

Properties of nickel-phosphorous coatings co-deposited by the electroless and electrochemical plating process

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Abstract— At present, despite numerous studies and practical application, the process of chemical nickel plating remains imperfect. The low nickel deposition rate, the high consumption of the solution components, and the complexity of the deposition process do not contribute to the widespread use of chemical nickel plating. At the same time, chemically deposited coatings are significantly different from the electrochemical: they possess valuable properties. In the paper, the intensification method of chemical nickel plating considered through the use of the co-deposition process with chemical and electrochemical methods. The co-deposition was carried out in an acidic electrolyte solution on an aluminum plate with the stationary potential shift from -0.01 to -0.25 V with the use of three electrode system. The presented technique of intensification due to the combination of nickel deposition processes by chemical and electrochemical methods is able to increase the deposition rate of the coatings, and also allows influencing their composition and mechanical properties.

Keywords— *nickel, aluminum, electroless deposition, potential, deposition rate.*

I. INTRODUCTION

Electroless nickel-phosphorus coatings are widely used to protect machine parts and mechanisms, since they have various valuable properties, such as uniformity, homogeneity, corrosion resistance, hardness, wear resistance [1-4].

Electroless nickel plating is an autocatalytic reduction process which proceeds by an electrochemical mechanism based on the nickel ions reduction by hypophosphite in aqueous solutions. The mechanism of electroless nickel plating reactions is very complex and is still being studied and refined [5, 6]. The nickel reduction with hypophosphite involves step reactions; therefore the electroless nickel plating of aluminium alloys is characterized by low speed and fast fading of the process, as well as low efficiency of nickel salts [7]. Thus, many factors influence the coating formation rate: the concentration of the main components, the pH of the solution, the temperature and the process time [8-10]. It should be noted that the process of electroless nickel plating takes a long time, and during its, there is a chemical reagents consumption, which is a disadvantage of the method [11].

In this paper, the influence of the stationary potential shift of the electroless nickel plating process on the deposited coatings properties is considered.

II. EXPERIMENTAL STUDIES

The deposition of a nickel-phosphorus coating during electroless and electrochemical co-deposition on an aluminium surface was carried out using a three-electrode cell and a P-5848 potentiostat. The silver chloride was used as the reference electrode, graphite rod – as auxiliary electrode, aluminum plate – as the working electrode. During the experiment, an acidic sulphate nickel plating solution was chosen as the electrolyte [12].

Preparation of the substrate for the process included: degreasing in carbon tetrachloride and alkaline solutions, alkaline and acid etching, double zincate treatment with the intermediate acidic etching [13]. Auxiliary and working electrodes, connected by a salt bridge with a reference electrode, placed in a potassium chloride solution, were immersed in preheated to operating temperature ($80\text{ }^{\circ}\text{C}$) electrolyte solution (250 ml).

After the surface potential of the aluminum had been established, the chemical nickel plating was performed for 3 minutes (to obtain nickel contact layer).

According to the determined shift, value of the potential was set on the voltage set block, and co-deposition of chemical and electrochemical nickel was carried out for 30 minutes. Then nickel coated aluminum plate was washed, dried and weighed. Gravimetric method was used to determine the average thickness of the coating. Each sample was heat treated at $350\text{ }^{\circ}\text{C}$ during one hour on air.

The phosphorus content in the coating was determined by energy dispersive spectroscopy (Oxford INCA Energy), sludge structure – by scanning electron microscopy (Tescan VEGA II LMU). The coatings roughness was investigated with a three-dimensional non-contact profilometer (Micro Measure 3D Station) with a measurement step of $0.1\text{ }\mu\text{m}$. The hardness of the annealed coatings was investigated with Nano Indenter G200; diamond pyramid was used as an indenter. The adhesive properties of the obtained samples were investigated

with a Micro-Scratch Tester MST-S-AX-0000. The load range was from 0 to 15 N, the loading rate – 15 N/min. The penetration depth was determined with an induction sensor. Cracking sounds were recorded with an acoustic sensor.

III. RESULTS AND DISCUSSION

Chemical nickel plating of aluminium occurs at a constant stationary potential which is equal to -0.48 V. When an aluminium plate with a zinc underlayer is immersed into an electroless nickel plating solution, the potential increases from -0.90 to -0.48 V due to the formation of a nickel layer on the surface of the plate. Consequently, the zinc underlayer is an activator and is replaced with nickel. Next, the process of electroless nickel plating is carried out without any electrochemical influence. In this case, the process rate will be low, but a slight shift of the stationary potential into the cathode region increases in the deposition rate occurs.

