



## SINTEZA ȘI CARACTERIZAREA ACOPERIRILOR AUTOCATALITICE DE NICHEL - FOSFOR CU CONȚINUT DE PARTICULE OXIDICE NANOMETRICE

### SYNTHESIS AND CHARACTERIZATION OF AUTOCATALYTIC NICKEL-PHOSPHORUS COATINGS CONTAINING NANOSIZED OXIDE PARTICLES

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This work emphasizes on the development of electroless nickel composite coatings with the incorporation of oxide nanosized hard particles embedded in Ni-P matrix to improve their performance. The preparation of electroless nickel composite coating bath, methods to introduce hard particles in the bath, factors that affect the particle incorporation in the coating and its effect on coating structure is discussed in detail. The nickel-phosphorus coatings alloy layer was deposited by an autocatalytic process, without external power input is from this point of view an major advantage over electrolytic nickel plating technology. However, the autocatalytic Ni-P coatings deposition has a drawback, namely the low speed of layer deposition. Our investigations were focused on enhancing the deposition speed and homogeneity of the Ni – P –XO coatings, where XO is a mixture of Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub> nanoparticles (ratio of 95: 5 by weight) deposited on low carbon content steel strip substrates.

The chemical cell (bath) was formulated for 10/L oxides admixture and then connected by immersing the pre-treated steel substrate in the electroless bath solution for 15, 30, 45 and 60 minutes, respectively. The pH of the solution was kept between 4.58 and 6.23. The temperature was controlled in the bath in 60 °C -98°C range. Different stirring intensities in 50 - 400 rpm range were tested. There was almost no difference between Ni-P coating adherence versus Ni-P-(Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub>) coating obtained by electroless plating. Moreover, electroless plating have nearly constant coating thickness across all surfaces, including edges and complex interior geometry. Nodularity of the Ni-P globules is reduced due to incorporation of second phase oxide nanoparticles.

Lucrarea pune accent pe dezvoltarea acoperirilor chimice compozite de nichel cu încorporarea de particule oxidice dure nanodimensionale într-o matrice de Ni-P pentru a le îmbunătăți performanța. Pregătirea băii de depunere chimică a acoperirilor nanocompozite de nichel, metodele de introducere a particulelor dure în baie, factorii care afectează încorporarea particulelor în stratul de acoperire și efectul acesteia asupra structurii acoperirii sunt discutate în detaliu. Stratul de aliaj nichel-fosfor a fost depus printr-un proces auto-catalitic, fără utilizare de energie externă și constituie din acest punct de vedere un avantaj major față de tehnologia de nichelare electrolitică. Totuși, depunerea auto-catalitică a acoperirilor de Ni-P are un dezavantaj și anume, depunerea acestora are loc cu o viteză redusă. Investigațiile noastre s-au concentrat pe creșterea vitezei de depunere chimică și a omogenității acoperirilor Ni-P-XO, unde XO este un amestec de nanoparticule de Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>, (în raportul gravimetric de 95: 5) depuse pe substraturi de bandă de oțel cu conținut scăzut de carbon.

În celula chimică (baie) s-a adăugat 10g/L de amestec oxidic și apoi a fost conectată prin scufundarea substratului de oțel pretratat în soluție, timp de 15, 30, 45, respectiv, 60 de minute. pH-ul soluției a fost menținut între 4,58 și 6,23. Temperatura a fost controlată folosind o baie de termostatare în intervalul 60 °C. -98 °C. Diferite intensități de agitare au fost testate în intervalul 50 – 400 rpm. Nu a existat aproape nicio diferență între aderența acoperirii Ni-P față de acoperirea Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> obținută prin depunere chimică. În plus, prin depunere chimică stratul are o grosime aproape constantă de acoperire pe toate suprafețele, inclusiv marginile și geometria interioară complexă. Nodularitatea globulelor de Ni-P este redusă datorită încorporării nanoparticulelor oxidice de fază secundară.

**Keywords:** Electroless Composite Coatings, Nickel, Nano-sized oxide powders, Process Parameters

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## 1. Introduction

The electroless nickel-phosphorus coatings alloy layer deposited by an autocatalytic process, without external power input, is more advantageous over electrolytic nickel-plating technology. An advantage of electroless nickel plating is the ability to coat interior surface of pipes, valves, and other parts of various materials, including metals (ferrous and nonferrous), plastics, glass and ceramics etc. [1-3] Particularly, the nickel-phosphorus coating successfully can replace in terms of quality and economical ones the electrolytic nickel coatings, hard chrome coatings and stainless steel strips, with features that recommend them for use in numerous industries such as: chemical and oil industry, polymer injections, aeronautics, automobile, food industry, electronics (hard drives substrates, printed boards), fire arms, cutting tools, etc) [4-5]. There is renewed interest in coatings with exceptional hardness, wear and impact properties for automotive and other mechanical applications [6]. Compared with the patented technologies, our contribution is focused on enhancing the deposition speed and homogeneity of Ni-P layers using different and new admixtures in the deposition bath, which could lead also to obtaining new layers of composite-type structures. The incorporation of nano size particles within Ni-P coatings significantly improves the coating properties and imparts new functional features to its performance. Several researchers have used the size of TiO<sub>2</sub> particles in the range of 15-300 nm, B<sub>4</sub>C particles in the range of 3-11 μm and the SiC particles in the range of 40-600 nm [7-11] and Al<sub>2</sub>O<sub>3</sub> particles in the range of 5-15 μm [12-15]. On the other hand, previous studies [16- 15] have shown that Al<sub>2</sub>O<sub>3</sub> toughened with ZrO<sub>2</sub>, TiC, WC, TaC develop an outstanding mechanical behaviour and excellent corrosion/ abrasion resistance as bulk ceramic. Insertion of zirconia into alumina as a sintering additive has been practiced for the densification of alumina ceramics. However, the concept of reinforcing alumina ceramics by dispersing zirconia particles or hard metal carbides (TiC, TaC) particles in the matrix is recognized in numerous studies [16 - 20]. The introduction of a small amount (1000-2000 p.p.m.) of zirconium in alumina, as a sintering additive, allows the formation of a solid solution that promotes the densification processes by introducing network defects. In contrast, ZTA microstructures are characterized by the presence of two distinct phases, which do not react with each other, but form a solid solution. The incorporation of nanosized particles within Ni-P coatings it is expected to significantly improve the coating properties and imparts new functional features to its performance [11-13]. Consequently, the development of nano-composites layers in arrays of nickel (Ni - P / Al<sub>2</sub>O<sub>3</sub>+ ZrO<sub>2</sub>) is challenging itself. To make these processes successful, better electroless technologies will be needed, improving

