COMPORTAREA ÎN DIFERITE MEDII DE COROZIUNE A ACOPERIRILOR Ni-P ȘI Ni-P-Al_2O_3 COMPOZITE DEPUSE PRIN METODA CHIMICĂ PE SUPRAFATA BENZILOR SUBȚIRI DIN OȚEL

CORROSION BEHAVIOR IN DIFFERENT ENVIRONMENTS OF Ni-P AND Ni-P-Al_2O_3 COMPOSITE COATINGS BY ELECTROLESS DEPOSITION ON STEEL STRIPS SURFACES

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This paper presents a study on the corrosion behaviour of coatings by electroless deposition on the steel strips surfaces. For Ni-P and Ni-P-Al_2O_3 composite and nanocomposite layers, the variation of corrosion rate in two representative corrosive environments: an acid environment (H_2SO_4 solution of 5% concentration) and basic environment (NaOH solution of 10% concentration), it has been established, respectively. The corrosion rate was appreciated by using the gravimetric method (mass loss) reported to the area submitted to corrosive attack and the process duration. The study was conducted over a period of 7 days (168 hours) for the acid environment and 28 days (672 hours) in basic environment. The macroscopic appearance of the corroded surfaces was also investigated. The experimental results have emphasized a better behaviour in basic environment of composite coatings, comparatively with the Ni-P coatings with high phosphorus content. In acidic environment, a remarkable behaviour presented the composite Ni-P-Al_2O_3 and Ni-P alloy coatings, while samples with nanocomposite coating of Ni-P-Al_2O_3 were completely destroyed.

In această lucrare se prezintă un studiu privind comportarea la coroziune a unor straturi de protecţie depuse prin metoda chimică pe benzi subţiri din oţel. S-a stabilit viteza de coroziune într-un mediu acid (sol. 5% H_2SO_4) şi unul bazic (sol. 10% NaOH) pentru straturi Ni-P şi straturi compozite şi nanocompozite cu faza dispersă Al_2O_3, în matrice Ni-P. Viteza de coroziune s-a apreciat gravimetric, prin pierderea de masă raportată la suprafaţa supusă atacului coroziv şi durata procesului. Studiul s-a efectuat pe o durată de 7 zile (168 de ore) pentru mediul acid şi 28 zile (672 de ore) în mediul bazic. Tipul de coroziune s-a stabilit prin analiza macroscopică a suprafeţelor corodate. In urma testului de coroziune la duratele îndelungate de testare s-a constatat o comportare mult mai bună în mediu bazic a acoperirilor compozite faţă de straturile clasice de Ni-P cu conţinut ridicat de fosfor. In mediu acid, un comportament remarcabil l-au prezentat probele cu acoperire compozită de tip Ni-P-Al_2O_3 şi cele pe bază* de *aliaje de Ni-P, în timp ce probele cu acoperire nanocompozită de Ni-P-Al_2O_3 s-au distrus complet.

Keywords: *electroless deposition of steel strips surfaces, composite coatings*

1. Introduction

Coatings based on Ni-P alloys as well as Ni-P-Al_2O_3 composite obtained by electroless method have many user features such as: hardness, high wear resistance, corrosion resistance, ductility etc.[1]. Currently, over 30% of the applications of these types of coatings are targeting their excellent resistance to corrosion [2]. High corrosion resistance of Ni-P coatings is due to the formation of nickel coating which acts as a barrier to oxygen diffusion on metal surface. Compared with electrolytic coatings, the chemical coatings are usually less porous and more resistant to corrosion (at equal thickness) and the alloys with high phosphorus content lead to superior corrosion resistance in most corrosive environments [3,4]. The amount of Al_2O_3 particles embedded in the Ni-P-Al_2O_3 composite increases with the increasing of particle concentration of coating solution, and particle size greatly influences the amount of incorporated particles. The researches in the field revealed improved properties of these coatings by using various reinforcing phases (Al_2O_3, TiO_2, SiC, Si_3N_4, B_4C). This paper investigated the corrosion behaviour of Ni-P-Al_2O_3 composite layers, comparatively to the Ni-P layers in acid environment (H_2SO_4 solution of 5% concentration) and basic environment (NaOH solution of 10% concentration) during 7 day or 28 days, for each corrosive environment.

