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ELECTRODEPOSITION OF NICKEL AND COBALT ALLOYS WITH ORGANIC LIGANDS IN SOLUTION

Electrodeposition of multicomponent nickel and/or cobalt alloys with nonmetallic inclusions from the complex electrolytes containing citric or malic acid was investigated. It has been confirmed that the decrease in the stability of metal complexes formed provides an increase in metal current efficiency. The use of malate complex electrolytes allows to diminish the effect of nickel and cobalt anomalous codeposition. Nickel-cobalt alloy electrodeposition from citrate electrolytes is accompanied by an overstoichiometric electrodeposition of nonmetallic components, phosphorus in particular.

Introduction. One of the most upcoming trends of modern galvanic processes development is replacement of coatings based on individual metal with multicomponent alloys including several metallic and/or nonmetallic components. In comparison with pure metals alloys have a wider range of physical and chemical properties. Besides, in case of cathodic coreduction, electrodeposition of components which are not liberated in the form of pure metals, for example, W or Mo [1], is possible. However, processes of controlled electrodeposition of alloys are much more difficult to perform than individual metal deposition. Experimental results of receiving and investigating multicomponent cathode layers do not always agree with theoretical regularities, which increases the significance of practical data of deposition effect on the properties of coatings of various composition.

The present paper deals with studying the processes of electrochemical preparation of multicomponent alloys based on metals of iron group and containing nonmetallic components. The two systems have been chosen for investigation:

- 1) four-component nickel- or cobalt-based alloys (Ni-Mo-P-S or Co-Mo-P-S);
- 2) three-component nickel- and- cobalt based alloys (Ni-Co-P).

The common feature of the alloys is the presence of insignificant amount of nonmetallic components in their composition. However, as far as codeposition of the metallic components is concerned the alloys under consideration differ significantly. Alloys of the first type contain molybdenum which does not deposit on the cathode separately, and at the same time differs greatly from the base metal (Ni or Co) in the values of standard electrode potential:



Alloys of the second type contain metallic components that are very close together in the metal galvanic series, which is the most favorable case for deterministic alloy deposition. From the technologi-

cal point of view the alloys concerned are united by the presence of organic ligand in the electrolyte, as well as lowered temperature of deposition in comparison with Watt's plating solution.

Potential fields of application of the alloys prepared differ. After deposition Ni-Mo-P-S or Co-Mo-P-S alloys were used as electrocatalysts for electrochemical preparation of hydrogen, and Ni-Co-P alloys were deposited onto copper substrates as micro wired coatings in the production of semiconductor electronic devices. However, in both cases the research was aimed at studying regularities of producing qualitative alloy coatings of the given composition at a lowered temperature from the electrolyte which does not contain a traditional additive agent (boric acid), its application having been restricted in Europe since 2004.

Main part. Electrodeposition of alloys was carried out under galvanostatic conditions, with cathode current density being 1–2 A/sq.dm and temperatures ranging from 20 to 30 °C, from complex electrolytes (pH 4 ~ 6) onto copper substrates. Nontoxic carboxylic acids (tribasic citric and bibasic malic) associated with the 4th class of hazard in the classification of detrimental substances were chosen as both complexing and buffering additives. Thus, alloys of the Ni-Mo-P-S or Co-Mo-P-S system were deposited from citrated electrolytes (Tab. 1), and those of the Ni-Co-P system - from the malate electrolytes (Tab. 2). The data obtained show that the electrolytes used are characterized by practically the same content of metal ions as well as concentration of the phosphorus-containing component (sodium hypophosphite). The substantial distinction between citrate and malate electrolytes in the concentration of organic ligand is caused by the need to maintain the electrolyte optimum pH value approaching 6 for molybdenum-containing alloys, and being 4-5 for nickel – cobalt coatings.

The tables show that the metal current efficiency was much lower for multicomponent alloys received from the citrate electrolyte (Fig. 1, alloys 1 ~ 4), than that from the malate electrolyte (Fig. 1, alloys 5, 6). Such a low value of the metal current efficiency in the citrate electrolyte is probably caused by several factors.