the selectivity and consistency of the deposits [14-17]. The environmental questions that the spent electroless solutions cause are also an important factor that the industry must consider when competing with alternative processes. The future of electroless plating looks bright and rewarding. New technologies are being developed for high performance needs, using alloys, composites and special "hard" electroless nickel coatings [18-23].

Obtaining of the thin steel strips, coated with nickel-phosphorous by chemical reduction in continuous flow is a technological challenge requiring new solutions, especially in increasing the rate of deposition layer solutions that will be proposed after achieving research. To increase the speed of the nickel bath will propose the troubleshooting consisting mainly of performing specific additives or coating bath application of alternative methods of agitation. This work is focused on understanding the influence of various processing parameters to obtain electroless complex nano-composite Ni - P / Al<sub>2</sub>O<sub>3</sub>+ ZrO<sub>2</sub> coatings.

## 2. Experimentals

Composition of coatings based on Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composites with dispersed nanometre sized alumina and zirconia powders were designed for electroless deposition by using an acid electrolyte based on nickel sulphate and sodium hypophosphite, in order to obtain uniform and adherent layers, which were achieved on thin low carbon ferrous strip of a 0.2 - 0.4 mm thickness. The composites considered in this paper are those in which alumina and zirconia are present as two distinct phases rather than as a solid solution.

### 2.1. Materials

#### 2.1.1. Ferrous substrate before electroless deposition

The microstructure of the surface of the steel substrate before pre-treatment and activation is shown in Fig. 1, which reveals a structure with fine stripes, characteristic of the cold rolled steel stripes on which impurities, oxidation stains, greases can be noticed. The chemical composition of the steel substrate was analyzed by XRF spectrometry, resulting in steel with a low content of C. (Table 1).

#### 2.1.2. Oxide component of composite coatings

The oxide additives used in the electroless deposition of Ni-P- Al<sub>2</sub>O<sub>3</sub>+ ZrO<sub>2</sub> composites had nanometre particle sizes and consisted of a nanometre mechanical alloying of alumina (Al<sub>2</sub>O<sub>3</sub>) with nanometre zirconia (ZrO<sub>2</sub>) mixed in a ratio of 95: 5 (% by weight).

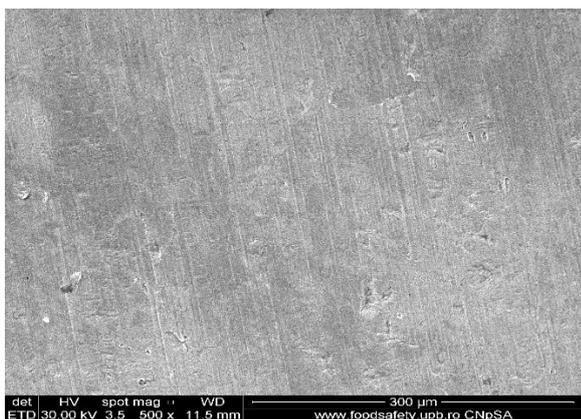


Fig. 1 - SEM image on steel substrate surface before pre-treatment and electroless deposition/Imagine SEM a suprafeței substratului de oțel înainte de tratament și depunere chimică  
 Magnification x 500/Mărire x500

Table 1

Chemical composition of the steel substrate analyzed by XRF spectrometry/ *Compoziția chimică a substratului de oțel analizat prin spectrometrie XRF*

Si, %	Mn, %	P, %	S, %	Cr, %	Ni, %	W, %	Fe, %
0.032	0.020	0.032	0.015	0.015	0.010	0.002	99.874

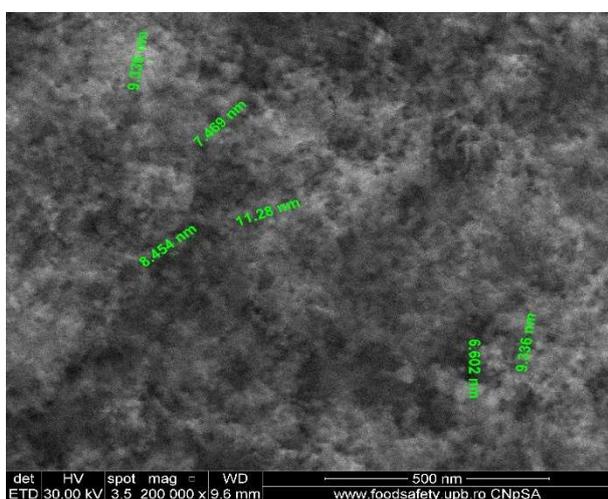


Fig.2 - SEM image on nanometre Al<sub>2</sub>O<sub>3</sub> powder/Imagine SEM a pulberii nanometrice de Al<sub>2</sub>O<sub>3</sub>  
 Magnification x 200,000/ Mărire x20000

