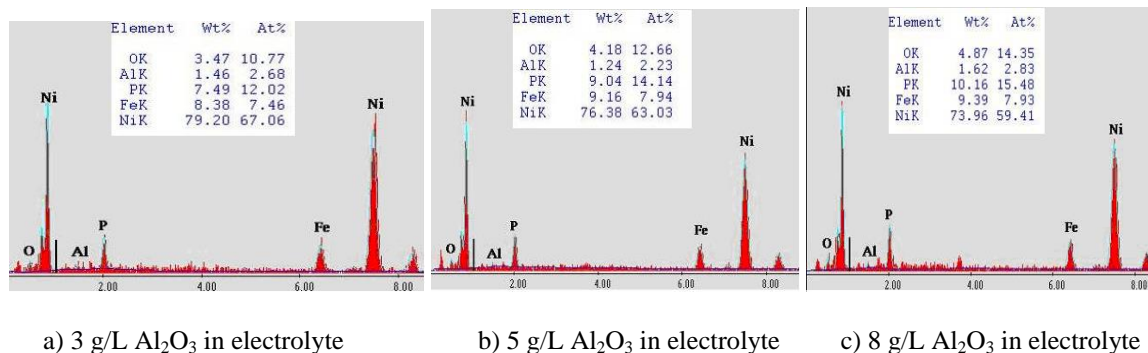


Fig. 2. EDS spectra of electroless Ni-P- Al_2O_3 composite coatings with Al_2O_3 disperse phase of $0.3 \mu\text{m}$ size

The EDS analysis of Ni-P- Al_2O_3 with 20 nm sized Al_2O_3 nanocomposite layers (Figure 3) showed that in comparison with the composite layers a non-significant variation of P and Ni content in the coating for Al_2O_3 content increase due to a better particle incorporation and dispersion in the layer, observed by metallographic analysis.

The alumina content in the nanocomposite layers shows that the inclusion degree of alumina particles in the nickel-plating baths with 3 g/L and 5 g/L is close and increases for 8 g/L, which is also observed when analyzing the composite samples with micrometric alumina dispersed phase.

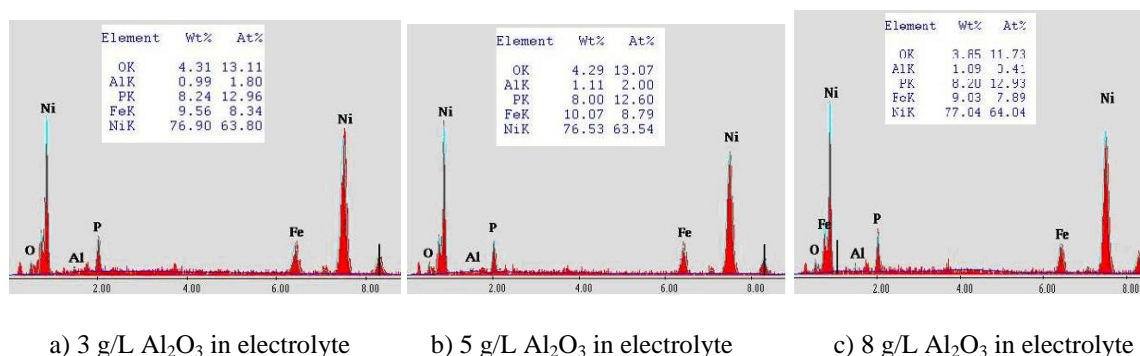


Fig. 3. EDS spectra of electroless Ni-P- Al_2O_3 nano-composite coatings with Al_2O_3 disperse phase of 20 nm size

3.2. Surface morphology

The macroscopic analysis of the coating layers surface realized by electroless nickel-plating, shows that composite and nanocomposite layers are less lustrous compared with Ni-P layers and the more opaque by Al_2O_3 increase in the layer. The composite and nanocomposite coatings surface is rougher compared to the smooth surface of Ni-P layers, especially when the alumina content is higher. The $0.3 \mu\text{m}$ sized alumina layers are rougher compared to those with 20 nm sized alumina. The optical microscopic analysis of the surface shows an uneven structure, with nickel areas in relief and depressions where alumina was included (Figure 1 and Figure 4).

