

DURIFICAREA ACOPERIRILOR CHIMICE NANOCOMPOZITE FĂRĂ ELECTROLIZĂ DE Ni-P-TiO₂ PE SUBSTRATURI DE OȚEL CU CONȚINUT REDUS DE CARBON

HARDENABILITY OF ELECTROLESS CHEMICAL Ni-P-TiO₂ NANOCOMPOSITE COATINGS ON LOW CARBON STEEL SUBSTRATES

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Our work was focused on enhancing the deposition rate, homogeneity, and hardenability on low carbon steel surfaces of Ni-P-TiO₂ nanocomposite comparatively with Ni-P coating. Two bath compositions were developed for the electroless deposition, namely Bath (A), composed of nickel sulphate and sodium hypophosphite aqueous solutions and various admixtures to stabilize and accelerate the deposition rate during plating, and Bath (T): Bath (A) to which nanosized TiO₂ particles were added in amount of 10 g/l. The deposition rates, co-deposition of particles, and roughness was influenced by the nano powder concentration, temperature, agitation rate, pH, and deposition duration in the bath. The adhesion and uniformity of the composite layers analyzed metallographically and by SEM are appropriate, so the interface of the composite layer with the support steel is perfectly continuous, without discontinuities and the layer is uniform. After deposition the coating was amorphous. Due to the heat treatment, the hardness of the electroless Ni-P-nanocomposite coating is significantly increased. The performance of the Ni-P-TiO₂ nanocomposite coatings is analyzed for their surface morphology, phase composition, wear and hardness to assess wear characteristics, and compared with Ni-P alloy coatings. The change in hardness with heat treatment exhibits a similar trend for these coatings, which suggests that the hardening mechanism upon annealing is the same for both electroless Ni-P and Ni-P-TiO₂ nanocomposite coatings.

Lucrarea are ca obiectiv îmbunătățirea vitezei de depunere, a omogenității și a durificării nanocompozitului Ni-P-TiO₂ pe suprafețe din oțel cu conținut redus de carbon, comparativ cu acoperirea Ni-P. Au fost dezvoltate două compoziții pentru baia de depunere fără electroliză, și anume baia (A), compusă din soluții apoase de sulfat de nichel și hipofosfit de sodiu și diverse adaosuri pentru a stabili și accelera viteza de depunere în timpul plăcii, și baia (T): baia (A) la care au fost adăugate particule de TiO₂ nanodimensionate într-o concentrație de 10 g/l. Vitezele de depunere, co-depunerea particulelor și rugozitatea au fost influențate de concentrația pulberii nanometrice, temperatură, viteza de agitare, pH și durata depunerii în baie. Aderența și uniformitatea straturilor compozite analizate metalografic și prin SEM sunt adecvate, astfel că interfața stratului compozit cu suportul din oțel este perfect continuă, fără discontinuități, iar stratul este uniform. După depunere, acoperirea a fost necristalină. Datorită tratamentului termic duritatea acoperirii fără electroliză de nanocompozit Ni-P este crescută în mod semnificativ. Performanța acoperirilor nanocompozite Ni-P-TiO₂ este analizată din perspectiva morfologiei suprafeței, compoziției fazale, uzurii și durității pentru a evalua caracteristicile de uzură și este comparată cu acoperirile aliate din Ni-P. Variația durității cu tratamentul termic prezintă o tendință similară pentru aceste acoperiri, ceea ce sugerează același mecanism de întărire la tratamentul termic pentru acoperirile nanocompozite fără electroliză de Ni-P și Ni-P-TiO₂.

Keywords: Electroless plating, Coatings, Ni-P-TiO₂ nano-composite layer, steel substrate

1. Introduction

Low carbon steel is extensively used in machine manufacturing, building, transportation, and oil-gas industry, due to its remarkable physical characteristics as well as inexpensive and easy manufacturing. However, it has few applications that require a high resistance to corrosion or high hardness [1]. Consequently, nickel-phosphorus (Ni-P) coatings were deposited on carbon steel using mechanically assisted electroless techniques, to increase hardness and corrosion resistance [2]. To enhance the mechanical characteristics of a material in the manufacturing of industrial equipment, using primarily carbon steel or low alloy steels, as well as

to make surfaces more resistant to abrasion and corrosion, electroless Ni-P plating can be applied [3,4]. These Ni-P coatings were deposited on carbon steel without the application of an external electrical current. This feature has, therefore, led to the development of special tools and new technologies in many industrial sectors. Chemical nickel plating is a process of electroless metal deposition and is widely used in the automotive industry, mining industry, electrotechnical and electronic industry, engineering, foundry industry and the military industry. Chemical nickel coatings are characterized by very even thickness distribution, which is especially appreciated for elements of complex shape, abrasion resistance, high hardness, high

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corrosion resistance in an aggressive chemical environment, good adhesion and solderability. Ni-P coatings can be manufactured using a variety of techniques, including electroplating and electroless chemical deposition [5,6]. The hardness of electroless deposits is particularly important when superior wear resistance is required. Metals can be protected from wear (abrasion) by covering them with metal matrix composites containing ceramic particles such as Al₂O₃, TiO₂, SiO₂, ZrO₂, SiC, Si₃N₄, B₄C, WC etc. However, these hard materials are too fragile and offer little or no adhesion for use as a coating. Therefore, a metal matrix is used to hold the oxide particles together and to facilitate good adhesion to the coated metal surface. Most electroless composite coatings mainly focus on the incorporation of either micron-sized particles or chemically prepared nanosized particles into the Ni-P matrix to yield desired engineering properties. The hardness and corrosion resistance were significantly improved by adding TiO₂ nanoparticles into Ni-P coatings on low alloyed steel or carbon steel substrates [7,8]. Another research group [9] indicated that the incorporation of TiO₂ nanoparticles in the Ni-P matrix did not have any influence on the structure and phase transformation behavior of electroless Ni-P coatings. This work aims to achieve Ni-P-nano-TiO₂ coating on a low carbon steel substrate utilizing the electroless deposition method. The performance of the nanocomposite coatings is analyzed for their