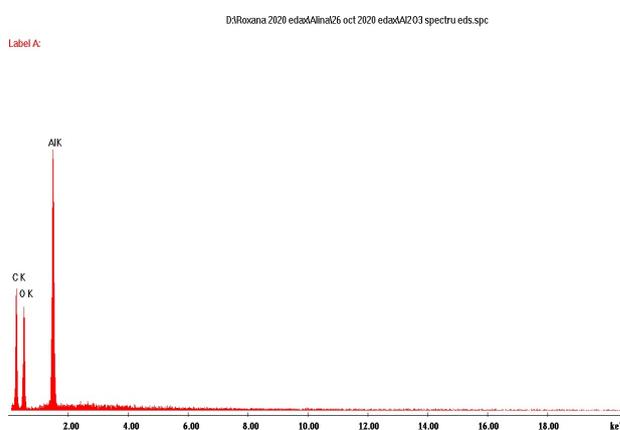


Fig.3 - EDAX image of the qualitative elemental analysis of the nanometre Al<sub>2</sub>O<sub>3</sub> powder/Spectru EDAX de analiză elementală calitativă a pulberii nanometrice de Al<sub>2</sub>O<sub>3</sub>

Elem	Wt %	At %	K-Ratio	Z	A	F
O K	51.49	64.16	0.1835	1.0311	0.3454	1.0008
Al K	48.51	35.84	0.2734	0.9659	0.5835	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte.	Error	P/B
O K	114.34	2.20	2.08	52.09	
Al K	355.00	7.25	1.18	48.94	

Fig.4 - EDAX quantitative elemental analysis of the nanometre Al<sub>2</sub>O<sub>3</sub> powder/Analiza cantitativă EDAX a pulberii nanometrice de Al<sub>2</sub>O<sub>3</sub>



Fig.5 - The macroscopic aspect of the nanometre Al<sub>2</sub>O<sub>3</sub> powder/ Aspectul macroscopic al nanopulberii de Al<sub>2</sub>O<sub>3</sub>

### Aluminium trioxide (alumina, Al<sub>2</sub>O<sub>3</sub>)

The electron microscopic appearance of the major oxide component (Al<sub>2</sub>O<sub>3</sub>) used in Ni-P-ZTA composite coatings is shown in Fig. 2, revealing particle sizes of approx. 10nm. The aluminous powder exhibits an analytical purity as confirmed by the qualitative (Fig.3) and quantitative EDAX analyses (Fig. 4). The macroscopic appearance of the nanometre Al<sub>2</sub>O<sub>3</sub> powder is shown in Fig. 5.

### Zirconium dioxide (zirconia, ZrO<sub>2</sub>)

The electron microscopic appearance of the minor oxide (ZrO<sub>2</sub>) used to prepare Ni-P-Al<sub>2</sub>O<sub>3</sub>+ ZrO<sub>2</sub> composite coatings is shown in Fig.6, revealing the particles size of approx. 5 nm. The zirconia powder showed an analytical purity as confirmed by EDAX qualitative quantitative analyses (Fig. 7 and Fig. 8). The macroscopic appearance of the nanometre ZrO<sub>2</sub> powder is shown in Fig. 9.

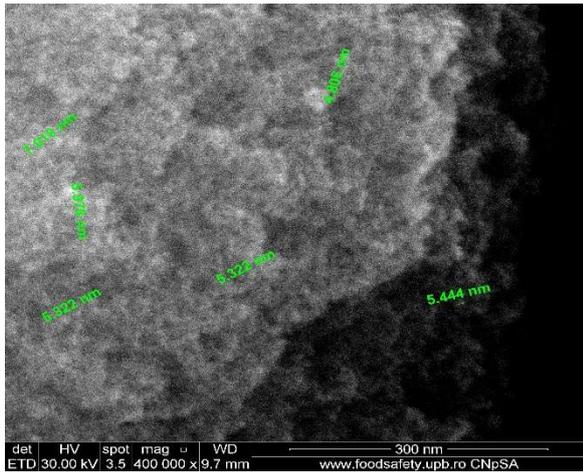


Fig.6 - SEM image on nanometre  $ZrO_2$  powder / Imagine SEM a nanopulberii de  $ZrO_2$   
Magnification x 400,000 / Mărire x 400000

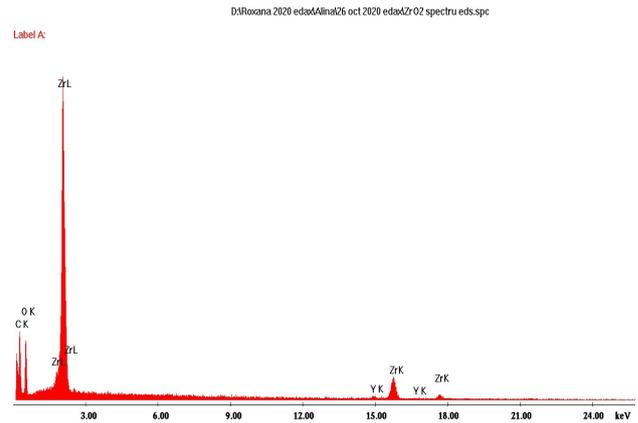


Fig.7 - EDAX image regarding the qualitative elementary analysis of the nanometre  $ZrO_2$  powder / Spectru EDAX de analiză elementală calitativă a pulberii nanometrice de  $ZrO_2$