According to researches, a series of experiments was conducted to establish a function of the average rate of nickel deposition from a solution, with the electrochemical potential being applied. Experimental results are presented in table 1.

TABLE I. THE NICKEL DEPOSITION RATE AND PHOSPHORUS CONTENT IN THE COATING ON THE POTENTIAL SHIFT

Sample No	Potential shift, V	Deposition rate, $\mu\text{m/h}$	Phosphorous content, wt%
1	0.00	10	4.60
2	-0.01	14	4.05
3	-0.03	16	1.54
4	-0.05	18	3.68
5	-0.08	20	4.02
6	-0.10	22	1.78
7	-0.15	24	0.00
8	-0.20	30	0.00
9	-0.25	40	0.00

It follows from the obtained data that the potential shift to the cathode region by the hundredths leads to an increase in the nickel deposition rate, since the potential is shifted under the effect of current, the chemical process is accompanied by the electrochemical process, and a share of chemical nickel in the composition of the deposit is reduced. Therefore, the chemical composition of the coating should change as well, i.e. a share of phosphorus should decrease. Therefore, a change in the chemical composition of the deposited coating

phosphorus content, which is consistent with the content of electrochemically deposited phosphorus in the coating.

At the potential shift of -0.10 V or more the amount of phosphorus in the coating decreased to a level less than the phosphorus detection limit (< 0 wt.%), which indicated the dominant electrochemical content in comparison with the content of electroless nickel in the coating or a high deposition rate, with which co-deposition of phosphorus is just impossible. Therefore, the coating deposition according to the mechanism presented in [14] at nickel co-deposition with a large stationary potential shift to the cathode region is not feasible.

The morphology of the obtained samples was investigated with the scanning electron microscopy. Figure 1 a shows a typical micrograph of the surface structure of the nickel coating, obtained with electroless deposition: the surface is uniform; the average crystallites surface size is $2 \mu\text{m}$. It was previously established that with the surface stationary potential shift, the nickel deposition rate increases, and therefore the structure of the coating changes. The closest in structure to the chemical coating sample is the one obtained at a cathode shift of -0.05 V (fig. 1 b). Other samples obtained at shifts less than -0.10 V differ from chemical ones (fig. 1 c as an example). The coating obtained with the potential shift by -0.08 V (fig. 1 c) is characterized by a non-uniform surface topography: the formation of hilly structures is due to the uneven deposition of nickel due to activation of nickel autocatalytic deposition at certain points on the surface.

At the stationary potential shift by -0.10 V (Fig. 1 d) and more, the microstructure is radically different from the electroless one and close to electrochemical.

The cathode shift of the surface stationary potential allows increasing the deposition rate, while the phosphorus content in the coating varies. Based on the obtained structural-morphological results, it was found that the samples of fig. 1a and fig. 1b are closest. At the same time, the phosphorus content in them is different: in the sample, without shift, the phosphorus content is 4.60 wt.%, and at the shift by -0.10 V – 3.68 wt. %

The deposited coatings are different in structure, therefore their physicochemical characteristics also differ. Thus, research of the influence of stationary potential shift on