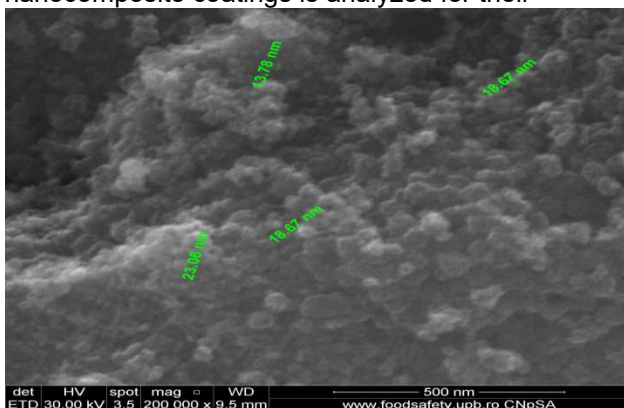


Fig.1 - SEM images of nanometric TiO₂ powder/ *Imagini electronmicroscopice SEM ale pulberii nanometrice de TiO₂*

surface morphology, phase composition, wear, and hardness to assess wear characteristics and compared with Ni-P alloy coatings.

2. Experimentals

Compositions of coatings-based Ni-P and Ni-P-TiO₂ composites, respectively, with dispersed nanosized titania (anatase) powder, were designed for electroless deposition by using an acid electrolyte based on nickel sulphate and sodium hypophosphite, to obtain uniform and adherent layers, which were achieved on a thin low carbon ferrous strip of a 0.2 mm thickness.

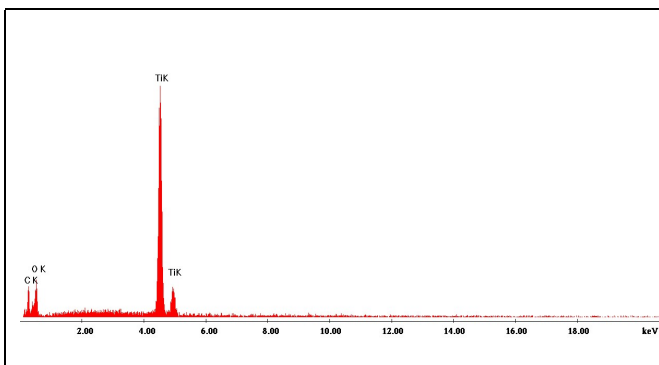
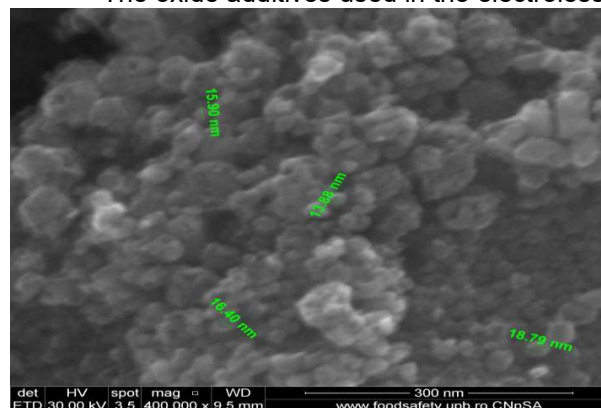
2.1. Materials

2.1.1. Ferrous substrate before electroless deposition.

Low Carbon specimens (20 mm x 20 mm x 0.2 mm) were used as substrates for electroless deposition. The substrates were cleaned with acetone, rinsed with distilled water, and ultrasonically cleaned to remove any contamination [10]. The chemical composition of the steel substrate with a low content of C was analyzed by XRF spectrometry and LECO method for C and S content, namely: 0.032% Si, 0.020% Mn, 0.032% P, 0.015% S, 0.015% Cr, 0.010% Ni, 0.002% W and 99.874% Fe.

2.1.2. Oxide components of composite coatings

The oxide additives used in the electroless



Elem	Wt %	At %	K-Ratio	Z	A	F
O K	47.13	72.74	0.0514	1.0714	0.1017	1.0001
TiK	52.87	27.26	0.4994	0.9243	1.0218	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte.	Error	P/B
O K	54.83	1.42	4.76	38.67	
TiK	723.71	7.68	1.29	94.22	

Fig.2 - EDAX image of nanometric TiO₂ powder and elemental analysis, by atomic % *Imagine EDAX a pulberii nanometrice de TiO₂ și analiza elementală, % atomice*

Table 1

Chemical composition of nano-TiO₂ / Compoziția chimică a nano-TiO₂

Content (reckoned as equivalent oxide), %	SiO ₂	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃
Nano TiO ₂	0.16	98.80	0.30	0.03	0.03	0.20	0.003	0.004	0.28

deposition of Ni-P-TiO₂ composites had nanometric particle size (Fig.1) and were of analytical grade, as confirmed by EDAX analysis (Fig.2).

X-ray fluorescence spectrometry (XRF) analyzes also revealed the presence of traces of Si, P, S, Cr, Ni, W (see Table 1).

2.2. The composition of the deposition bath

In this study, two bath compositions were developed for the electroless deposition, Ni-P alloys as the reference for the Ni-P-TiO₂ composite system, namely:

Bath(A); 26.28 g / l nickel sulphate, 21.53 g/l sodium hypophosphite, 9 g / l sodium acetate, 15 g/l ammonium sulphate, 0.3 g / l sodium citrate, 0.1 g/l sodium dodecyl sulfate and 1 g/l lead acetate.

Bath (T); Bath (A) to which 10 g/L nano-TiO₂ (~ 30 nm) was added. Preliminary tests were performed with 1 g/l, 5g/l and 10 g/l nano-TiO₂ and the best deposition rate was recorded for 10 g/l nano-TiO₂. For this reason, our trials were carried out for 10 g/l nano-TiO₂ admixture. The electrochemical bath solutions were freshly prepared from analytical-grade chemicals and double distilled water. The use of a complexing agent, such as sodium citrate, propylene glycol and urea in the electrolytically deposited Ni-P bath, determines the stability during plating. We introduced electrolytes such as sodium acetate, lead acetate and ammonium sulphate to stabilize the suspension. To keep the oxide particles that tend to deposit at the bottom of the deposition bath in suspension, we used a sodium dodecyl sulfate surfactant. The pH of the bath solution was 5.98.