Elem	Wt %	At %	K-Ratio	Z	A	F
O K	31.39	72.24	0.0454	1.1347	0.1275	1.0004
Y K	6.33	2.62	0.0576	0.9063	1.0039	1.0000
ZrK	62.28	25.14	0.5643	0.9022	1.0042	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte.	Error	P/B
O K	63.05	10.61	2.17	5.94	
Y K	8.69	4.68	7.30	1.86	
ZrK	67.33	4.41	1.93	15.26	

Fig.8 - EDAX quantitative elemental analysis of the nanometre  $ZrO_2$  powder / Analiza cantitativă EDAX a pulberii nanometrice de  $ZrO_2$



Fig.9 - The macroscopic aspect of the nanometre  $ZrO_2$  powder / Aspectul macroscopic al nanopulberii de  $ZrO_2$

## 2.2. Electroless bath composition

Two bath compositions were developed for the electroless deposition of Ni-P alloys as a standard for the Ni-P-  $Al_2O_3$ +  $ZrO_2$  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 sulphide and 1 g / l lead acetate.

Sodium acetate has been introduced into the bath as a buffer solution for pH and prevents excess concentration of free metal ions.

Sodium citrate was used as complexing agents which form metastable complexes with nickel ions and release them slowly for the reaction, which helps to maintain the stability of the electroless bath and deposition time. The deposition rate and reaction mechanism are influenced by the complexing agent [5]. Lead acetate was used as stabilizers in electroless bath. Suitable and precise amount of stabilizer in the bath increases the deposition rate of electroless coatings, whereas excess amount decreases the deposition rate [5]. Sodium Dodecyl Sulphide is added as wetting agents (surfactant) in the electroless bath. The important functions of surfactant are to lower the surface tension of a liquid, allowing the easier spreading and reduce the interfacial tension

between the liquid and solid surfaces. In the electroless nickel bath, presence of surfactant promotes the coating deposition reaction between the bath solution and the surface of the specimen.

**Bath (B);** Bath (A) to which 10 g / L nano-ZTA was added. The electrochemical bath solutions were freshly prepared from analytical grade chemicals and with double distilled water.

## 2.3. Obtaining of electroless composite layers

Pre-treatment of samples for chemical coating with Ni-P-Ox alloy consists of:

- chemical degreasing at 80 °C – 90 °C, followed by washing in hot (80 - 90 °C) and cold water;

- pickling in 20% hydrochloric acid and washing in hot water, at the temperature of the nickel plating bath, in order to keep its temperature constant when immersing the sample in the solution for chemical nickel plating.

The preparation of the steel support strip has a decisive role in obtaining an adherent, uniform and continuous coating. A large part of the nickel plating defects is caused by the inadequate preparation of the surface of the support material [13,14].

The electrochemical cell (B bath) was connected by immersing the pre-treated steel

substrate and activating it in 250 ml of solution for 15, 30, 45 and 60 minutes, respectively. The pH of the solution was between 4.58 and 6.23. The temperature was controlled using a thermostatically controlled bath at 80°C. The deposition under continuous stirring is necessary for the continuous removal of the native hydrogen in the type of 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, 400 rpm. The weight of the deposited composite coating was evaluated by changing the weights of the substrates before and after the electroless process

#### 2.4. Characterization methods

The pH of electrolytes was measured over time, using the HACH sensION156 Portable pH/Conductivity Meter. The samples of thin steel strip coated with Ni-P- Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> 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, TOXEL, Cu BASE). In order to investigate the morphology, micro-composition and thickness of the coatings were studied by using Scanning Electron Microscope: Quanta Inspect F coupled with Energy-Dispersive X-ray Spectroscopy EDXS. The prepared samples were weighed before starting the experiment by a Sartorius electronic balance, with standard deviation of ≤ 0.02 mg and measured for a corresponding area (1 cm<sup>2</sup>) determination. The initial weight was used to calculate the sample weight variation after the electroless test and determination of deposition index.

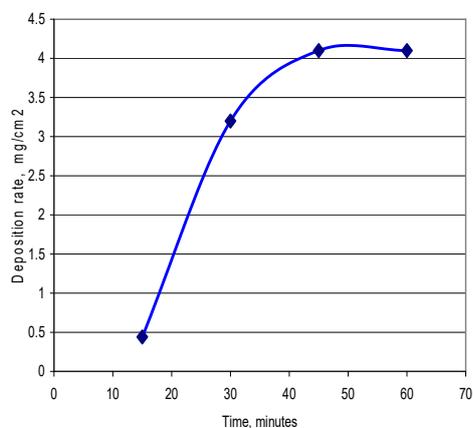


Fig 10 - Electroless deposition rate of Ni-P-nano Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite coating as a function of time at pH 5.18 and temperature of 80°C / Viteza de depunere chimică a compozitului Ni-P nano Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> funcție de timp la pH 5,18 și temperatura de 80 °C

### 3. Results and and discussion

In acidic baths, on a substrate with adequate characteristics, deposition can take place with nickel and hypophosphite in a wide concentration range, without the simultaneous and uncontrolled reduction of nickel in the entire volume of the bath: for nickel, between 3 and 100 g / L , and for hypophosphite, between 10 and 100 g / L. From a stoichiometric point of view, each mole of nickel consumes 3 moles of hypophosphite. Therefore, theoretically a ratio of 0.33 would be required. In practice, it is recommended that the value of this ratio be maintained between 0.25 and 0.60. According to [2] the highest deposition rate is obtained at the ratio of 0.45. To optimize the deposition process, the bath component has become increasingly complex, the bath being completed with various additives: complexing agents, accelerators, stabilizers, buffers, pH regulators, wetting agents, etc. This led to the improvement of the process characteristics and the properties of the deposits: the stability of the bath, the immersion duration, the bath' temperature and pH evolution, the control of the deposition speed, the structure of the deposit made, the smoothness and the shine of the surface, etc. It turned out that each component of the bath has a specific influence in the chemical deposition process and will be discussed as follows.