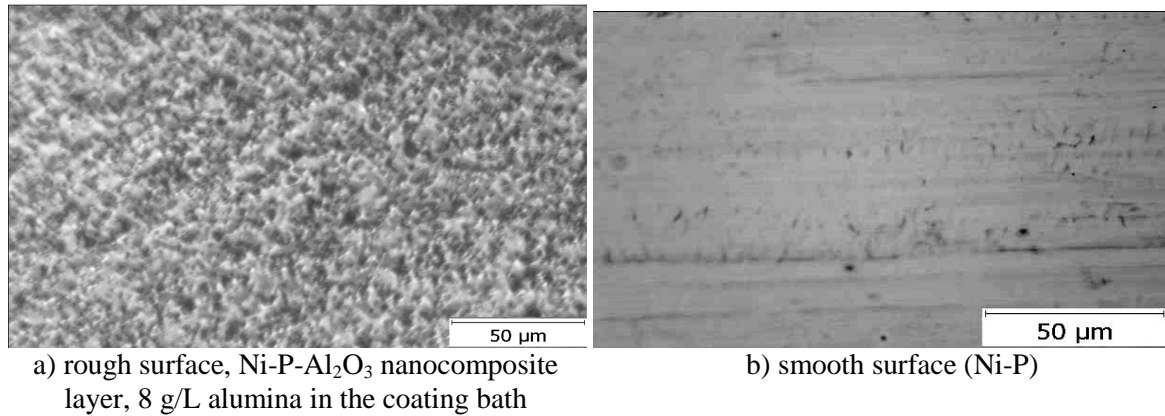


Fig. 4. Comparative aspects of samples surface coated with Ni-P and with Ni-P-Al₂O₃

The surface's unevenness in the presence of alumina, regardless of its dimensions is obvious in the layers section, as can be observed in Figure 5. In Figure 5b and 5c is observed that where alumina is present indentations appears in the surface. This phenomenon appears because alumina does not ensure an auto-catalytic support for nickel deposition [15].

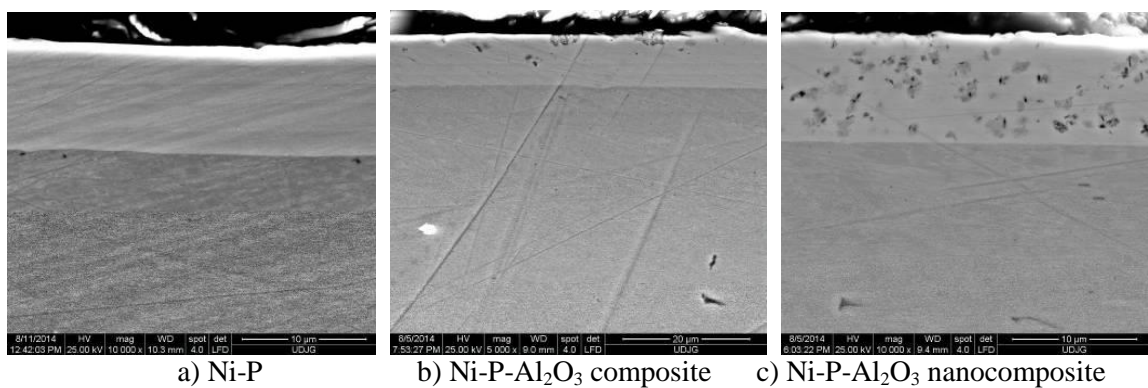


Fig. 5. The influence of Al₂O₃ on surface smoothness

The optical microscopy analysis of the surface shows for both composite coatings (Figure 6) and for nanocomposite coatings (Figure 7) an increase of included alumina particles quantity for alumina quantity in the electroless bath.