2.3. Obtaining Ni-P and Ni-P-TiO₂ coatings by electroless deposition

Iron and its alloys are the most frequently plated substrates. From a surface preparation standpoint, they can be grouped as low alloy and carbon steels, cast iron, and high alloy steels. The principles of preparing ferrous surfaces are based on successive steps for soil removal, deoxidation, and surface activation. The way these steps are carried out will depend on the type of alloy processed [10].

The electrochemical cell (T-bath) was connected by immersing the pretreated steel substrate and activating it in 100 ml of solution for 15, 30, 45 and 60 minutes, respectively.

The pH was measured using a pH meter (Hanna Instruments) and adjusted with NH₄OH solution. The temperature was controlled using a thermostatically controlled bath at 80°C. The deposition under continuous stirring is necessary for

the continuous removal of native hydrogen from the chemical reaction of the metal substrate with the acid bath. Tests were performed with different stirring intensities at 50, 100, 150, 200, 250, 300, 350, and 400 rpm and it was established that a stirring at 300 rpm is optimal for a laminar flow of the solution from the electroless bath. The weight of the deposited composite coating was evaluated by changing the weights of the substrates before and after the electroless process shown in reference [11]. The heat treatment of deposited Ni-P and Ni-P-TiO₂ coatings was performed in a Nabertherm electric furnace with an internal reaction chamber built especially for good insulation from the rest of the oven. Argon was introduced into the reactor to prevent oxidation. The gases were washed, at the exit of the enclosure, in a vessel with water. The samples were placed on a refractory ceramic support through which the inert gas easily circulated inside. The gas concentration was uniform throughout the enclosure volume, thus ensuring good protection on the sample surface. The heat treatment was applied at temperatures of 250°C and 400°C followed by cooling in the furnace until the ambient temperature.

2.4. Characterization of Ni-P and Ni-P-TiO₂ composite coatings

The weight of phosphorus was calculated by subtracting the weights of nickel and alumina or titanium from the total weight deposited. The results were confirmed for some samples with EDX analysis. The mass deposited "G" on the surface unit area during the plating period represents the deposition rate as the difference of the weights of the substrates before and after the electroless process.

The pH of the electrolytes was measured over time, using the HACH sensION156 Portable pH/Conductivity Meter. The samples of thin steel strip coated with Ni-P-TiO₂ 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 analyzer (DMCA) and commercial software Super Q, analytical programs (IQ+, WROXI, Ni-Fe-Co). To investigate the morphology, micro-composition and thickness of the coatings were studied using Scanning Electron Microscope: Quanta Inspect F coupled with Energy- Dispersive X-ray Spectroscopy EDXS. The prepared samples were

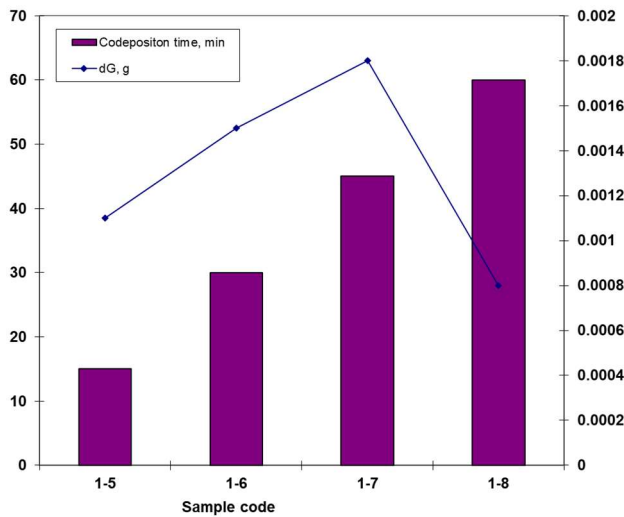


Fig. 3 - Electroless deposition rate of Ni-P-nanoTiO₂ composite coatings versus time/Viteza de depunere chimică a acoperirilor compozite Ni-P-nanoTiO₂ în funcție de timp.

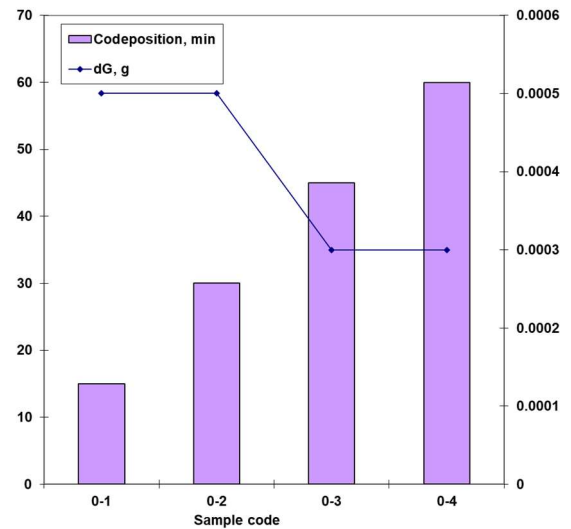


Fig. 4 - Electroless deposition rate of Ni-P coatings versus time/Viteza de depunere chimică a acoperirilor de referință Ni-P în funcție de timp

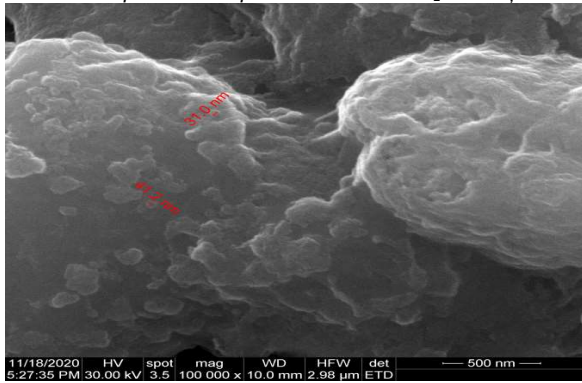


Fig. 5 - Microstructure of Ni-P-nanoTiO₂ composite coating after 15 minutes of electroless deposition/Microstructura acoperirii compozite Ni-P-nanoTiO₂ după 15 minute de depunere chimică

