UDC 544.654.2

## HARD AND DECORATIVE NI-P COATINGS ELECTRODEPOSITED FROM THE METHANESULFONATE ELECTROLYTE

#### ZHIGALOVA A.A., SKNAR Y.E., SKNAR I.V. Ukrainian State University of Chemical Technology, Dnepropetrovsk, Ukraine; zhigalova1028@gmail.com

The regularities of electrodeposition Ni-P coatings from the methanesulfonate and sulfate electrolytes were investigated. As a phosphorus-containing component we used sodium hypophosphite. It has been shown that increasing concentration of sodium hypophosphite in electrolytes leads to an increase in phosphorus content in the coatings. Increasing the electrodeposition current density of current density leads to reduction of phosphorus content in the coatings.

Cathodic voltamperograms were taken for the methanesulfonate and sulfate electrolytes. Addition of sodium hypophosphite to the electrolyte leads to a shift of the total voltamperogram in the region of positive potential. It was established that boric acid in the methanesulfonate electrolyte reduces the difference in nickel and nickel-phosphorus discharge overvoltage.

Hard and decorative Ni-P coatings are characterized by high internal stresses. The internal stresses increase with increasing concentration of sodium hypophosphite in electrolytes. Nickel-phosphorus coatings are characterized by high values of microhardness. The highest values of the microhardness of coatings are observed at a concentration of sodium hypophosphite 0,12 mol/l. The microhardness of the coatings obtained from the methanesulfonate electrolyte is higher than that of the coatings obtained from the sulfate electrolyte. The extent of nickel-phosphorus coatings brightness deposited from the methanesulfonate electrolyte reaches 20% and slightly lower in the case of the sulfate electrolyte. Results suggest that the physical-chemical properties of the coatings obtained from the methanesulfonate electrolyte higher in comparison with coatings obtained from the sulfate electrolyte.

Nickel-based coatings have a very valuable physical-chemical, mechanical and magnetic properties. For this reason, researchers are paying particular attention to the study of the electrochemical coatings based on Ni [1]. Considering this one of the most promising material is a nickel-phosphorus alloy. Ni-P coatings are characterized by high values of microhardness, wear resistance, increased protective and magnetic properties [2, 3]. To obtain high-quality coatings Ni-P alloy is necessary to establish patterns between the various factors electrodeposition coating process, their structure and properties.

## Experimental procedure

In this work, we added to the electrolytes sodium hypophosphite in an amount of 0; 0.03; 0.05; 0.07; 0.12 mol/l. Electrodeposition of Ni-P alloys was performed at pH3, T=333K and at current densities 2, 3, 5, 7 A/dm<sup>2</sup> for each concentration of sodium hypophosphite. Phosphorus content in Ni-P coatings deposited from the methanesulfonate and sulfate electrolytes was determined by a photocolorimetric method. In the study of the kinetics of the Ni-P coatings electrodeposition was used polarization curves analysis method. Internal stresses are defined by a flexible cathode method [4]. The brightness degree of Ni-P coatings measured relatively silver mirror using a photoelectric gloss meter. Microhardness determined using PMH-3 device.

#### **Results and Discussion**

Increasing the concentration of sodium hypophosphite in electrolytes increases the phosphorus content in the coatings. It is found that the phosphorus content does not differ in the coatings deposited from the methanesulfonate and sulfate electrolytes (figure 1). At a current density 2A/dm<sup>2</sup> at a concentration of 0.03 mol/l sodium hypophosphite in the electrolyte can be observed incorporation of phosphorus in an amount of 4.7% by weight in the coatings obtained from the methanesulfonate electrolyte and 4.5% by weight in the coatings deposited from the sulfate electrolyte. Further increase concentration NaH<sub>2</sub>PO<sub>2</sub> to 0,12 mol/l phosphorus content increases in deposits less. On the content of coatings affected by current phosphorus in the density of electrodeposition. Increasing the current density leads to a reduction of phosphorus content in the coatings.

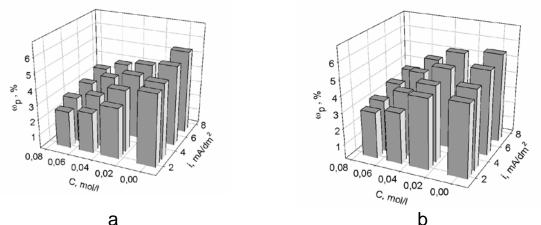
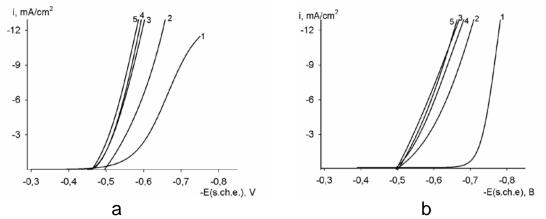


Figure 1. The phosphorus content in the Ni-P coatings deposited from the methanesulfonate (a) and sulfate (b) electrolytes

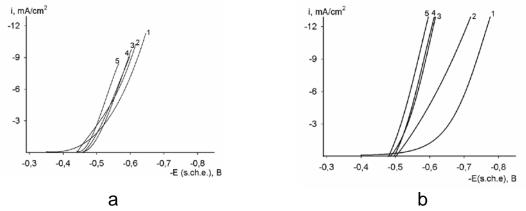
We have found that the overvoltage of nickel electrodeposition from methanesulfonate electrolyte is 100 mV lower than in the case of the sulfate electrolyte. (figure 2).



