

## INFLUENCE OF ELECTROLYSIS PARAMETERS ON THE PROPERTIES OF Ni-P ALLOYS OBTAINED FROM METHANESULFONATE ELECTROLYTES

SAVCHUK O. O., SKNAR Yu. E., SKNAR I. V., BEZIK A. O.,  
CHEREMYSINOVA A. O.

Ukrainian State University of Chemical Technology, Dnipro, Ukraine  
zhigalova1028@gmail.com

The characteristics of electrodeposition of Ni-P alloy coatings from a methanesulfonate electrolyte have been investigated. It is shown that increasing the concentration of phosphorus compounds in the electrolyte increases the phosphorus content in coatings. It was found that the increase in current density leads to a reduction of phosphorus in the deposits. The dependences of the properties of deposits nickel-phosphorus on temperature, current density and concentration of sodium hypophosphite in the methanesulfonate electrolyte have been obtained.

It is shown that increasing the concentration of sodium hypophosphite and temperature leads to increased internal stresses and microhardness alloy Ni-P. Changing the structure-dependent properties of polycrystalline deposits is associated with the formation of distorted crystal lattice. The distortion of coatings is due to the increase of phosphorus content in the deposit. The surface of the Ni-P alloy obtained from the methanesulfonate electrolyte at 313 K is more brilliant compared with coating deposited at 333K. Lowering the temperature of electrolysis extends the range of concentrations of sodium hypophosphite in which there are high values of the gloss.

Electrolytic metal alloys with phosphorus have a number of valuable properties. Among these coatings a special place belongs to the Ni-P alloy. This alloy is characterized by high corrosion resistance, microhardness, wears resistance, good protective and magnetic properties [1]. In the codeposition of nickel and phosphorus microcrystalline coating is obtained. The amorphous structure of the Ni-P deposits significantly affects the magnetic properties of the films [2].

Physical-chemical properties of Ni-P coatings depend on the composition of the electrolyte and conditions of electrolysis. Determining the relationship between different factors of the process of making such coatings, their composition and properties are an important subject of research. Most work in this area is dedicated to coatings obtained from sulfate electrolytes. However, today, new prospects open up for

electrolytes based on methanesulfonic acid [3, 4]. This makes the relevance of research of electrodeposition of Ni-P alloys from methanesulfonate electrolyte and their properties.

### **Research methodology**

Electrodeposition of Ni-P alloy was performed from a methanesulfonate electrolyte with concentration of sodium hypophosphite  $C$ , mol/dm<sup>3</sup>: 0; 0.03; 0.05; 0.07; 0.12. The composition of the methanesulfonate electrolyte: 1.00 M Ni(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 0.30 M NaCl, 0.70 M H<sub>3</sub>BO<sub>3</sub>,  $C$  M NaH<sub>2</sub>PO<sub>2</sub>.

Operating conditions were pH3,  $T = 313$  and  $T = 333$  K,  $i = 20, 30, 50, 70$  mA/cm<sup>2</sup>. Coating thickness was 25  $\mu$ m.

The phosphorus content of the coatings deposited on copper foil in galvanostatic mode was determined by the X-ray fluorescence method [5] using the "SPRUT" spectrometer.

Internal stresses in nickel-phosphorus coatings were determined by the flexible cathode method.

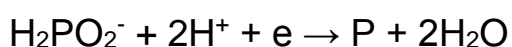
The Vickers hardness was measured with a PMT-3 device at a load of  $P = 100$  g.

The gloss of the coatings was measured to a silver mirror using a photoelectric gloss meter FB-2.

### **Results and Discussion**

In the electrodeposition of coatings from the methanesulfonate electrolyte containing from 0.03 to 0.12 mol/dm<sup>3</sup> sodium hypophosphite, uniform, smooth, well-adherent Ni-P deposits are formed. An increase in the concentration of sodium hypophosphite in electrolytes leads to an increase in the phosphorus content of the coatings. The phosphorus content in the deposits obtained at  $T=333$ K,  $i=20$  mA/cm<sup>2</sup> and 0.07 mol/dm<sup>3</sup> NaH<sub>2</sub>PO<sub>2</sub> is 4.4 wt.%. The concentration of sodium hypophosphite in the electrolyte equal to 0.12 mol/dm<sup>3</sup> corresponds to 7.1 wt.% of phosphorus in the coating. Reducing the temperature to 313K contributes to a decrease in the phosphorus content. In this case, when the concentration of sodium hypophosphite in the methanesulfonate electrolyte is 0.07 mol/dm<sup>3</sup> the phosphorus content in the deposit is 3.4 wt.%, at 0.12 mol/dm<sup>3</sup> the content is 5.2 wt.%.