#### 3.1 Duration of the electroless deposition process

The samples were kept for different periods in order to assess the degree of incorporation and dispersion of Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub> in the Ni-P matrix, depending on the time parameter. The mass deposited on the unit surface during the plating period represents the *deposition rate* as the difference of the weights of the substrates before

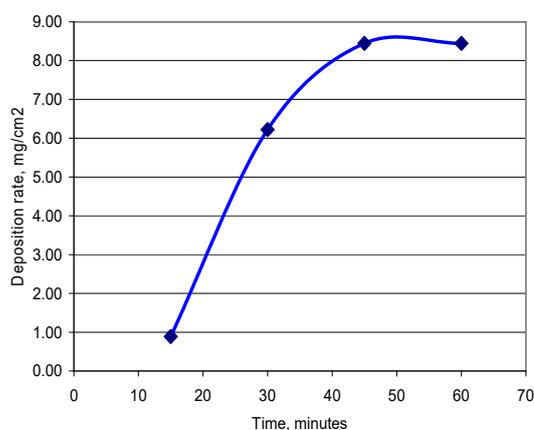


Fig 11 - Electroless deposition rate of Ni-P-nano Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite coating as a function of time at pH 6.23 and temperature of 80 °C / Viteza de depunere chimică a compozitului Ni-P nano Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> funcție de timp la pH 6,23 și temperatura de 80 °C

and after the electroless process. The electroless deposition rate of the Ni-P-ZTA coating as a function of time can be seen in Fig. 10 and Fig. 11. The highest increase in the deposition rate is achieved after 45 minutes, while at 60 minutes there is a decrease of deposition rate. Increasing the pH of the deposition bath from 5.18 to 6.23 at the same temperature of the immersion bath leads to a doubling of the deposition rate.

### 3.2. The influence of temperature of electroless bath

Most reactions involved in the chemical deposition process are endothermic. As a result, increasing the temperature accelerates the deposition, as shown in Fig. 12, and in Fig. 13, respectively. The deposition rate increases exponentially with the bath temperature. Most of the acid baths operate at 80 – 90 °C. Alkaline baths can be operated at lower temperatures, of only 40 °C, this being the reason why alkaline baths are used for depositing layers on plastic supports. If the temperature is allowed to rise well above 90 °C, there is damage to the electroless plating solution or intensification of its decomposition process. When the bath temperature rises above the value recommended by normal operation, even if the other variables remain constant, deposits with low phosphorus content are obtained [2]. A low pH has been established to obtain a high P content in the coating because it increases the corrosion resistance of the layer by changing the electronegativity of nickel. The pH of the work bath was corrected with citric acid. The temperature was maintained at lower values (80°C) to avoid destabilizing the bath. Long maintenance times were also tested to see the differences in the inclusion of nanoparticles of Al<sub>2</sub>O<sub>3</sub>+ ZrO<sub>2</sub> mixture in the layer, depending on this working parameter.

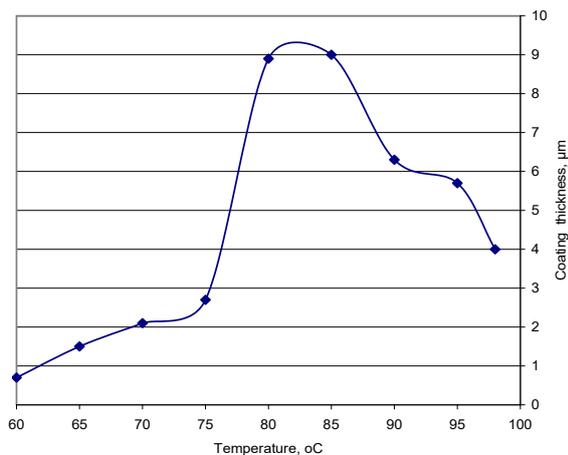


Fig.12 - Variation of layer thickness depending on temperature at pH - 4.58 and after 15 min immersion / *Variația grosimii stratului în funcție de temperatură la pH-4,58 după imersare timp de 15 min*

The temperature of the nickel plating solution must be closely monitored to obtain significant and high quality deposits. Working temperatures above 90 °C lead to the decomposition of the nickel-plating bath and at too low temperatures, below 65 °C the deposition of nickel is very slow or non-existent.

### 3.3. Influence of plating bath pH

The temperatures as well as the pH of the solution in the deposition bath during the production process are important parameters by the influence it exerts on the rate of deposition. A high pH value of the coating solution can lead to abnormally high deposition rates of the Ni-P layer, which can lead to high roughness, pitting, and / or uneven and localized deposits (in the form of flakes). a pH too low will cause slow deposition rates and dull deposits. In Fig. 14 and Fig. 15 is shown the evolution of the layer thickness depending on the pH of the bath after 15 minutes and respectively 60 minutes of immersion in the nickel bath. The increase in layer thickness is determined by the increase in the rate of the nickel reduction reaction as the pH increases. The decrease of the pH below 4 in the specific working conditions mentioned, leads to the significant decrease of the layer thickness, the deposition process becoming very slow.