2. Experiments

2.1. Obtaining of composite coatings

Coatings based on Ni-P alloys and Ni-P-Al_2O_3 composites with different contents of dispersed micro- and nanometer sized alumina were obtained by electroless deposition by using an acid electrolyte based on nickel sulphate and

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sodium hypophosphite, in order to obtain uniform and adherent layers, which were achieved on thin steel strip of a 0.2 mm thickness.

In the case of Ni-P-Al_2O_3 composites coatings, in the chemical nickel bath have been added alumina particles of 0.30 μm and 20 nm respectively, in the amount of 3 g/l; 5 g/l and 8 g/l, for each dimension separately. Since the introduction of Al_2O_3 powder in the electrolyte causes rapid destabilization of nickel plating bath, this phenomenon was avoided by increasing the amount of stabilizer (lead acetate). Before introducing in the nickel bath, the alumina particles of high grade (99.98%) were mixed in 50 ml electrolyte by magnetic stirring with a speed of 600 rot/min, to allow an optimal dispersion and wetting of Al_2O_3 particles. Magnetic stirring at laboratory level is needed to remove the hydrogen from the deposition bath and to maintain chemical homogeneity of the electrolyte. Surface preparation of thin steel strip, which has a decisive role in obtaining a adherent, uniform and continuous coating, it consisted of: chemical degreasing at 80-90^{0}C, followed by washing in hot water and cold, pickling in 20% concentration hydrochloric acid and washing in warm water, at nickel plating bath temperature.

The samples of thin steel strip coated with the Ni-P alloys with different concentrations of P, as well as the Ni-P-Al_2O_3 composite layers with different sizes and concentrations of Al_2O_3 particles were symbolised as: 32, 40, 42, 84, 87, 94, 100,106 and 112.

The experimental coating conditions, pH, solution temperature, immersion time of the samples and the stirring speed are given in Table 1.

2.2. Characterization of the coatings deposited on the surface of samples

The pH of electrolytes was measured over time, using the HACH sensION156 Portable pH/Conductivity Meter. The meter can measure absolute millivolts (mV). Absolute millivolts are displayed with 0.1 mV resolution in the range of -2000 to 2000.

Before the corrosion tests, the samples of thin steel strip coated with Ni-P and Ni-P-Al_2O_3 layers were characterized regarding the chemical composition, layer thickness, macroscopic appearance, uniformity and adhesion.

The chemical composition of the layers was determined by X-ray Fluorescence (XRF) Panalytical AXIOS X-ray fluorescence spectrometer operating at 60 KV and current of up to 160 mA with dual multi-channel analyser (DMCA) and commercial software Super Q, analytical programs (IQ +, WROXI, Ni-Fe-Co, TOXEL, Cu BASE).

In order to investigate the morphology and microcomposition of the layers, and thickness coating for the samples 32 and 106 were studied by using Scanning Electron Microscope: Quanta Inspect F coupled with Energy-Dispersive X-ray Spectroscopy EDXS.

Table 1

Experimental condition of Ni-P alloys and Ni-P-Al_2O_3 composite coatings

Condiţiile experimentale de acoperire cu aliaje de Ni-P şi respectiv Ni-P-Al_2O_3

Sample code *Cod probă*	Type of protective coatings applied on steel strip *Tipul stratului de protecţie aplicat pe banda din oțel*	pH value *Valoare pH*	Solution *temperature Temperatura soluţie* (^{0}C)	Immersion time *Timp de imersie* (min)	Stirring speed *Viteza de rotaţie* (rot/min
32	Ni-P layer with low-phosphorus (7%) *Strat Ni-P cu conţinut mic de fosfor (7%)*	5.0	82 - 84	10	-
40	Ni-P layer with medium phosphorus content (9%) *Strat Ni-P cu conţinut mediu de fosfor (9%)*	4.0	82 - 83	10	200
42	Ni-P layer with high phosphorus content (12%) *Strat Ni-P cu conţinut mare de fosfor (12%)*	3.5	85 - 87	20	100
87	**Ni-P-Al_2O_3** composite layer, obtained **with 3g/l** Al_2O_3 **(0,3** μm**)** *Strat compozit* ***Ni-P-Al_2O_3, cu 3g/l Al_2O_3 de 0,3 μm***	5.5	83	20	600
84	**Ni-P-Al_2O_3** composite layer, obtained **with 5g/l** Al_2O_3 **(0,3 μm)** *Strat compozit* ***Ni-P-Al_2O_3, cu 5g/l Al_2O_3 de 0,3 μm***	5.0	83	20	600
94	**Ni-P-Al_2O_3** composite layer, obtained with **8g/l** Al_2O_3 **(0,3 μm)** *Strat compozit* ***Ni-P-Al_2O_3, cu 8g/l Al_2O_3 de 0,3 μm***	5.0 - 6.0	83	20	600
100	**Ni-P-Al_2O_3** nanocomposite layer, obtained with **3g/l** Al_2O_3 **(20 nm)** *Strat nanocompozit* ***Ni-P-Al_2O_3, cu 3g/l Al_2O_3 de 20 nm***	5.0	80	20	600
106	**Ni-P-Al_2O_3** nanocomposite layer, obtained with 5g/l **Al_2O_3** (20 nm**)** *Strat nanocompozit* ***Ni-P-Al_2O_3, cu 5g/l Al_2O_3 de 20 nm***	5.0 - 6.0	80	20	600
112	**Ni-P-Al_2O_3** nanocomposite layer, obtained with 8g/l **Al_2O_3** (20 nm**)** *Strat nanocompozit* ***Ni-P-Al_2O_3, cu 8glL Al_2O_3 de 20 nm***	5.0 - 6.0	81	20	600