During the electrodeposition of the Ni-P alloy the formation of phosphorus occurs with the consumption of hydrogen ions:

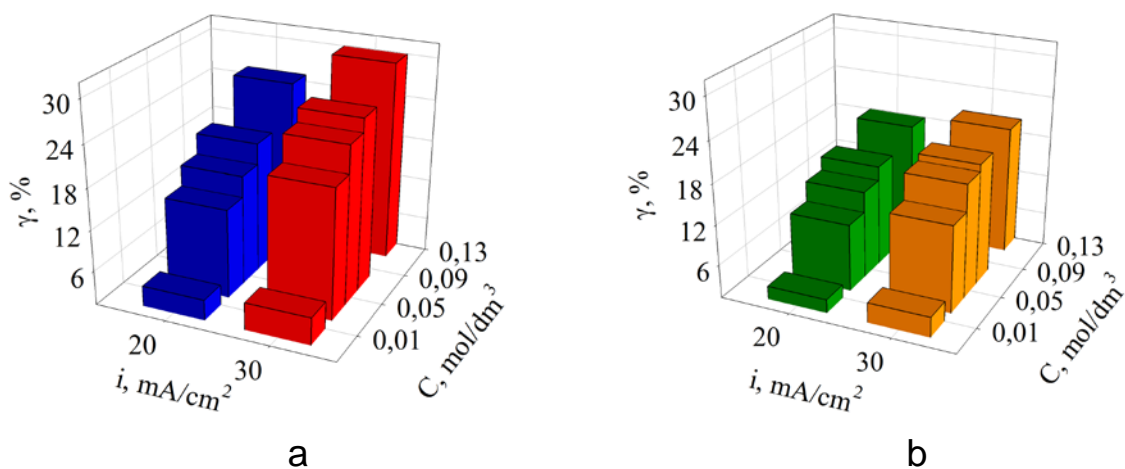


The effect of temperature on the composition of the alloy, first of all, can be due to a change in the concentration of H<sup>+</sup>-ions in the near-electrode layer. As the temperature decreases, the ion diffusion rate

decreases and the rate of the phosphorus formation reaction decreases.

An increase in current density leads to a decrease in the phosphorus content of Ni-P alloy. Perhaps this is due to the fact that sodium hypophosphite electroreduction occurs at the limiting current. The increased speed of metal matrix deposition at constant velocity of entering the phosphorus in the deposit leads to decreasing of phosphorus content in the coatings.

The composition of the Ni-P alloy affects the properties of the coating. As can be seen from Fig. 1, increasing the concentration of sodium hypophosphite in the electrolyte leads to an increase in the gloss.



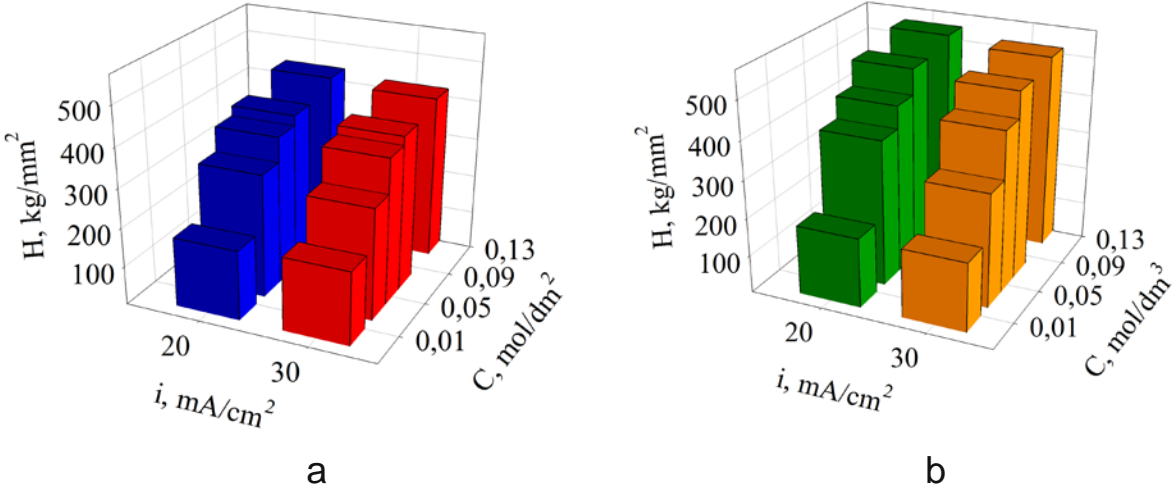
**Fig. 1.** Effect of deposition current density and sodium hypophosphite on the gloss of nickel-phosphorus deposits obtained from methanesulfonate electrolytes at 313K (a) and 333K (b).

The grain size of nickel-phosphorous coatings decreases significantly with increasing phosphorus content in the alloy, which manifests itself in increasing the reflectivity of coatings. As for reducing the grain size to short wavelength light waves that is 0.4 microns, the surface roughness is imperceptible and the coating is glossy. To reduce the grain size of coating, it is also helpful to reduce the temperature of electrolysis and increase the current density. Thus obtained experimental data reflect the cumulative effect of all these factors. High values of gloss nickel-phosphorus coatings are observed for a larger range of concentrations of sodium hypophosphite in the electrolyte at a temperature of 313°K.

One of the most important and most frequently used characteristics of materials strength is microhardness. Microhardness is often used as a parameter to study and compare the strength properties of alloys.