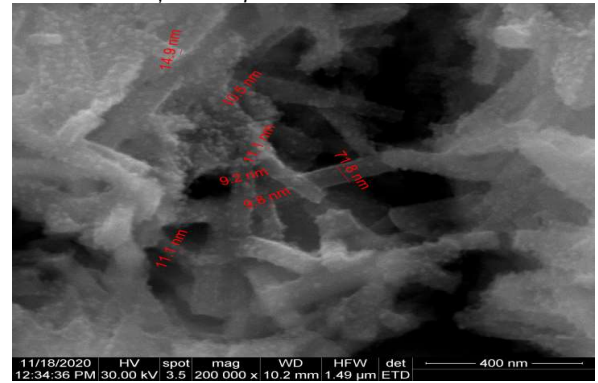


Fig. 6 - Microstructure of Ni-P-nanoTiO₂ composite coating after 30 minutes of electroless deposition/Microstructura acoperirii compozite Ni-P-nanoTiO₂ după 30 minute de depunere chimică

weighed before starting the experiment on a Sartorius electronic balance, with standard deviation of ≤ 0.02 mg and measured for a corresponding area (1 cm²) determination. The initial weight was used to calculate the sample weight variation after the electroless test and determination of the deposition index. Mineralogical analysis of nickel composite deposits with TiO₂ dispersion phase by electroless method was performed with a Panalytical XPERT ProMPD diffractometer. The microhardness of the nanocomposite coatings was tested with a Vickers digital CV Instruments hardness gauge at loads of 25 g, 50 g, and 100 g.

3. Results and discussions

3.1. Electroless deposition rate of nickel composite coatings

The electroless deposition rate of the Ni-P-TiO₂ coating as a function of time is shown in Fig. 3. There is an increase in the deposition rate after 15 minutes (sample 1-5), 30 minutes (sample 1-6) and 45 minutes (sample 1-7), with a maximum at the end and after that there is a capping of the deposition, at 60 minutes (sample 1-7), probably due to the

formation of electrochemical reaction products on the surface that prevents the reaction of the substrate with the solution in the bathroom. For comparison with systems containing oxide additives, Fig. 4 shows the electroless deposition rate of the reference Ni-P coating (without oxide addition performed in the bath of composition A). An increase in the deposition rate is observed after 15 minutes (sample 0-1), 30 minutes (sample 0-2), after which a deposition limit occurs, at 45 minutes (sample 0-3) and 60 minutes (sample 0-4), probably due to the formation of electrochemical reaction products on the surface.

3.2. Microstructure and morphological analysis of nickel composite coatings

The SEM images of the Ni-P-nanoTiO₂ composite coating surface after 15 minutes and 30 minutes of electroless deposition, respectively, are shown in Fig. 5 and Fig. 6.

The electroless chemically deposited Ni-P microstructure is amorphous, with weakly crystallized nanometric structural elements with sizes of 30-40 nm after 15 minutes and 9-15 nm after 30 minutes, respectively. The activation

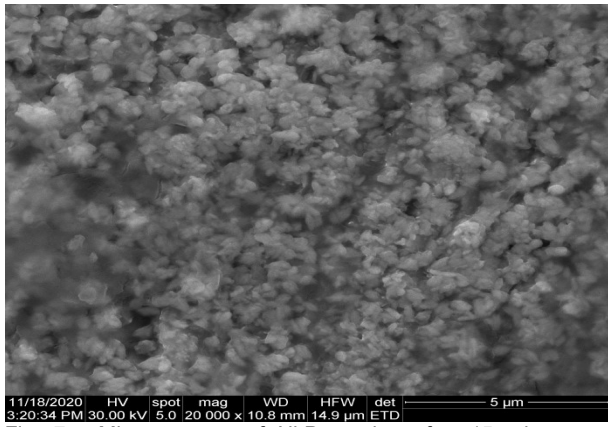


Fig. 7 - Microstructure of Ni-P coating after 15 minutes of electroless deposition/Microstructura acoperirii compozite Ni-P după 15 minute de depunere chimică

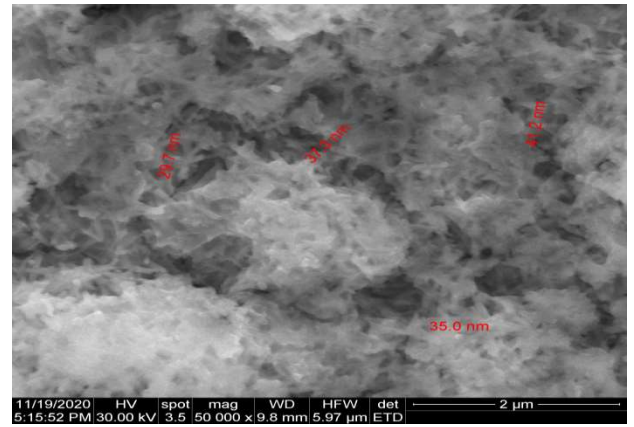


Fig. 8 - Microstructure of Ni-P-nanoTiO₂ composite coating after 30 minutes of electroless deposition/Microstructura acoperirii compozite Ni-P după 30 minute de depunere chimică

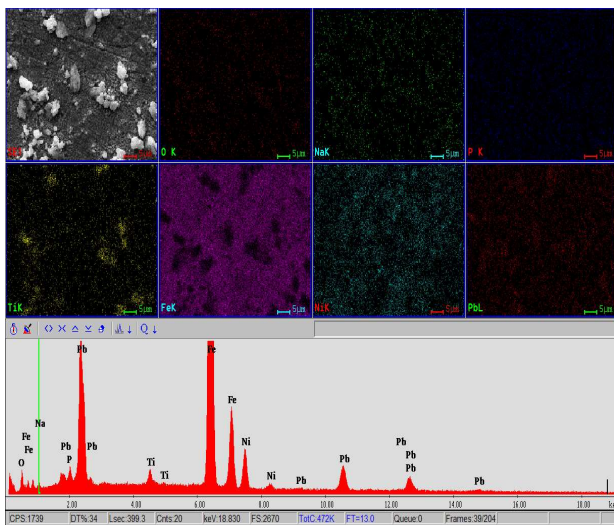


Fig. 9 - EDS global image of the distribution of the component elements in Ni-P-nanoTiO₂ coating after 15 minutes of electroless deposition/ Imagine globală EDS a distribuției elementelor componente din depunerea compozită Ni-P-nanoTiO₂ după 15 minute