2.3. Testing the resistance to chemical corrosion in different environments

Chemical corrosion resistance tests on the investigated coatings were performed respectively, in acid and basic corrosive environments, being generally performed tests for nickel layers deposited on steel strips by chemical method. Chemical corrosion test for resistance of the layers deposited on the surface of thin cold-rolled strip steel was performed according to ASTM G 31-72 "Standard Practice for Laboratory Immersion Corrosion Testing of Metals (revised in 2004), which includes the procedures and the factors influencing corrosion laboratory tests by immersion, particularly the mass loss tests.

In order to assess the corrosion resistance of coated samples were followed the next steps:

- *Sample preparation* - The samples were degreased with a concentrated solution of ethanol and acetone to remove entirely the impurities from the passive layer. The edges of the cuts and the edge of the mounting hole of the samples were protected by a strong varnish and then were dried for 24 hours at room temperature.
- *Weighing and measuring the size of samples* - the prepared samples were weighed before starting the experiment by an electronic balance, with standard deviation of ≤ 0.02 mg and measured for corresponding area determination. The initial weight was used to calculate the sample weight variation after the corrosion test and determination of corrosion rate (gravimetric index).
- *Immersion of samples* in individual containers containing acid environment for 168 hours (7 days) and in a basic environment for 672 hours (28 days).
- *Removing samples* from acid or basic environment, repeatedly washed with warm water and rinsed with distilled water, and finally dried with hot air and weighing. The loss of mass Δm is the difference between the initial mass and after corrosive attack. The temperature and the pH of corrosion environment were monitored in of each time interval.
- *Macroscopic inspection* of samples after the corrosion tests.

The acid environment was prepared as a 5% solution of H_2SO_4 (by weight ratio: 52.1 g solution of 96% H_2SO_4 + 948 g distilled water) using a cooling bath. The solution of H_2SO_4 was at a pH of 0.36 at room temperature (18,54^{0}C). The basic environment was prepared as a 10% solution of NaOH (by weight ratio: 8.0843 g NaOH + 792 g distilled water) and the NaOH solution had a pH of 13.03 at room temperature (20^{0}C).