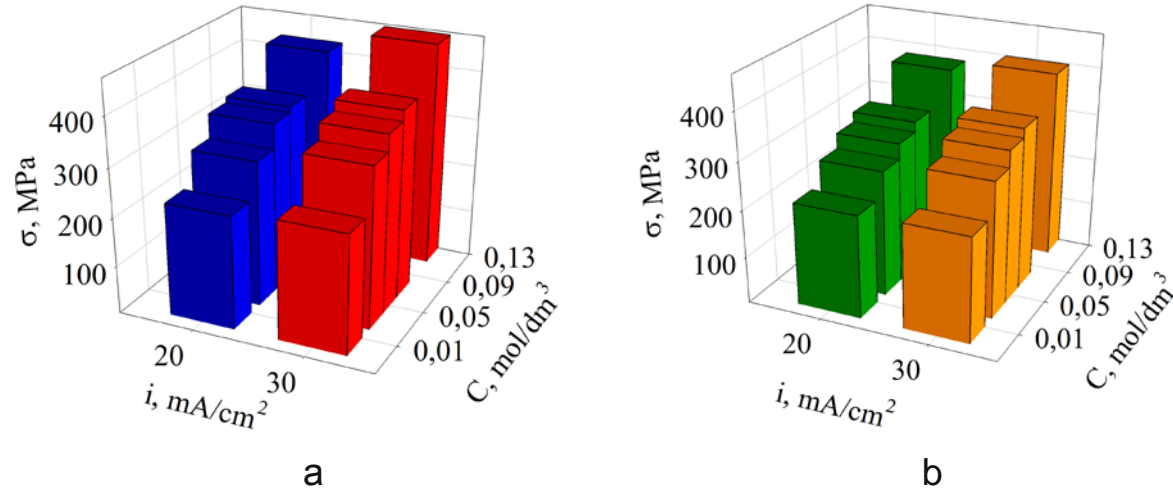
Experimental evidence obtained for coatings deposited from methanesulfonate electrolyte (Fig. 2) indicate that the microhardness

increases with the concentration of sodium hypophosphite in the electrolyte and increasing the temperature electrolysis. The increase in current density causes a slight decrease in microhardness values. Perhaps such regularities are associated with the change in the amount of phosphorus that is embedded in the deposits during electrodeposition.



**Fig. 2.** Effect of deposition current density and sodium hypophosphite on the microhardness of nickel-phosphorus deposits obtained from methanesulfonate electrolytes at 313K (a) and 333K (b).

The nickel-phosphorus alloy is characterized by high values of internal stresses. The internal stresses increase with increasing concentration of sodium hypophosphite in the electrolyte (Fig. 3).



**Fig. 3.** Effect of deposition current density and sodium hypophosphite on the internal stresses of nickel-phosphorus deposits obtained from methanesulfonate electrolytes at 313K (a) and 333K (b).

Obviously, this is due to structural changes in the crystal lattice of coatings, which occur as a result of the inclusion of phosphorus deposits

to a greater extent, the higher the concentration of sodium hypophosphite in the electrolyte. Internal stresses determine the number of performance coatings - strength, brittleness, ductility. The nature of internal stresses in the electrodeposited polycrystalline films are associated with defects in the structure, inclusions of various kinds of foreign elements, changing phase composition. In the Ni-P coatings it is a compression of the deposit that causes internal stress stretching. With increasing the temperature of electrolysis there is a slight decrease in internal stresses.

Thus, the new electrolyte based methanesulfonic acid is promising for electrodeposition of the Ni-P coatings with high gloss and microhardness. Reducing the internal stresses in the deposit is possible by raising the temperature of electrolysis.

### **Conclusions**

Results of the study of the Ni-P alloy electrodeposition from methanesulfonate electrolyte have shown that increasing the concentration of phosphorus compounds in the electrolyte increases the phosphorus content in coatings. The increase in current density results in the reduction of phosphorus in coatings. It is shown that increasing the concentration of sodium hypophosphite and temperatures leads to increased microhardness and internal stresses associated with an increased amount of phosphorus in the coatings. Reducing the temperature of electrodeposition from 333 K to 313 K promotes sodium hypophosphite concentration range in which there are high values of the degree of gloss.

### **References**

- [1] Li L, Zhang Yi, Deng S, Chen Y. Effect of ammonium on low temperature electrodeposition of Ni-P alloys // *Materials Letters*, vol.57, pp.3444-3448, 2003.
- [2] Carbajal J.L., White R.E. Electrochemical production and corrosion testing of amorphous Ni-P // *Journal of The Electrochemical Society*, vol.135, pp.2952-2957, 1988.
- [3] Danilov F. I., Sknar I. V., Sknar Yu. E. Kinetics of nickel electroplating from methanesulfonate electrolyte // *Russian Journal of Electrochemistry*, vol.47, pp. 1035-1042, 2011.
- [4] Danilov F. I., Sknar I. V., Sknar Yu. E. Electroplating of Ni-Fe alloys from methanesulfonate electrolytes // *Russian Journal of Electrochemistry*, vol.50, pp. 293-296, 2014.
- [5] Mikhailov I. F., Baturin A. A., Mikhailov A. I., Fomina L. P. Perspectives of development of X-ray analysis for material composition // *Functional Materials*, vol. 23, pp. 5-14, 2016.