**Figure 2.** The cathodic voltamperograms obtained in the methanesulfonate (a) and sulfate (b) electrolytes at the presence of sodium hypophosphite, mol/l: 1 - 0; 2 - 0,03; 3 - 0,05; 4 - 0,07; 5 - 0,12.

Introduction of the sodium hypophosphite in the electrolyte leads to a shift depending on the voltamperogram towards positive potentials. Increasing the concentration of sodium hypophosphite in the electrolyte is more than 0,05 mol/I had little effect on the course of the polarization dependencies. It was found that boric acid reduces the difference in discharge overvoltage for nickel and nickel-phosphorus alloys obtained from the methanesulfonate electrolyte (figure 3).

The nickel-phosphorus alloys deposited from the methanesulfonate electrolyte characterized by high values of internal stresses. Internal stresses increase with increasing concentration of sodium hypophosphite in the electrolyte. Obviously, this is due to structural changes in the crystal lattice of coatings. A similar effect was observed when using the sulfate electrolyte.



**Figure 3.** The cathodic voltamperograms obtained in the methanesulfonate (a) and sulfate (b) electrolytes at the presence of 0,7 mol/l boric acid and sodium hypophosphite, mol/l: 1 - 0; 2 - 0,03; 3 - 0,05; 4 - 0,07; 5 - 0,12.

The brightness degree of Ni-P coatings deposited from the methanesulfonate electrolyte reaches 20% and slightly lower in the case of the sulfate electrolyte (figure 4). The highest values of the brightness degree correspond low current density. It may be due to the decrease of phosphorus content in Ni-P coatings at higher current density.

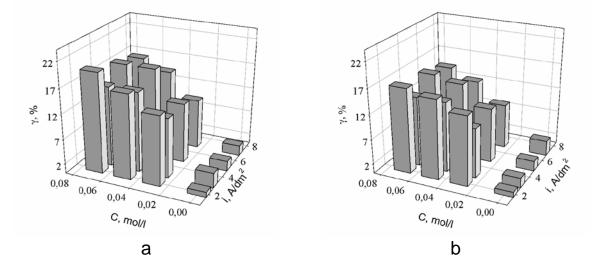
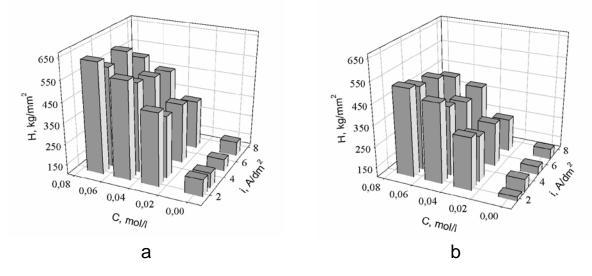


Figure 4. The brightness degree in the Ni-P coatings deposited from the methanesulfonate (a) and sulfate (b) electrolytes

Nickel-phosphorus coatings have high microhardness (figure 5). Microhardness increase with increasing concentration of sodium hypophosphite in the electrolytes. Microhardness of coatings deposited from methanesulfonate electrolyte exceeds the microhardness of coatings deposited from the sulfate electrolyte.



*Figure 5. Microhardness of the Ni-P coatings deposited from the methanesulfonate (a) and sulfate (b) electrolytes* 

# Conclusions

It is established that the nickel-phosphorus alloys deposited from the methanesulfonate and sulfate electrolytes under identical conditions similar in composition. According to the kinetics research rate of electroreduction of the nickel ions(II) at the presence of sodium hypophosphite in the electrolyte increases. Similar dependences are obtained for the sulfate electrolyte. The addition of boric acid to the methanesulfonate electrolyte reduces the differences in the kinetics of the Ni-P and nickel electrodeposition. In the sulfate electrolyte such effect is not observed. Ni-P coatings deposited from the methanesulfonate electrolyte have higher physical-chemical properties than coatings deposited from the sulfate electrolyte.

## Reference

[1] Djokic Stojan S. Electrodeposition of amorphous alloys based on the iron group of metals. // J. Electrochem. Soc., 1999, vol.146, pp.1824-1828

[2] Revesz A., Lendvai J., Loranth J., Padar J., Bakonyi I. Nanocrystallization studies of an electroless plated Ni–P amorphous alloy. //J. Electrochem. Soc., 2001, vol.148, pp. 715-720.

[3] Thomas M. Harris, Quoc D. Dang. The mechanism of phosphorus incorporation during the electrodeposition of nickel-phosphorus alloys. //J. Electrochem. Soc., 1993, vol.140, pp. 81-83.

[4] Shmelev N.M. The controller of works in electroplating. Metallurgy, Moscow, 1966. 175 p.