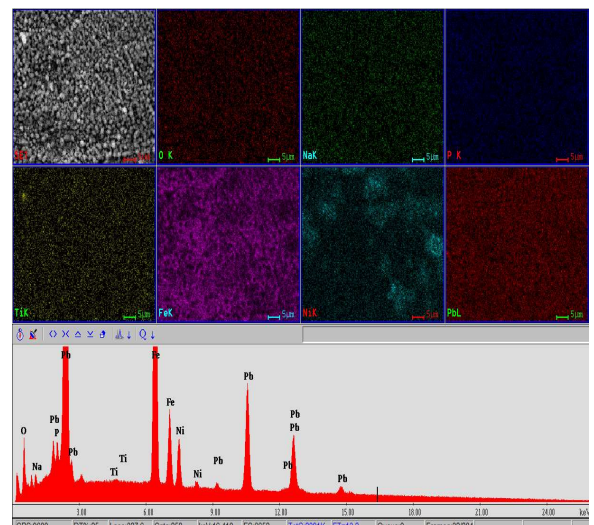


Fig. 10 - EDS global image of the distribution of the component elements in Ni-P-nanoTiO₂ coating after 30 minutes of electroless deposition/ Imagine globală EDS a distribuției elementelor componente din depunerea compozită Ni-P-nanoTiO₂ după 30 minute

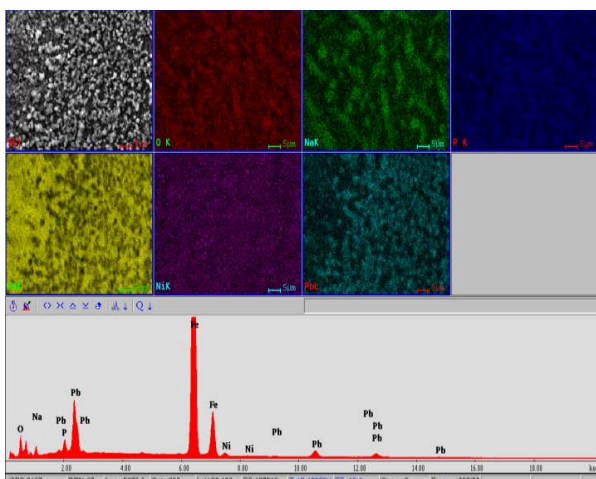


Fig. 11 - EDS global image of the distribution of the component elements in Ni-P coating after 15 minutes of electroless deposition/ Imagine globală EDS a distribuției elementelor componente din depunerea compozită Ni-P după 15 minute

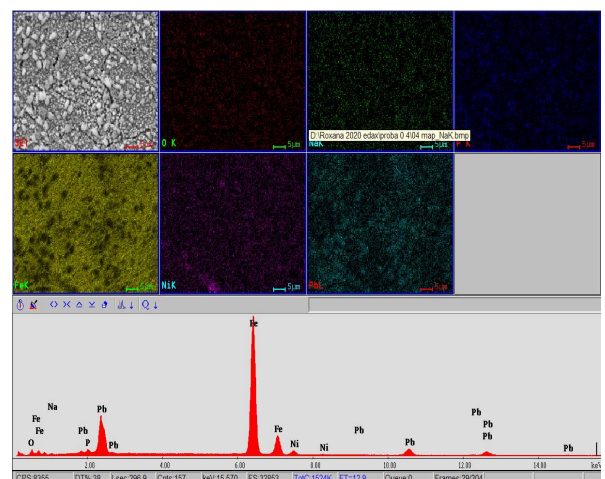


Fig. 12 - EDS global image of the distribution of the component elements in Ni-P coating after 30 minutes of electroless deposition/ Imagine globală EDS a distribuției elementelor componente din depunerea compozită Ni-P după 30 minute

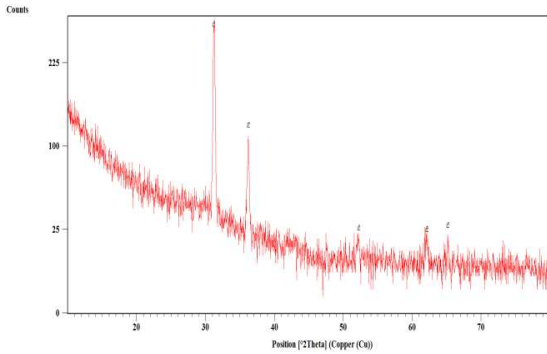


Fig. 13 - X-ray diffraction pattern of Ni-P-TiO₂ coating after 30 minutes of electroless deposition/ *Diffractograma de raze X a acoperirii cu Ni-P-TiO₂ după 30 de minute de depunere*

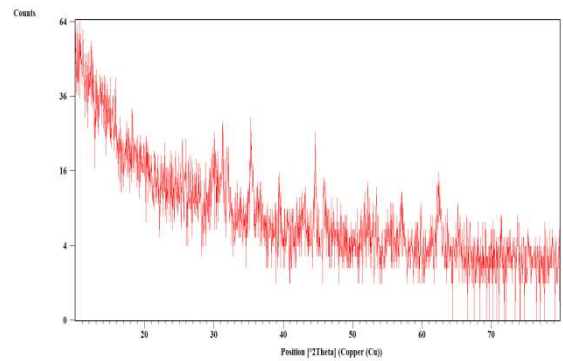


Fig. 14 - X-ray diffraction pattern of Ni-P-TiO₂ coating after 30 minutes of electroless deposition and heating at 250°C in Ar for 1 hour/ *Diffractograma de raze X a acoperirii cu Ni-P-TiO₂ după 30 de minute de depunere tratată la 250 °C în Ar 1 oră*

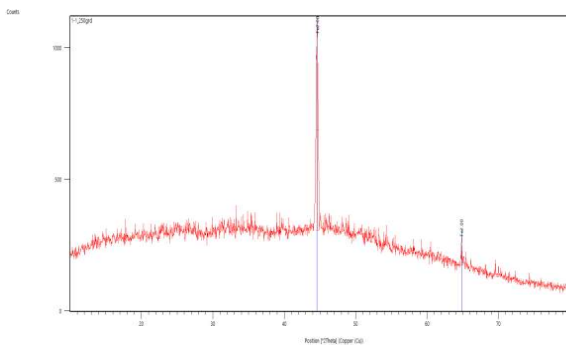


Fig. 15 - X-ray diffraction pattern of Ni-P coating after 30 minutes of electroless deposition/ *Diffractograma de raze X a acoperirii cu Ni-P după 30 de minute de depunere*