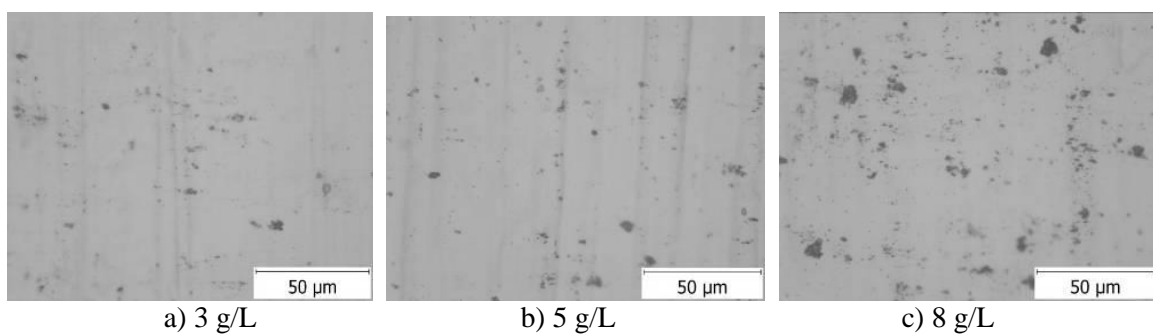


Fig. 6. Optical micrographs of Ni-P-Al₂O₃ composite coatings surface

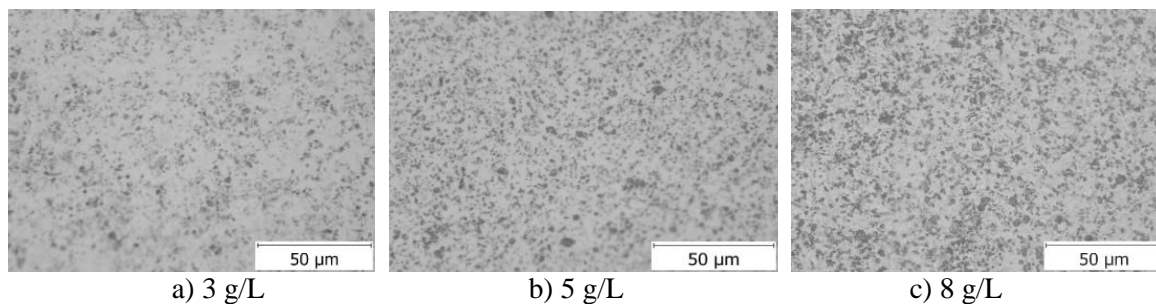


Fig. 7. Optical micrographs of Ni-P-Al₂O₃ nanocomposite coatings surface

It is also observed that compared with the 0.3 μm sized alumina composite layers, the nanocomposite layers presents a significantly higher inclusion degree of 20 nm sized alumina, regardless the alumina content in the electrolyte. The dispersion of nanometric alumina particles is also much better compared to the micrometric alumina.

2.3. The analyses of layer thickness and of coating layers adherence

The layer thickness and the adherence were realized by metallographic analyzing of composite and nanocomposite layers in cross section. The analysis was done based on the micro- and nanometric alumina particles quantity introduced in the electroless bath, while the other parameters with known influence [19] respectively, duration, temperature and pH of the process were maintained at constant values.

Figure 8 presents the influence of 0.3 μm sized alumina quantity on the layer thickness and Figure 9 that of the 20 nm sized alumina.