Obtaining the Ni - P - Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> layers shows a relatively long coating duration to achieve a layer thickness of 10-14 µm for an immersion time of 45 - 60 min. The reactions associated with the process of reducing nickel sulphate require time. However, working conditions can be met to ensure the formation of a considerable layer and at short deposition times of 15 minutes. As presented on Fig.14 and Fig.15, it is observed that for acid baths a pH of 6 at a working temperature of 80°C is favourable for the layer thickness as a function of the immersion duration of the samples.

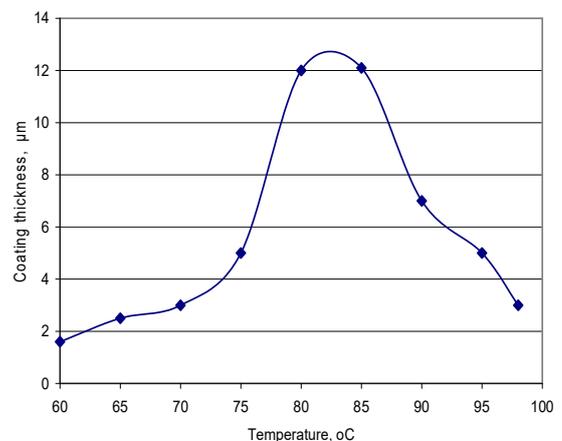


Fig.13 - Variation of layer thickness depending on temperature at pH - 6.28 and after 15 min immersion / *Variația grosimii stratului în funcție de temperatură la pH- 6,28 după imersare timp de 15 min*

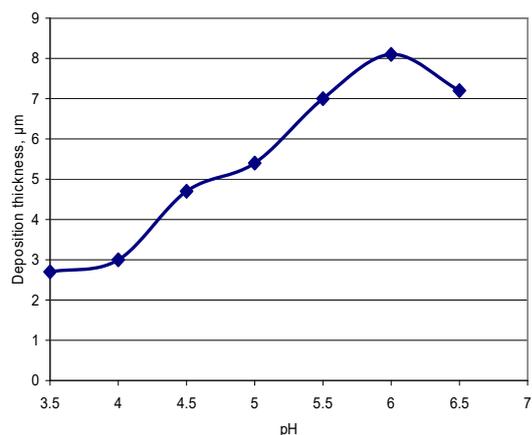


Fig. 14 - Evolution of the layer thickness depending on the pH of the plating bath after 15 minutes of immersion at temperature of 80°C / *Evoluția grosimii stratului în funcție de pH-ul băii de depunere după imersare timp de 15 min la temperatura de 80°C*

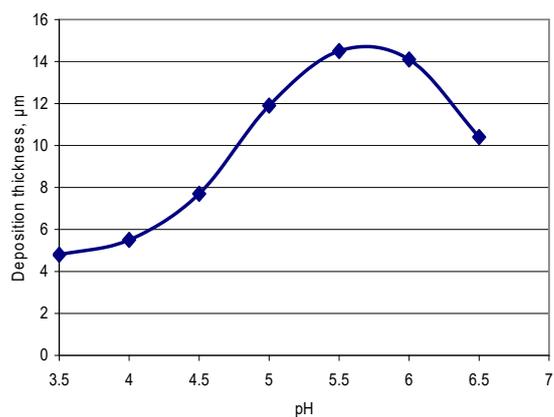


Fig. 15 - Evolution of the layer thickness depending on the pH of the plating bath after 60 minutes of immersion at temperature of 80°C / *Evoluția grosimii stratului în funcție de pH-ul băii de depunere după imersare timp de 60 min la temperatura de 80°C*

### 3.4. Influence of bath stirring speed

Stirring is necessary to remove hydrogen from the deposition bath and maintain the homogeneity of the chemical composition of the electrolyte. In industrial practice, air bubbling is indicated as being more effective in entraining hydrogen gas to the surface of the electrolyte and passing into the atmosphere. At the laboratory level, mechanical agitation was applied. To maintain the stability of nanometre-sized particle dispersion throughout the nickel plating bath required the application of a high agitation speed and it was established that a stirring at 300 rpm is optimal for a laminar flow of the solution from electroless bath as well as for the surface deposition uniformity and the parallel ridges are less visible, recording increase of the deposited layer. Higher speeds being able to lead to non-uniform coatings, respectively with variable layer thicknesses.

### 3.5 Microstructural and morphological analysis of composite deposits

The SEM electron microscopic images of the Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite coatings after 15 minutes and 60 minutes of electroless deposition, respectively, are shown in Fig. 16 and Fig. 17. There is a quasi-amorphous structure. 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-nanoAl<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite deposition after 15 minutes of electroless deposition in Fig. 18

respectively after 60 minutes of electroless deposition in Fig. 19, where a relatively uniform distribution of the elements P, Ni, Al, O occurs. Also, there are interferences of Fe from the steel substrate, Pb and Na, respectively, which were used in the form of lead acetate and sodium acetate to stabilize the electrochemical bath. A long deposition (60 min) led to uneven and localized deposits (as flakes), probably due to the presence of these stabilizer bath deposition. Pb ions stabilize the bath, preventing the decomposition of the solution by inhibiting the deposition / protection of catalytically active nuclei. Sodium acetate has been introduced into the bath because it acts as a buffer solution for pH and prevents excess concentration of free metal ions. For Ni deposits, it prevents exceeding the concentration of Ni ions, stabilizing the baths and preventing the precipitation of Ni phosphate. Nodularity of the Ni-P globules is reduced due to incorporation of second phase oxide nano sized particles.