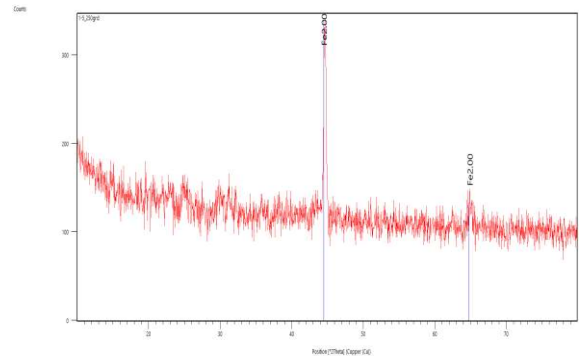


Fig. 16 - X-ray diffraction pattern of Ni-P coating after 30 minutes of electroless deposition and heating at 250°C in Ar for 1 hour / *Diffractograma de raze X a acoperirii cu Ni-P-TiO₂ după 30 de minute de depunere tratată la 250°C în Ar 1 oră*

energy of the crystallization is reduced due to the presence of co-deposited particles in the composite coating. The SEM images of the Ni-P composite coating after 15 minutes and 30 minutes of electroless deposition, respectively, are shown in Fig. 7 and Fig. 8.

The electroless chemically deposited Ni-P structure is amorphous. However, this amorphous structure is metastable and may undergo a crystalline transition only when the temperature is increased. The relative homogeneity of the deposition can be appreciated from the global EDS image of the distribution of the component elements present in the Ni-P-TiO₂ composite deposition after 15 minutes of electroless deposition in Fig. 9 and after 30 minutes of electroless deposition in Fig. 10, respectively, where there is a relative uniform distribution of the elements P, Ni and Ti, O. Additionally, there are some interferences of Fe in the steel substrate and Pb, respectively, which was used as agent in the form of lead acetate to stabilize the electrochemical bath. For comparison, the global EDS image of the distribution of the component elements present in the Ni-P composite deposition is given after 15 minutes of electroless deposition in Fig. 11 and after 30 minutes of electroless deposition in Fig. 12, respectively,

where a relatively uniform distribution is observed: elements P, Ni, Fe, O, and traces of Pb.

The X ray diffractogram of nickel composite deposits with TiO₂ dispersion phase by the electroless method after 30 minutes of deposition is shown in Fig. 13, respectively, after heat treatment at 250°C in Fig. 14. X-ray diffraction pattern of Ni-P coating after 30 minutes of electroless deposition is given in Fig. 15 and in Fig. 16, respectively, the diffractogram for the sample of Ni-P coating after heating at 250°C in Argon for 1 hour. In all four cases there is noticed the quasi-amorphous structure, with interferences of some lead compounds used to stabilize the bath.

The incorporation of TiO₂ particles into Ni-P type matrices is a convenient method for preparing composite coatings to improve the mechanical and physical properties of the deposition. The activation energy of the crystallization is lower due to the presence of co-deposited particles in the composite layer. The processes of co-deposition of secondary phase particles occur at low temperature when the chemical interaction between the particles and the metal matrix is not favored. The particles are only physically trapped in the Ni-P matrix; therefore, a heat treatment of these coatings is necessary to promote phase transformations [12-14] that will

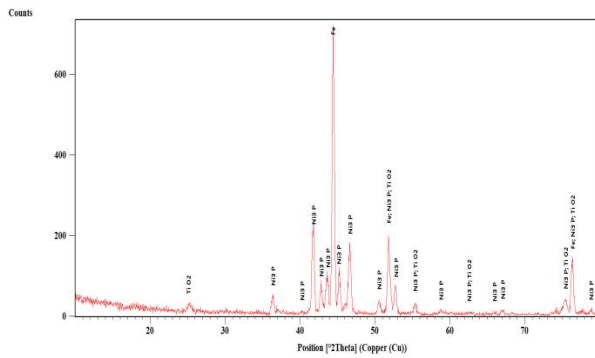


Fig. 17 - X-ray diffraction pattern of Ni-P- TiO₂ coating after heating at 400°C in Ar 1 hour/ *Difractograma de raze X a acoperirii cu Ni-P-TiO₂ tratată la 400°C în Ar 1 oră*

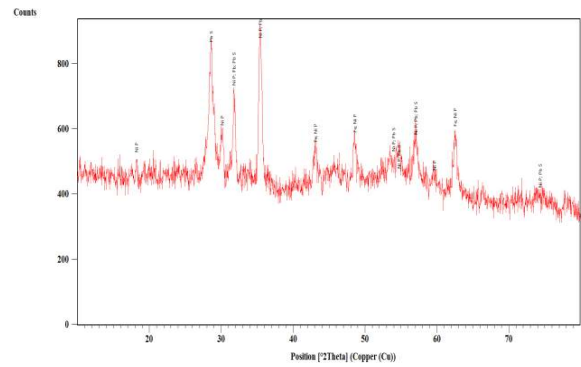
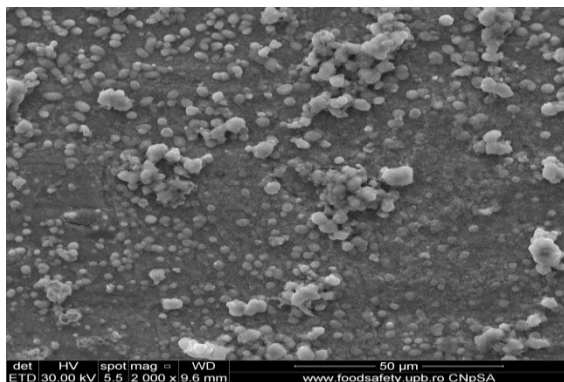
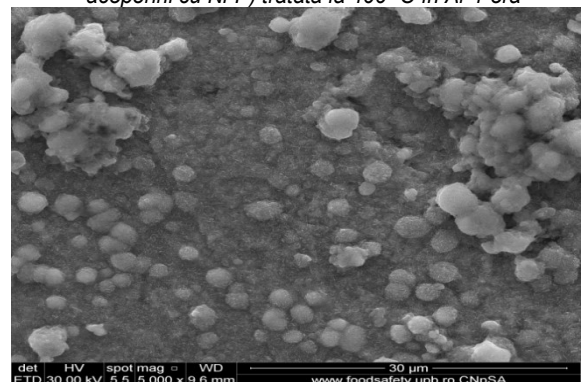