3. Results and discussion

3.1. The chemical composition and morphology of coatings

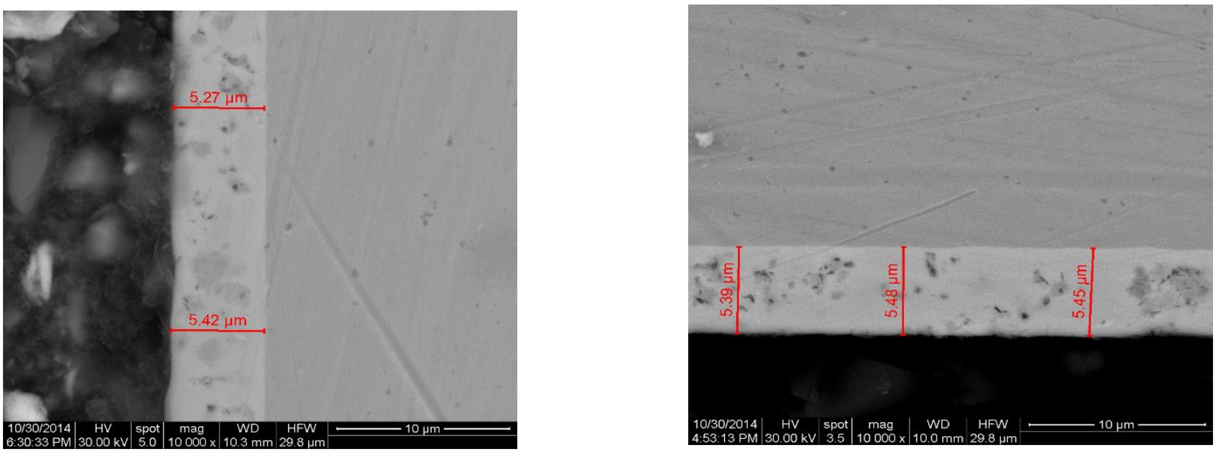
The chemical composition of layers was analyzed by XRF (Table 2) on samples coded 32 and 106 and it showed a Ni content in the range 90.814% and 91.957%, the P content of 8.918% and 6.887%, and the an amount of 0.900% Al for the sample 106.

Table 2

Chemical composition of experimental Ni-P and Ni-P-Al_2O_3 composite coatings

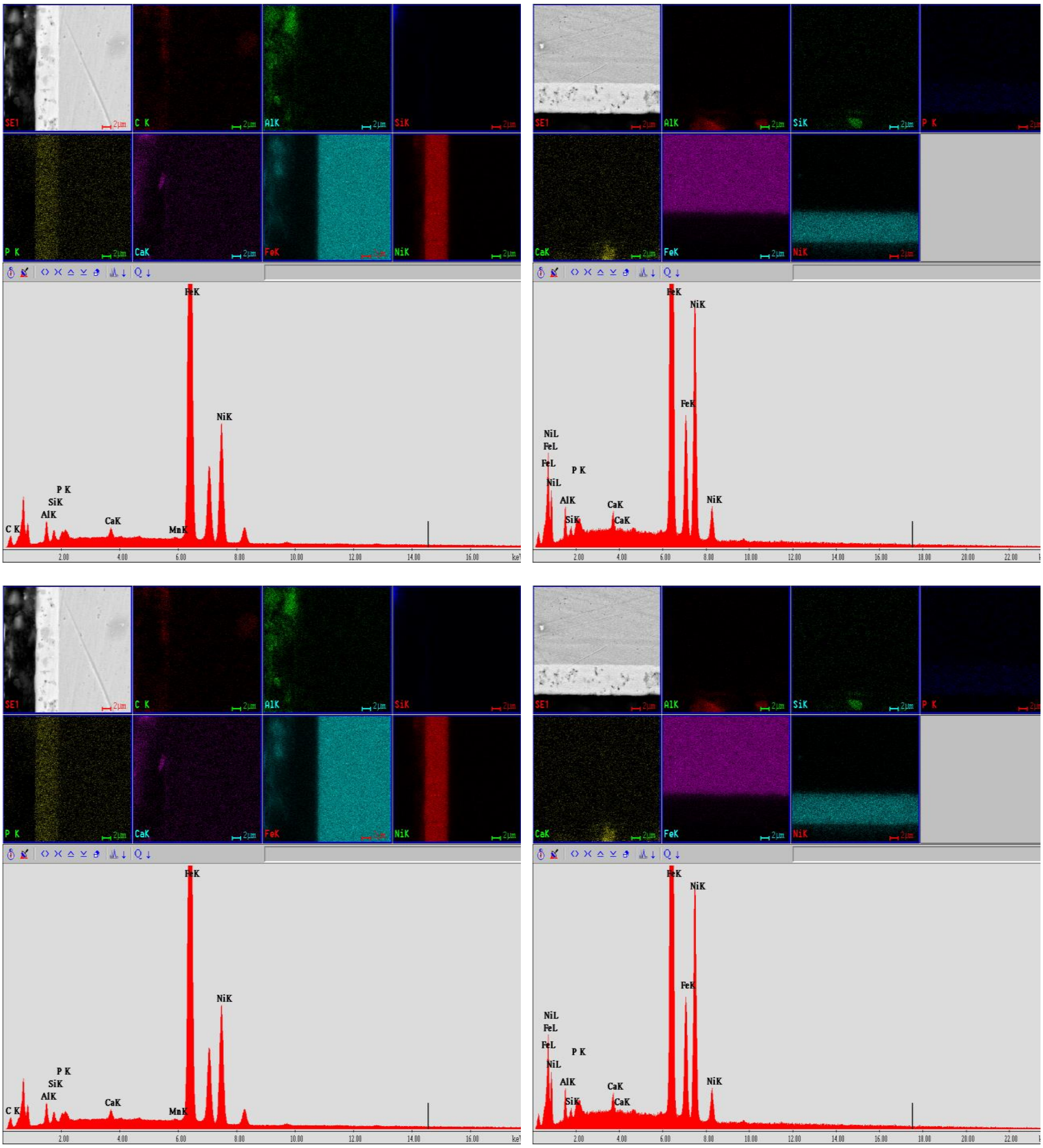
Compoziţia chimică a straturilor experimentale de aliaje Ni-P şi Ni-P-Al_2O_3