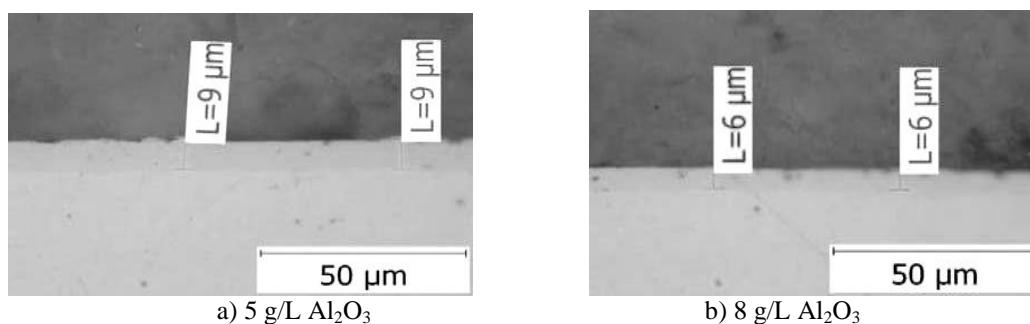


Fig. 8. The influence of micrometric Al₂O₃ on layer thickness composite coatings

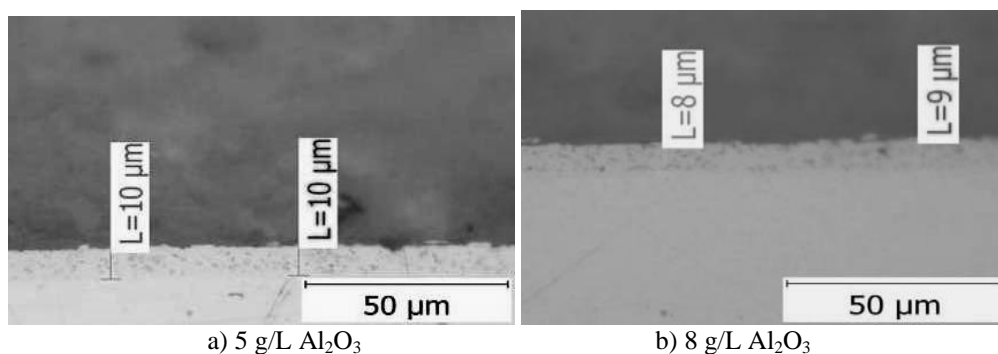


Fig. 9. The influence of nanometer-size Al₂O₃ on layer thickness of nanocomposite coatings

Because when Al_2O_3 content is increased, in the nickel-plating bath the coated nickel decreases, is observed from Figure 8 that the thinnest layers results at 8 g/L of Al_2O_3 .

Unlike composite layers, little differences are observed in the case of nanocomposite ones for layer thickness depending on the alumina content, possibly due to closer values of the Ni and P contents of these layers.

Regarding the adhesion of deposited layer, the metallographic analysis shows for both types of layers a perfectly continuous interface with the steel, without discontinuities which shows a good adherence to the steel substrate.

2.4. The microstructural analysis

The analysis realized using the scanning electron microscopy (SEM) for layers section (Figure 10), shows that in the composite layers the alumina quantity increases in the layer when the particle content increases in the nickel-plating bath. It is also observed that for 3 g/L and 5 g/L alumina in the electrolyte, the inclusion degree is very low and the most particles are on the layer surface and even agglomerated. For 8 g/L more particle are included in the layer but still agglomerated. As already noted for the layer thickness, the decrease of this characteristic is observed when Al_2O_3 particle content is increased.