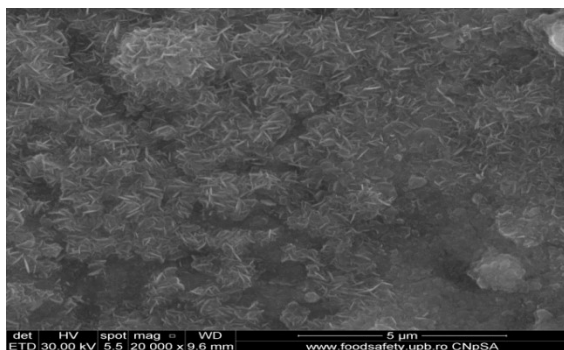
Fig. 18 - X-ray diffraction pattern of Ni-P coating after heating at 400°C in Ar 1 hour/ *Difractograma de raze X a acoperirii cu Ni-P) tratată la 400°C în Ar 1 oră*



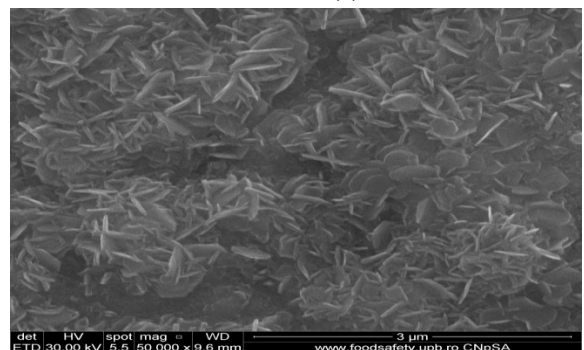
a



b-detail of (a)



c – detail of (b)



d – detail of (c)

Fig. 19 - SEM images of Ni-P-TiO₂ coating after heating at 400°C in Ar 1 hour/ *Imagini electronmicroscopice de baleiaj ale acoperirii Ni-P- TiO₂ tratate la 400°C în Ar 1 oră*

influence the properties of the deposited layers. The temperature at which the heat treatment is performed, and the concentration of the oxide particles have a significant influence on the hardness of these layers [7]. After heat treatment, the microhardness of the Ni-P-TiO₂ layers increases significantly due to the precipitation of hard Ni₃P particles as shown in the X-ray diffraction patterns as given in Fig. 17 and Fig. 18. The microhardness of composites with oxide nanoparticles obtained by chemical nickel plating depends on three factors: the level of incorporation of particles, the temperature at which the heat treatment is performed and the uniform distribution, with fewer particle agglomerations [8]. Co-deposition of oxide particles in the Ni-P matrix changes the roughness and morphology of the surface of composite deposits from a smooth and soft state to a hard

state with nodular aspects in the Ni-P-TiO₂ composite coating. The increase in hardness is attributed to the recrystallization of nickel and the precipitation of fine particles of nickel phosphides intermetallic compounds. The optimal duration of treatment recommended by most researchers is one hour [15,16]. At temperatures above 400°C, the size of the particles of phosphides grows and reduces the hardness. Also, the decrease in lattice defects and coarsening of the Ni₃P particles reduce the hardness when these coatings are annealed beyond 400°C. [16].

Nanocomposite coating samples were selected for Vickers microhardness testing: Ni-P-TiO₂ as deposited for 30 minutes, Ni-P-TiO₂ heated at 250°C, Ni-P heated at 400°C compared with the