In addition, adhesion test showed that there was almost no difference between Ni-P coating and Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> coating by electroless plating.

Mineralogical analysis of nickel composite deposits with dispersion phase of Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> mixture by electroless was investigated by XRD analysis. The X-ray pattern of nickel composite layers by the electroless plating after 60 minutes of deposition is shown in Fig. 20. There is a quasi-amorphous structure, with interferences of mostly rhombohedral Al<sub>2</sub>O<sub>3</sub> and tetragonal ZrO<sub>2</sub>.

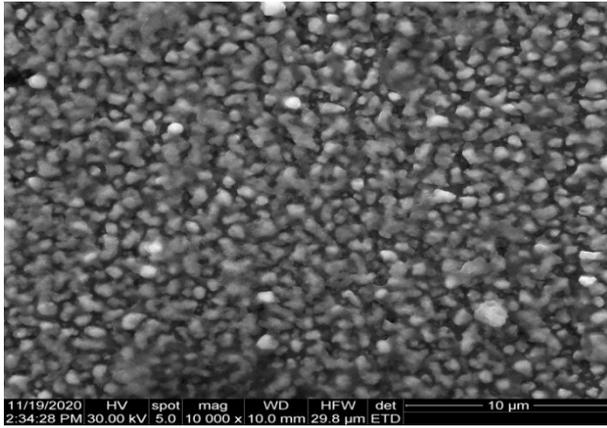


Fig. 16 - Microstructure of composite coating Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> after 15 minutes of electroless deposition / Morfologia SEM a stratului compozit de Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> după 15 de minute de depunere chimică

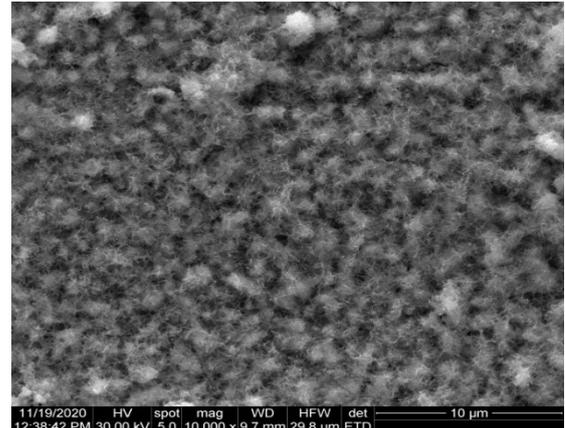


Fig. 17 - Microstructure of composite coating Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> after 60 minutes of electroless deposition / Morfologia SEM a stratului compozit de Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> după 60 de minute de depunere chimică

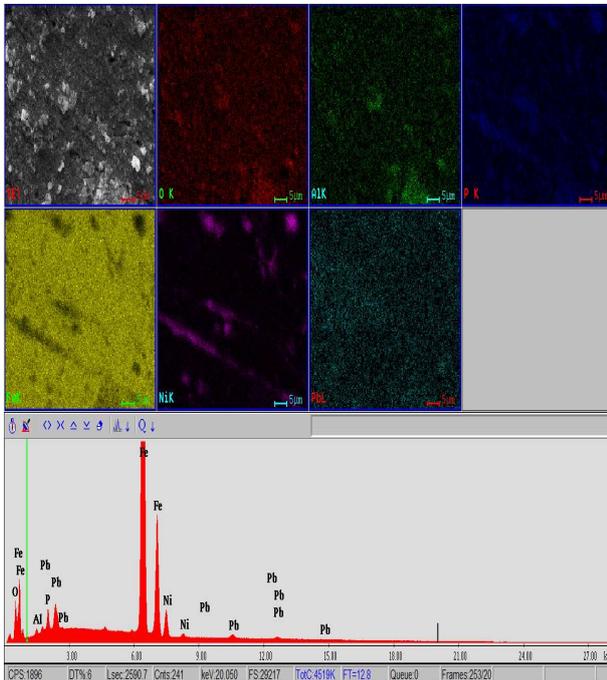


Fig. 18. - EDS global image of the distribution of the component elements present in the Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite deposition after 15 minutes of electroless deposition /Spectrul EDS global al distribuției elementale din compozitul Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> deșus timp de 15 min

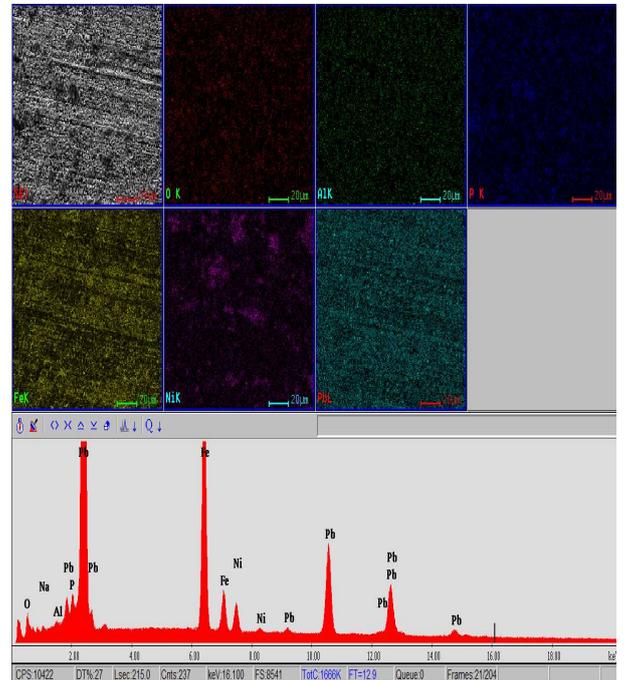


Fig. 19. - EDS global image of the distribution of the component elements present in the Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite deposition after 60 minutes of electroless deposition /Spectrul EDS global al distribuției elementale din compozitul Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> deșus timp de 60 min