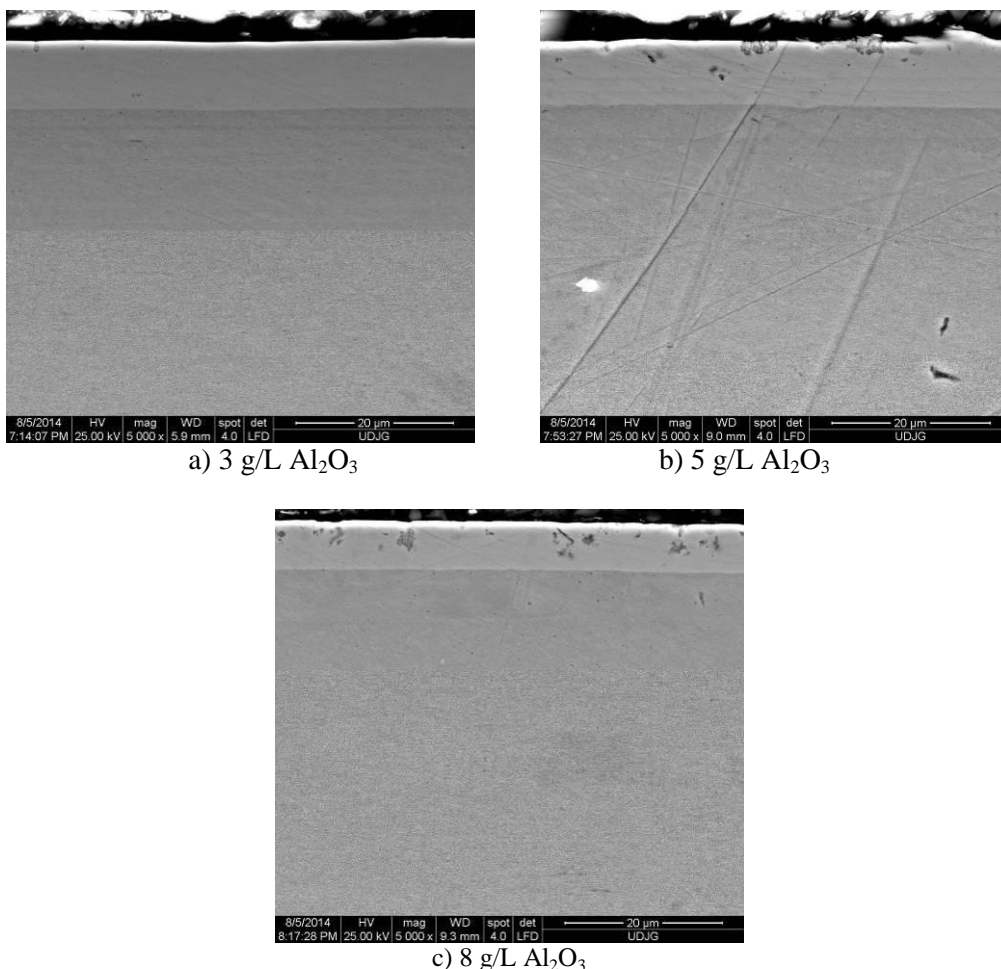


Fig. 10. SEM micrographs of cross-section of electroless Ni-P- Al_2O_3 composite coatings at different Al_2O_3 (0.3 μm) amounts in bath

The cross-section analysis of the nanocomposite layers shows both a very good inclusion degree of alumina and its uniform dispersion in the whole coated layer. SEM images presented in Figure 11 shows an increase of the alumina quantity in the layer for particle quantity increasing in the nickel-plating bath.