Sample code *Cod probă*	%Ni	Al%	Si%	P%	S%	Mg%	Cr%	Mn%	Cu%	Pb%
32	90.814	0.011	0.025	8.918	0.011	0.021	0.037	0.154	0.010	-
106	91.957	0.900	0.050	6.887	0.008	0.076	-	-	-	0.121



a) X 10.000 b) X 10.000

Fig. 1 - SEM image of coating thickness of Ni-P and composite Ni-P-Al_2O_3 layer of 32 and 106 samples
Imagine SEM a grosimii stratului de Ni-P şi Ni-P-Al_2O_3 a probelor 32 și 106.



a) b)

Fig. 2 - EDS overall image showing the distribution of chemical elements on 32 and 106 samples with Ni-P and Ni-P-Al$_2$O$_3$ coating/ *Imagine EDS de ansamblu a distribuţiei elementelor stratului de Ni-P şi Ni-P-Al$_2$O$_3$ a probelor 32 și 106.*

The thickness of the Ni-P coating layer in the case of the sample 32 was 5.27 to 5.42 microns (Fig.1.a), while for the composite Ni-P-Al$_2$O$_3$ (20 nm - 5 g/l) layer in the case of the sample 106 was in the range 5.39 to 5.45 microns (Fig.1.b). In the corresponding coating area of sample 32 should be noticed the presence of Ni and P (Fig. 2.a) and in case of sample 106, the appearance of Ni, P and Al as shown in Fig.2.b.

3.2. Assessment of corrosion resistance in acidic environment

The corrosion behaviour in both corrosive environments -acid and basic- were taken the samples from nine types of coatings, as shown in Table 1.

For each layers type was determined the gravimetric index (corrosion rate) in acid solution of H_2SO_4 with concentration of 5% on all samples subjected to corrosion. The results after 168 hours (7 days) of corrosion are shown in Table 3.

Table 3

Results of corrosion behaviour after 168 hours in the acid solution 5% H_2SO_4
Rezultate privind comportarea la coroziune după 168 h în soluţie H_2SO_4 de conc. 5%

Sample code *Cod probă*	Weight loss/ *Pierdere de masă* Δm, [g]	Surface area/ *Suprafaţa* S, [cm^2]	Gravimetric index (Corrosion rate), *Indicele gravimetric,* $v_{cor.}$ [g/m^2h]
32	0.3454	10.09	2.04
40	0.2035	9.99	1.21
42	0.1227	9.47	0,77
87	0.3852	10.26	2.23
84	0.3289	9.77	2.01
94	0.3267	9.72	2.00
100	1.5505	10.87	8.49
106	1.4056	9.50	8.81
112	1.4298	9.82	8.67

It can be noticed from these data, the best resistance to corrosion in acidic environment, highly corrosive of samples 40 and 42 samples coated with Ni-P alloy, with high phosphorus content , (corrosion rate = 0.77 - 1.21 g/m^2h) and the weakest samples 100, 106 and 112 with nanocomposite coating of Ni-P-Al_2O_3 (corrosion rate = 8.49 - 8.81 g/m^2h.

The variation of the corrosion rate over time, depending on the chemical composition of the coating layer shows that the samples with the composite coating Ni-P-Al_2O_3 **(0,3 µm)** had a better corrosion behaviour compared to the nanocomposite coating Ni-P-Al_2O_3 **(20 nm)** (Fig. 3).