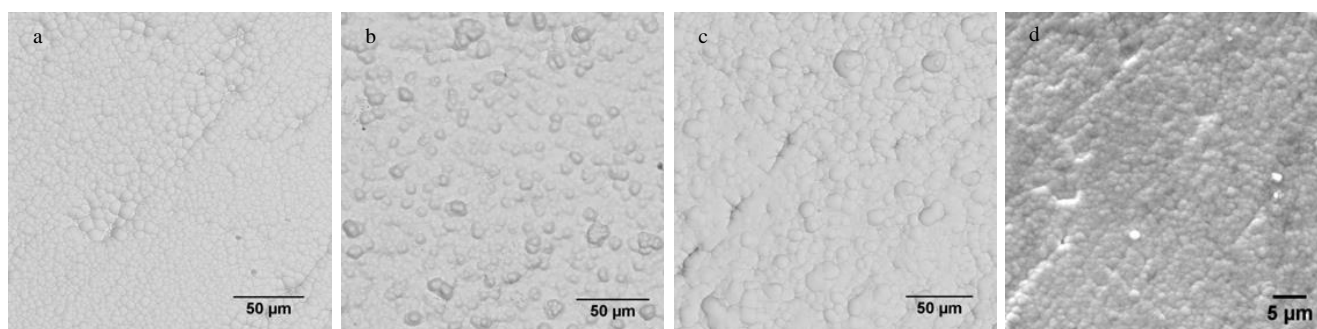


Fig. 1. Surface microstructure of the deposited coatings: a) electroless nickel; b) with surface potential shift by -0.05 V; c) with surface potential shift by -0.08 V; d) with surface potential shift by -0.10 V.

should be observed, i.e. the phosphorus content decreases. This is reflected in the results (table 1), in which at the potential shift by -0.03 V (at -0.51 V) the phosphorus content in the coating decreased. The further potential shift of the sample surface to -0.08 V caused an increase in the

roughness, hardness and wear resistance of coatings was carried out.

Table 2 presents the results of the roughness measure in comparison to the stationary potential shift of the surface,

from which it follows that with the increase of cathodic displacement, an increase and decrease in the roughness was observed.

TABLE II. THE SURFACE ROUGHNESS ON THE SURFACE POTENTIAL SHIFT

Sample No	Note	Roughness Ra, μm
1	aluminium plate	0.545
2	electroless nickel $E_{\text{cath}} = 0.00 \text{ V}$	0.493
3	cathodic potential shift $E_{\text{cath}} = 0.01 \text{ V}$	0.851
4	0.03 V	0.671
5	0.05 V	0.665
6	0.08 V	0.622
6	0.10 V	0.373
8	0.15 V	0.217
9	0.20 V	0.335
10	0.25 V	0.242

The aluminium plate, prepared according to the mentioned method, was selected as the reference sample. During chemical nickel plating, the surface roughness decreased by $0.05 \mu\text{m}$, which corresponds to the statement about the soothing properties of electroless nickel plating [3, 15]. Consequently, the samples obtained by electroless and electrochemical nickel co-deposition should be close by the value to the electroless deposited coating.

At the same time, at the cathode shift of the sample potential by 0.01 V from the stationary potential (-0.48 V) of the process of electroless nickel plating, the surface roughness increases by a factor of 2 due to changes in the qualitative and quantitative composition of the coating. The further increase in cathode shift to -0.08 V leads to slight surface roughness decrease, but at the shift equal to -0.10 V , the roughness decreased by a factor of 2. These changes are explained by the increase in the share of electrochemically deposited nickel in comparison with the share of electroless deposited nickel.

Chemical nickel is known to have a fine-crystalline structure with an α -nickel lattice, in which nickel and phosphorus atoms are evenly distributed [16]. Therefore, during the electrochemical influence, nickel is not uniformly formed: deposition occurs not over the entire area, but on individual crystals.

According to theoretical data, nickel coatings need to be thermally treated after the deposition, since heating contributes to the pores closure and the recrystallization process during the annealing process [17–20]. Table 3 presents the results of the investigation of the microhardness dependence on the surface potential shift. The control samples were an aluminium plate and an electroless nickel plated aluminium plate.

The deposited at 0.01 V cathode shift sample has less hardness than the control one. Thus, a small electrochemical influence on the aluminium plate decreases the quality of the obtained coatings. Increase of cathode shift leads to the increase of the coating hardness. It should be noted that the sample obtained with the potential shift by 0.05 V had a hardness higher than the control samples by about 100 MPa .

TABLE III. THE MICROHARDNESS ON THE SURFACE POTENTIAL SHIFT

Sample No	Note	Microhardness, MPa
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1	aluminium plate	1051
2	electroless nickel $E_{\text{cath}} = 0.00 \text{ V}$	1097
3	cathodic potential shift $E_{\text{cath}} = 0.01 \text{ V}$	587
4	0.03 V	790
5	0.05 V	1170
6	0.08 V	1587
7	0.10 V	1674
8	0.15 V	2194
9	0.20 V	4600
10	0.25 V	6827

The further shift of the stationary potential to the cathode region, starting from 0.08 V , contributed to the deposition of coatings with a hardness that exceeded the hardness of the control samples, which is positive for the exploitation characteristics of the coating.