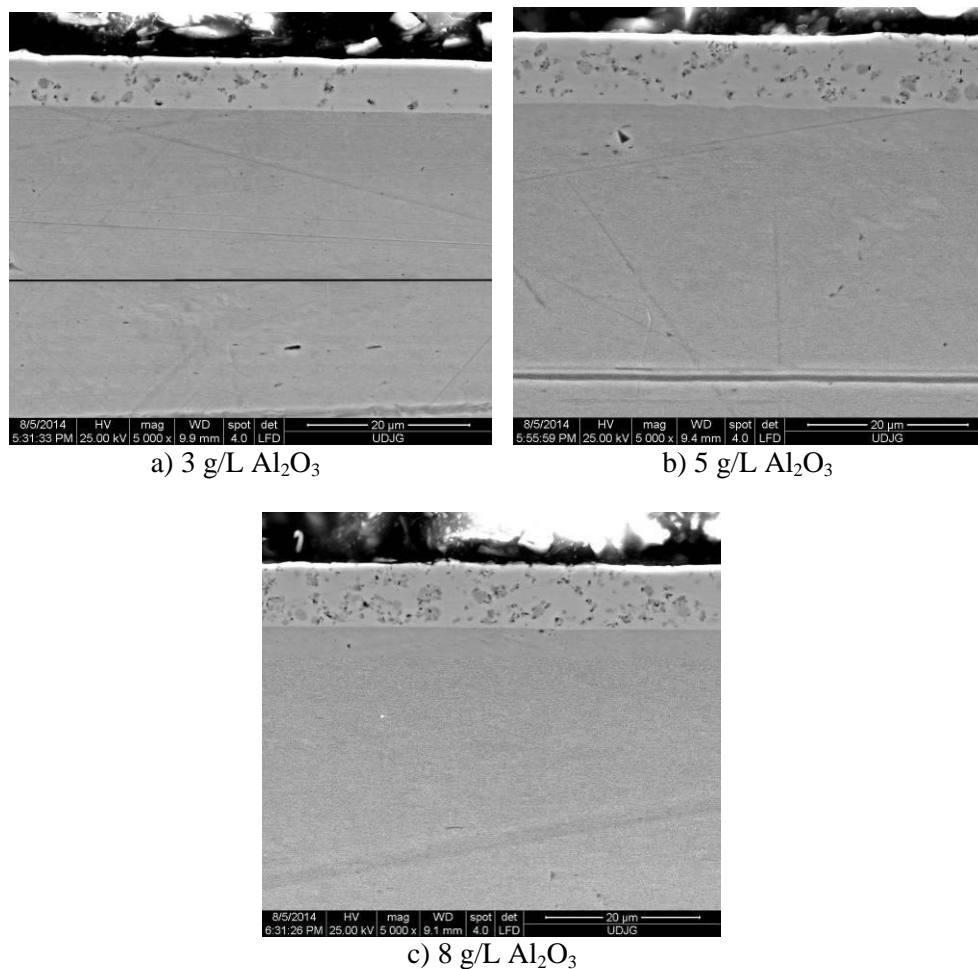


Fig. 11. SEM micrographs of cross- section of electroless Ni-P-Al₂O₃ nano-composite coatings depending on Al₂O₃ (20 nm) amounts in bath

3.5. The corrosion behavior

The corrosion resistance was measured by using a PGP 201 type potentiostat connected to an electrochemical cell with three electrodes: working electrode (the tested sample); platinum counter-electrode and a calomel Hg/Hg₂Cl₂ saturated reference electrode. The samples were cleaned with acetone before immersion in the testing solution, respectively 3.5% NaCl.

The results of the analysis (Figure 12 and Table 4) shows an increase of the corrosion resistance for alumina content increase both for micrometer-size Al₂O₃ and for nanometer one. Due to a better inclusion degree of the nanometer-size Al₂O₃, the best corrosion behavior in 3.5% NaCl is presented by the layers obtained for 8 g/L of 20 nm sized alumina coating bath.

Table 4. Electrochemical parameters of the coatings derived from Tafel plots

Coating	E cor [mV]	Rp [kohm cm ²]	I cor [μA/cm ²]	β _a [mV/decade]	β _c [mV/decade]
Ni-P + 3g/L Al ₂ O ₃ 0.3 μm	-444.5	7.00	2.02	65.3	109.1
Ni-P +5g/L Al ₂ O ₃ 0.3 μm	-410.3	13.51	1.55	146.0	104.4
Ni-P +8g/L Al ₂ O ₃ 0.3 μm	-386.2	17.98	1.13	159.3	84.5
Ni-P+ 3g/L Al ₂ O ₃ 20 nm	-472.5	2.75	1.70	33.2	36.9
Ni-P +5g/L Al ₂ O ₃ 20 nm	-489.2	5.05	1.19	33.1	49.1
Ni-P +8g/L Al ₂ O ₃ 20 nm	-470.4	5.87	1.04	33.7	40.3