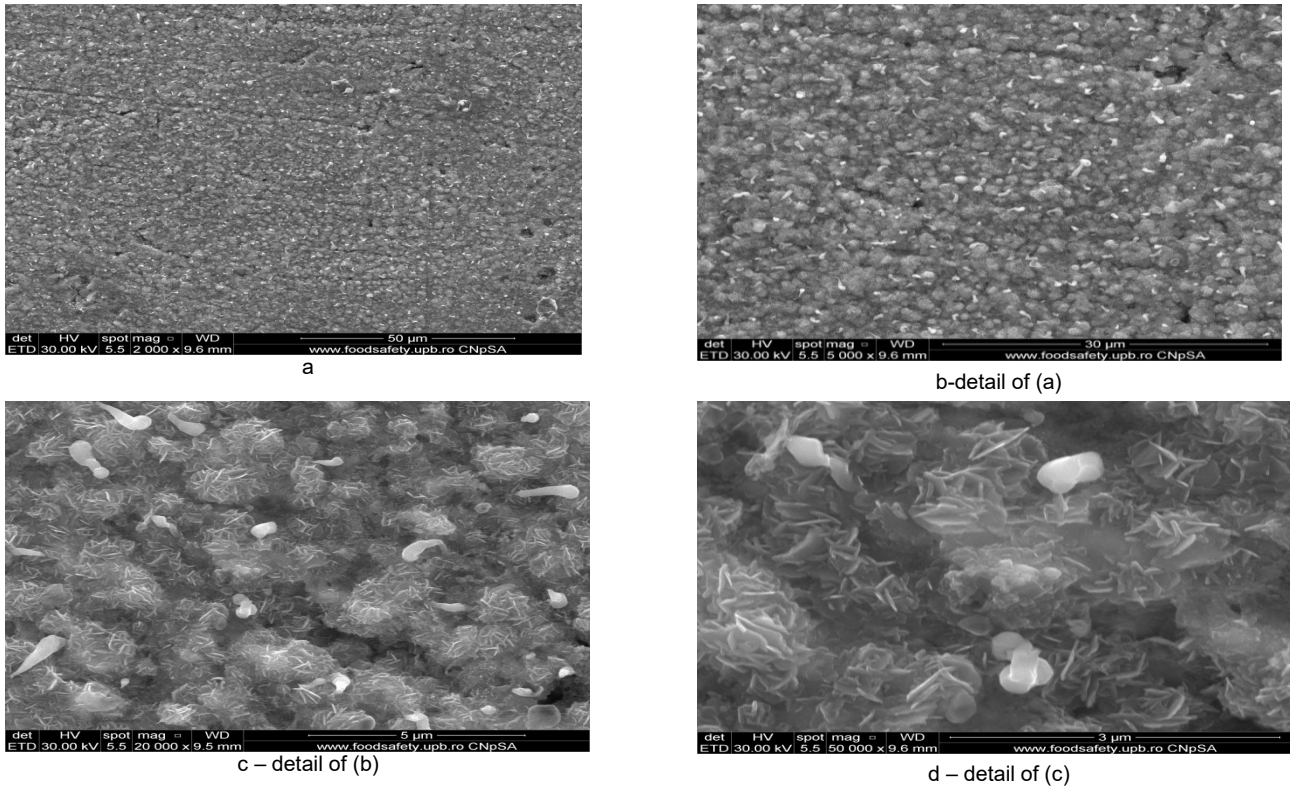


Fig. 20 - SEM images of Ni-P coating after heating at 400°C in Ar 1 hour/
 Imagini electronmicroscopice de baleiaj ale acoperirii Ni-P tratate la 400°C în Ar 1 oră

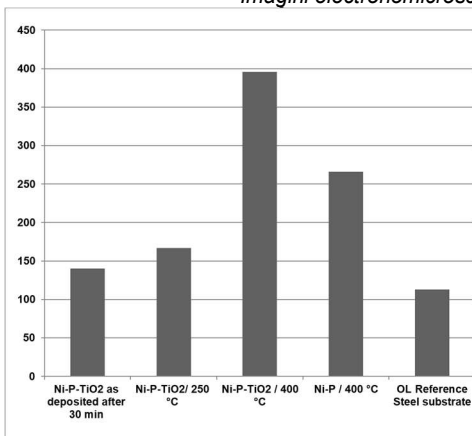


Fig.21 - Vickers microhardness on Ni-P-TiO₂ coating samples as deposited for 30 minutes, Ni-P-TiO₂ heated at 250°C, and Ni-P-TiO₂ heated at 400°C compared to Ni-P sample heated at 400°C and OL substrate (uncovered steel strip) / Microduritatea Vickers pe probele de acoperiri Ni-P-TiO₂ depuse 30 minute, Ni-P-TiO₂ tratate la 250°C, și Ni-P-TiO₂ tratate la 400°C comparativ cu proba Ni-P arsă la 400°C și substratul OL (bandă de oțel neacoperită).

laminated steel, OL-type, substrate (uncovered steel strip). The test results at 50 g loads are shown in Fig. 21. It was found that all samples coated with nanocomposites have improved hardness compared to the uncoated OL sample. Compared with the OL uncovered reference sample, it can be recorded that the highest microhardness for the Ni-P-TiO₂ coating heat-treated at 400°C, is more than 3.5 times higher, respectively, the Ni-P nanocomposite coating heat-treated at 400°C being more than 2.4 times, the samples last longer than

the reference test. A low phosphorus content (1% P) favors the development of a higher micro hardness. After proper heat treatment, the coating becomes crystalline and the hardness and wear resistance are greatly improved by incorporating particles into electroless chemically deposited metals, which is a convenient method for preparing composite coatings since the particles improve the mechanical and physical properties of the coating. At temperatures above 400°C, the size of the particles of phosphides grows and reduces the hardness [16]. Treatment at higher temperatures and over a longer period leads to a progressive decrease in hardness, which can be attributed to the increase in nickel grains and phosphorus. Post-deposition heat treatment had a significant impact on the hardness of the electroless Ni-P coating. One of the important characteristics of electroless coatings is the possibility of obtaining very high hardness values through an appropriate heat treatment [13]. This provides a unique wear and erosion resistance. The parameters of the post heat treatment (time and temperature) are defined by the phosphorus content. If the phosphorus content stays in one phase region, i.e., below 4.5 or above 11, there would be only one reaction in which the β or γ phase is transformed to α and NiP₃. This transformation occurs at 400°C for low phosphorus and 330-360°C for high phosphorus content alloys [14]. However, in the region between 4.5 and 11 wt.% phosphorus, there is another transformation in which β is transformed to α-nickel. This transformation occurs at 250-290°C and causes the precipitation of fine particles throughout the coating.

Fig. 21 shows the effect of heat treatment temperature on the hardness of Ni-P and Ni-P-TiO₂, respectively, coatings.

Many sources also reported that the maximum hardness of Ni-P is obtained after a heat treatment at 400°C for one hour [13, 15-16].

4. Conclusions

One of the outstanding characteristics of electroless plating coatings is their high hardness, especially after heat treatment. There are three major parameters affecting the hardness of these coatings, namely, phosphorus content, time, and the temperature of the applied post heat treatment. The Ni-P-TiO₂ nano-composite coatings were successfully obtained by the incorporation of TiO₂ nanoparticles into the Ni-P matrix using electroless plating technique.

Our work has demonstrated that the microhardness of the Ni-P-TiO₂ composite coatings was significantly increased, and their wear resistance was also greatly improved, compared with reference Ni-P coatings.

Heat treatment is an important factor that affects the thickness, hardness, structure, and morphology of the deposit on the steel surface. The optimal heat treatment regime was for one hour at 400°C for maximum hardness of the coating layers. The increase in hardness is attributed to the recrystallization of nickel and the precipitation of fine particles of nickel phosphides intermetallic compounds. Compared with the OL uncovered reference sample, it can be recorded that the highest microhardness for the Ni-P-TiO₂ coating heat-treated at 400°C, is more than 3.5 times higher, respectively, the Ni-P nanocomposite coating heat-treated at 400°C being over 2.4 times more, they last longer than the reference test.

Acknowledgements: *This work was supported by a grant of the Romanian Ministry of Education and Research, CCDI-UEFISCDI, Project No 317 PN-III-P2.2.-PED -2019-3409, within PNCD III.*

The authors are grateful to CSIII Roxana Trușcă and Lecturer dr. ing. Adrian V. Surdu for their help to this paper.

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