In addition to the roughness and microhardness, one of the important coating characteristics is adhesion. Therefore, the greater the adhesion of the coating to the substrate, the longer its service life is.

Table 4 shows the results of adhesion characteristic measurements of deposited nickel coatings.

TABLE IV. ADHESIVE CHARACTERISTICS OF THE COATING AT VARIOUS POTENTIAL SHIFTS

Samples	Force, N		
	Cracks	Partial coating loss	Overall coating loss
electroless nickel $E_{\text{cath}} = 0.00 \text{ V}$	0.50	0.89	1.61
cathodic potential shift $E_{\text{cath}} = 0.01 \text{ V}$	0.30	0.62	1.09
0.03 V	1.20	1.83	3.77
0.05 V	1.92	1.96	3.15
0.08 V	1.98	2.99	4.49
0.10 V	0.39	–	2.54
0.15 V	0.46	0.79	2.52
0.20 V	0.27	1.35	2.15
0.25 V	1.95	2.52	3.51

As can be seen from the obtained data, the adhesion characteristics increase with an increase in the surface potential shift to a value of -0.08 V . After this value, there was a decrease in the strength characteristics of the coatings. It should be noted that a slight electrochemical influence of 0.01 V on the surface does not contribute to an increase in strength characteristics.

IV. CONCLUSION

The effect of the electrode potential shift to the cathode region on the deposition rate, composition and structure of deposited coatings was investigated. It is established that with a potential shift from the stationary value by -0.03 V , the phosphorus content in the nickel coating decreases from 4.60% to 1.54% , and with a further increase of the potential shift value to -0.08 V , the phosphorus content increases up to 4.02% , probably due to direct electrochemical reduction of hypophosphite. At the same time, the samples obtained at shifts of -0.15 V , -0.20 V and -0.25 V do not contain phosphorus. It was also shown that the potential shift to the cathode region leads to electroless and electrochemical nickel co-deposition, which contributes to the deposition rate increase from 10 to $40 \mu\text{m/h}$ (4 times).

The morphology of the deposited nickel coatings was investigated with scanning electron microscopy. Surface irregularities are formed during simultaneous electroless and

electrochemical deposition of nickel. At the same time, with an increase in cathodic polarization to -0.08 V, the size of nickel crystallites increases, a further shift allows to obtain coatings differ from electroless one. It is noted that the closest in morphology and microstructure to the electroless deposited coating is the sample obtained with the surface shift to the cathodic region by -0.05 V.

Microstructure investigations showed that the sample closest to the control is the deposited at the shift of -0.05 V; further physicochemical study allowed to determine prose of co-deposited coatings over electroless one.

The study of roughness allowed establishing that the small cathode shift near the stationary potential leads to an increase in the surface roughness by a factor of 2, which indicates a possible change in the qualitative and quantitative composition of the coatings. With an increase in the cathodic shift to -0.08 V, the surface roughness decreases slightly, but at the shift of -0.10 V, the roughness decreases by a factor of 2. These changes can be explained by the fact that such a shift leads to the case when the share of electrochemically deposited nickel exceeds the share of electroless nickel.

The study of microhardness showed that with an increase in the cathode shift, the hardness of the coatings increases. It should be mentioned that the sample deposited with the potential shift by 0.05 V without heat treatment is almost twice softer than the control one, but after annealing the hardness become higher than the control samples by about 100 MPa. Further displacement of the stationary potential to the cathode region starting from 0.10 V, contributes to the deposition of coatings with a hardness that even before heat treatment exceeds the hardness of the control samples. In the case of the shift by -0.10 V, the sample without annealing is harder by 100 MPa, and with heat treatment – by 700 MPa, which positively affects the exploitation properties of the coating.

The study of adhesion showed that with a change in the stationary potential shift up to -0.08 V, the wear resistance of the coatings increases. The further shift of the stationary potential to the cathode region leads to a decrease in wear resistance. Therefore, it can be concluded that the adhesion characteristics and wear resistance of the co-deposited coatings could be increased with the use of small potential shift near the stationary value.

Investigation of different physicochemical properties of nickel coatings showed that properties of co-deposited coatings could exceed one of electroless nickel. Therefore, the method of co-deposition of electroless and electrochemical nickel at certain values of the shift of the surface potential to the cathode region makes it possible to obtain coatings with lower phosphorus content but with better physicochemical characteristics.

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