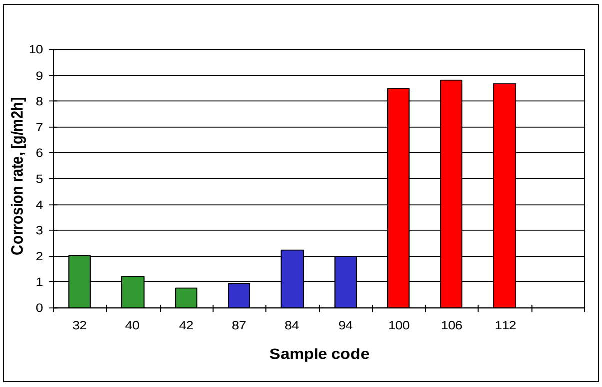


Fig. 3 - The corrosion rate in acid environment (H_2SO_4 solution, c = 5%) depending on the type of protective coatings/ *Viteza de coroziune în soluţie de H_2SO_4 conc.5% funcţie de tipul stratului de protecţie .*

Direct observation of the samples showed that after the corrosion test for 168 hours in acidic environment have shown remarkable resistance the samples 40, 42, 32 coated with Ni-P alloy. Unlike these samples they maintained their appearance, samples 84, 87, 94 coated with composites began the degradation of layers and the appearance of corrosion products, while samples 100, 106 and 112 with nanocomposite coatings were completely destroyed (Fig. 4).

Localized corrosion of nickel coatings is specific because it provides to the steel support a cathodic protection, so any unevenness porosity or layer will result in a powerful corrosion effect of steel substrate. In the case of composite layers, it should be emphasize that as alumina dispersed phase is finer creates more surface discontinuities favouring a generalized corrosion. Localized corrosion attacks observed on samples can be caused by microscopic defects - microporosity or discontinuities of the layer.

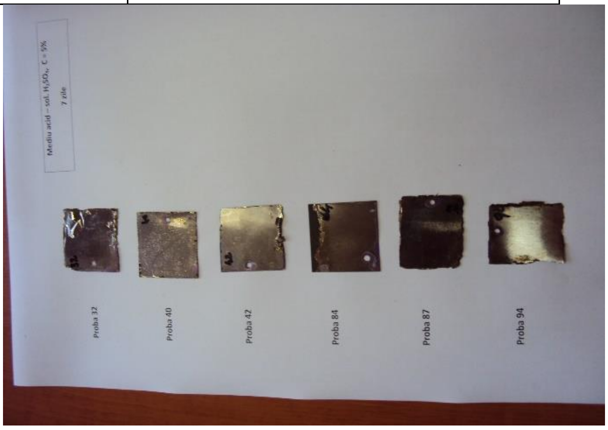


Fig. 4 - The surface layers appearance of Ni-P and Ni-P-Al_2O_3 composite coatings after 168 hours etching in 5% H_2SO_4 solution /*Aspectul suprafeţelor straturilor de Ni-P şi compozite Ni-P-Al_2O_3 corodate chimic în sol. 5% H_2SO_4 după 168 de ore*

3.3. Assessment of corrosion resistance in basic environment

For each layers type of the samples subjected to corrosion it was determined the gravimetric index (corrosion rate) in basic solution of NaOH with 10% concentration. The results after 672 hours (28 days) are shown in Table 4.

The basic environment not drastically affected the corrosion resistance of coated samples as well of uncoated reference sample throughout the investigations. It can be highlighted that all coated samples tested for corrosion to 672-hour in a basic environment (NaOH solution of conc.10%) had a very good behaviour, a remarkable corrosion behaviour having the samples 84, 87 with Ni-P-Al_2O_3 composite coating and sample 42 with Ni-P alloy coating (corrosion rate = 0.0073 – 0.0114 g/m^2h), compatible with all coated samples (Fig. 5).

A most significant mass loss is recorded for the samples 106 and 112, with **Ni-P-Al_2O_3**

Table 4

Results of corrosion behaviour after 672 hours in basic solution of 10% NaOH/
Rezultate privind comportarea la coroziune după 672 ore în soluţie NaOH de conc.10%

Sample code Cod probă	Weight loss/Pierdere de masă Δm, [g]	Surface area/ Suprafaţa, S, [cm^2]	Gravimetric index (Corrosion rate), Indicele gravimetric, v_{cor} [g/m^{2}h]
32	0.0037	4.38	0.0126
40	0.0033	3.27	0.0150
42	0.0057	7.47	0.0114
87	0.0038	6.02	0.0094
84	0.0033	6.76	0.0073
94	0.0044	4.70	0.0139
100	0.0043	5.58	0.0115
106	0.0079	6.99	0.0168
112	0.0037	4.38	0.0126