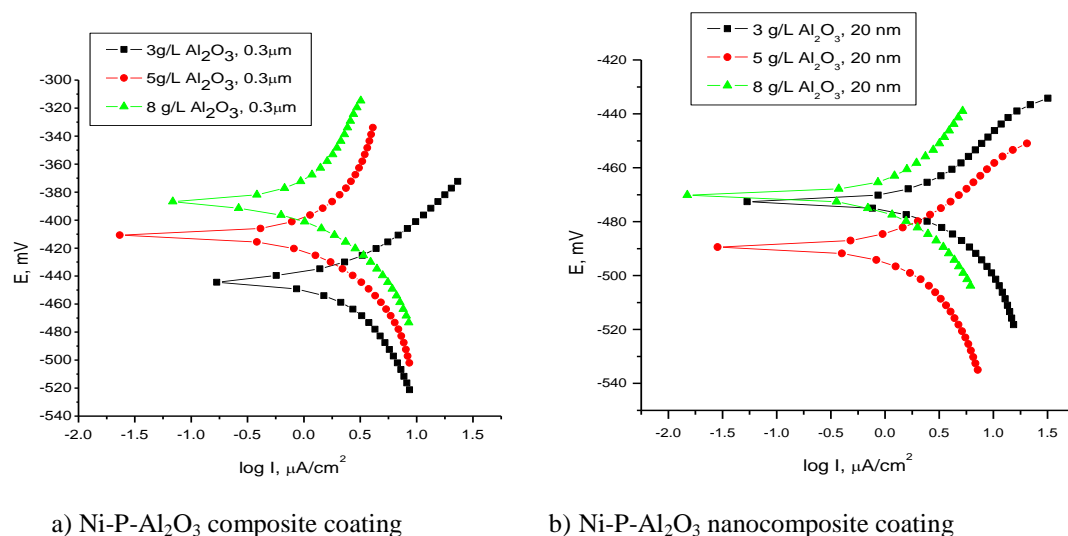


Fig. 12. Potentiodynamic polarization curves of composite and nanocomposite layers in 3.5% NaCl

The anodic polarization curves (Figure 13) shows for the nanocomposite samples a clear passivation due to the presence of higher alumina content on the surface. Corrosion tests by mass loss evaluation in different corrosive environments (which will be the subject of another work) confirmed these results. However, in strong acid environments in HCl solutions, Ni-P coatings with high phosphorus content presented a higher corrosion resistance compared to the composite and nanocomposite coatings with 0.3 μm and 20 nm sized alumina.

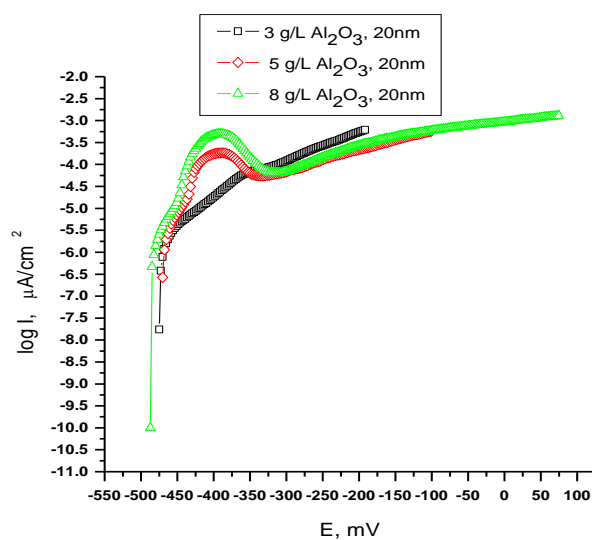


Fig. 13. Anodic polarization curves of Ni-P-Al₂O₃ nanocomposite layers

4. Conclusions

- The introduction of Al₂O₃ powder in the electrolyte can rapidly destabilize the nickel-plating bath requiring the increase of stabilizer quantity compared to the bath used for obtaining Ni-P layers.
- Maintaining the particle dispersion (especially the nanometric ones) in the whole nickel-plating bath required the utilization of a high stirring rate, namely 600 rpm.

- The quantity of Al₂O₃ particle included in the Ni-P-Al₂O₃ composite or nanocomposite is increasing when the concentration of particles in the coating solution is increasing, regardless the Al₂O₃ particles sizes.
- The particles sizes influences the inclusion degree, the research results showing a better inclusion of 20 nm sized particles than 0.3 μm sized ones.
- The inclusion and dispersion degree of nanometric alumina is significantly better than micrometric one and depends less on the alumina content in the electrolyte.
- The results from EDS analysis showed a lower P and Ni content in the coating than the one obtained in the same working conditions but without Al₂O₃.
- It was noted a decrease in Ni content and an increase of the P content in the coating for 0.3 μm sized Al₂O₃ content increase in the nickel-plating bath and implicitly in the layer. The introduction of 20 nm sized alumina does not significantly modify the chemical composition of the layers.
- The layers adherence and uniformity is appropriate and the layer thickness decreases insignificantly for nanometric alumina quantity increasing in the electrolyte.
- The corrosion resistance increasing for alumina content increasing both for micrometric and nanometric alumina.
- Due to the better inclusion degree of the nanometric alumina, the best corrosion behavior in 3.5% NaCl is that of the layers obtained in coating baths with 8 g/L of 20 nm sized alumina.

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