After 15 minutes of electroless deposition (Fig. 16), some nodular structures are distributed uniformly in the composite coating. The appearance of cauliflower-like nodules, which is typical of amorphous material, was observed After 60 minutes of electroless deposition (Fig. 17). The nodular structures are very small in size which was not visible in low magnification. The oxide particles were trapped in nodular boundaries and cause the particles to be agglomerated. Consequently, the presence of particles in nodular boundaries affects on nodules growth accordingly [14, 23]. The SEM images of the surface morphology in conjunction

with the elemental composition obtained from EDS (Fig. 18 and Fig. 19) clearly confirm the presence of Al<sub>2</sub>O<sub>3</sub> particles in the Ni-P matrix. Fe peaks were detected in coatings, in which the coating thickness was less than the diffusion depth of EDS ray resulting in observing the substrate's peak. Also, Na and Pb peaks were detected, originating from stabilizers, buffers and complexing agents used in electroless bath. According to the XRD analyses (Fig. 20), the coating after 60 minutes of deposition has mainly an amorphous feature. However, the nano-sized co-deposited particles of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> diffraction peaks can be seen on the XRD pattern.

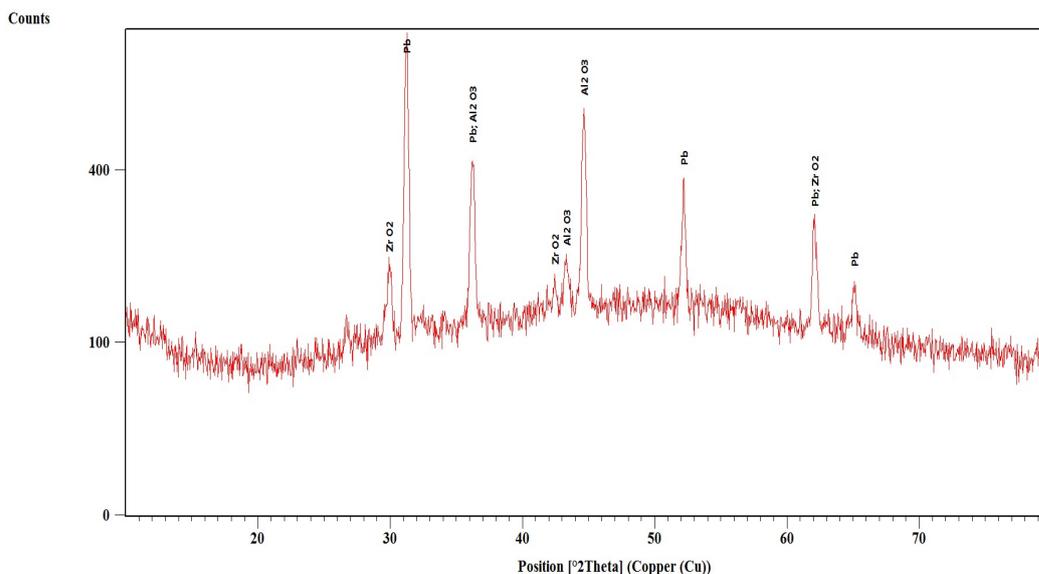


Fig. 20 - X ray diffraction pattern of Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> composite deposition after 60 minutes of electroless deposition  
 Difractograma de raze X a stratului compozit Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> după 60 de minute de depunere chimică.

#### 4. Conclusion

The deposition of nickel-phosphorus composite coatings by an autocatalytic process, without external power input is effective and from this point of view proves advantage over electrolytic nickel plating technology. The idea of co-deposition of various second phase particles in electroless nickel deposits and thereby taking advantage of their inherent uniformity, hardenability, wear resistance and corrosion resistance has led to the development of electroless nickel composite coatings. Electroless nickel composite layers on low carbon steel strips substrates have emerged as suitable coatings in particular situations to improve their performance. The oxide nano-particles co-deposited in electroless Ni-P coatings using in-situ co-precipitation reaction appears to be uniform and finely distributed particles in Ni-P matrix. However, the autocatalytic phosphorus nickel coatings deposition has a high drawback, namely the low speed layer deposition. In electroless coating process, the specimen or substrate is immersed in to specific solution called electroless bath. Our work focuses the troubleshooting and consists mainly of performing specific electroless bath composition formulation having a source of metallic ions, reducing agent, complexing agent, wetting agent or surfactant, additives, and stabilizer. In the electroless nickel composite coatings nickel sulphate was used as source of metal. Sodium hypophosphite was used as reducing agents in electroless nickel baths due to higher deposition rates, increased stability, and greater simplicity of bath control.

The preparation of electroless nickel composite coating bath, methods to introduce hard

particles in the bath, factors that affect the particle incorporation in the coating and its effect on coating structure is discussed in detail. Morphology characterization and phase structure analysis of the composite coatings demonstrated that 10 wt % nano Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> particles had an important influence on the growth process and phase structures and grain size of the coatings. Nodularity of the Ni-P globules is reduced due to incorporation of second phase particles. There was almost no difference between Ni-P coating adherence versus Ni-P-Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> coating obtained by electroless plating. Electroless plating have nearly constant coating thickness across all surfaces, including edges and complex interior geometry. In perspective, the composite coating is the excellent technique to improve the mechanical and tribological properties of industrial components and parts and will be assessed in our future works.

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