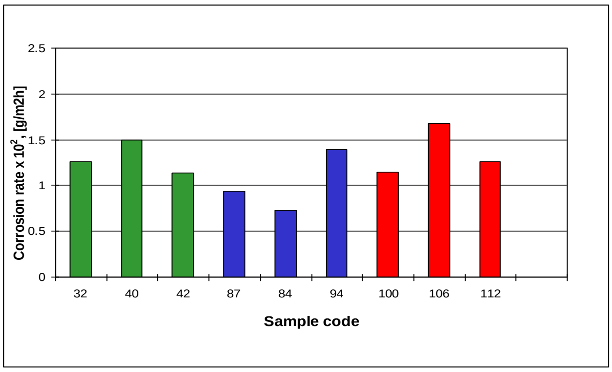


Fig. 5 - The corrosion rate in basic environment (NaOH solution, c = 10%) depending on the type of protective coatings/ *Viteza de coroziune în soluţie de NaOH conc.10% funcţie de tipul stratului de protecţie.*

nanocomposite coating (corrosion rate = 0.0126 – 0.0168 g/m^{2}h).

Macroscopic analysis shows that all coated samples tested for corrosion in a basic medium had a much better resistance to corrosion than in acidic environment, even at prolonged duration for 28 days (**Fig. 6**).

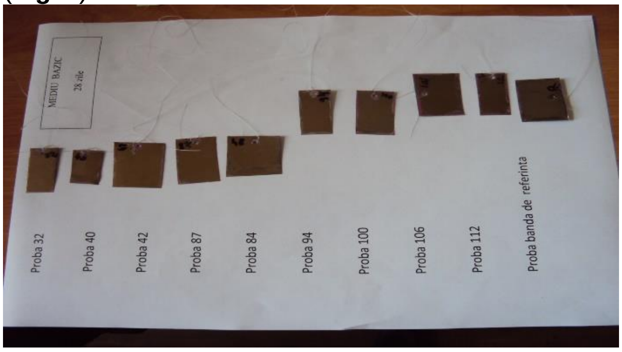


Fig. 6 - The surface layers appearance of Ni-P and Ni-P-Al_2O_3 composite coatings after etching in 10% NaOH solution/ *Aspectul suprafeţelor straturilor de Ni-P şi compozite Ni-P-Al_2O_3 corodate chimic in soluţie de NaOH de concentraţie 10%.*

4. Conclusions

4.1. Testing of resistance to chemical corrosion of experimentally layers was performed in two types of corrosive environments, namely in: acid and basic conditions. In both corrosive environments the samples with nanocomposite layer of alumina in the Ni-P matrix they showed weaker corrosion behaviour compared to Ni-P layers with high phosphorus content. It should be noticed that uncoated reference sample was destroyed in the acidic environment since after the first day of testing.

4.2. After the corrosion test in acid environments, H_2SO_4 solution with 5% concentration, a remarkable behaviour have shown after 7 days of testing for the samples 84, 87, 94 and 40, 42, 32, with **Ni-P-Al_2O_3 (0,3 μm)** composite coating and Ni-P alloys, while the samples 100, 106 and 112 with nanocomposite coating **Ni-P-Al_2O_3 (20 nm)** were completely destroyed. It should be noted that uncoated reference sample was destroyed in the acidic environment since after the first day of testing.

4.3. All coated samples tested for corrosion in a basic medium (NaOH solution with 10% concentration) had a very good behaviour, a remarkable behaviour for the samples 84, 87 and 42 even in periods of 28 days testing.

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REFERENCES

1. W. Reidel, Electroless Nickel Plating, ASM international, Metals Parks, Oh. 1991.
2. R. Taheri, Evaluation of Electroless Nickel-Phosphorus (EN) Coatings, Thesis, University of Saskatchewan, Saskatoon, 2003.
3. G.O. Mallory,.and J.B. Hajdu, Electroless Plating: Fundamentals and Applications, Cambridge University Press, Cambridge, 1990.
4. M. Schlesinger Electroless Deposition of Nickel, Modern Electroplating, Fifth Edition Edited by Mordechay Schlesinger and Milan Paunovic, 2010
5. *** Electroless Nickel Deposit Properties, State of EN Science, Rev 4.1 7/97.