Table 1
Composition of citrate electrolytes for deposition of Ni- or Co- based coatings

Coating component	Electrolyte component	
	Nature	Concentration, m/l
Ni	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.2
Co	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.2
Mo	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.02
P	$\text{Na}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	0.02
S	$(\text{NH}_2)_2\text{CS}$	10^{-4}
-	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	0.28

Table 2
Composition of malate electrolytes for deposition of Ni or Co based coatings

Coating component	Electrolyte component	
	Nature	Concentration, m/l
Ni	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.18
Co	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.08
P	$\text{Na}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	0.02
-	$\text{C}_4\text{H}_6\text{O}_5$	0.05

First of all, using ligands of complex composition is characterized by the decrease in the metal current efficiency if compared with simple electrolytes [2]. Secondly, molybdenum which, on the one hand, is characterized by low electrochemical equivalent and, on the other hand, considerably reduces overpotential of a parallel hydrogen liberation process at the cathode, was codeposited into alloys of the system involved [3]. However, in complex malate electrolyte high metal current efficiency for nickel - cobalt alloys was recorded even at room temperature. It may be caused by favorable thermodynamic characteristics of the Ni-Co pair, but at the same time, it is probably due to good buffering properties of malic acid in the electrolyte for depositing iron group metals, despite lowered pH value of the malate electrolyte, as well as because of low stability of malate systems in comparison with citrate ones. In all cases codeposition of nonmetallic components into alloys resulted in the reduction of metal current efficiency (Fig. 1, alloys 2, 3, 5). The most substantial decrease in current efficiency has been recorded for the Co-Mo-P-S alloy (by 48% in comparison with that for the Co - Mo one), slightly less - for the Ni-Mo-P-S alloy (by 35% in comparison with Ni-Mo) and absolutely insignificant - for the Ni-Co-P alloy (by 9% in comparison with Ni-Co).

According to raster electronic microscopy (Fig. 2) the most extended surface with roundish poly-disperse grains is typical of the Co-Mo-P-S alloy. Nickel-based alloys have more flattened surface

irrespective of the nature of a complexing compound. However, the Ni-Co-P alloys were characterized by increased fracturing in comparison with the Ni-Mo-P-S alloys, while in individual nickel coatings generated from malate electrolytes fracturing was slightly observed.

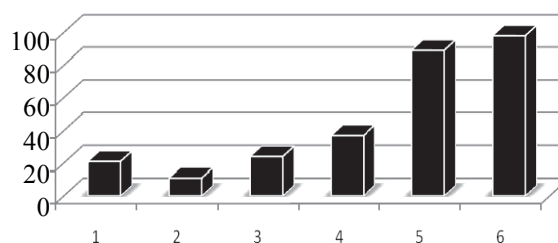
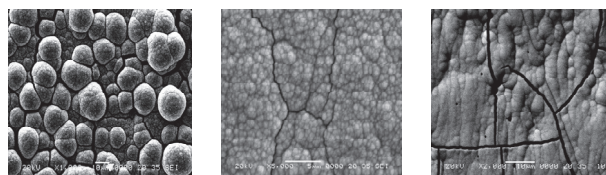


Fig. 1. Metal current efficiency for alloys: 1 - Co-Mo; 2 - Co-Mo-P-S; 3 - Ni-Mo; 4 - Ni-Mo-P-S; 5 - Ni-Co; 6 - Ni-Co-P



1 2 3

Fig. 2. Electron microscope image of alloy surfaces (coating thickness 2–3 μm):

1 – Co-Mo-P-S; 2 – Ni-Mo-P-S; 3 – Ni-Co-P

It should be noted that the increased current efficiency for the Ni-Co-P alloy, as well as the results of other researches [4] are indicative of a favorable effect of Co on the microstructure of nickel - cobalt alloys due to the decrease in hydrogen absorption of coating surface and reduction of internal stresses in its structure. The reason of the detected tendency to microfracturing of visually qualitative Ni-Co-P coatings can be associated with the decrease in cathode polarization while depositing nickel alloy due to cobalt which is characterized by lowered overpotential of crystallization.

The chemical composition of electrodeposited coatings was analyzed by means of X-ray energy dispersive microanalysis. The analysis results (Fig. 3) have shown that metal and nonmetal codeposition in the systems concerned differed. When depositing from citrate electrolytes the basic metal portion was 85% both for Co and for Ni. In malate electrolytes, when the nickel salt concentration was approximately the same, the basic metal portion of the alloy was only 75%, which was probably caused by more intensive codeposition of the second metal because cobalt and molybdenum significantly differ in cathodic polarization value. The very low content of molybdenum in the nickel alloy in comparison with the cobalt one comes under

notice. Such result is in good agreement with the adsorptive film hypothesis of codeposition of refractory metals into an alloy, according to which the refinement of cobalt alloys in comparison with those of nickel is explained by the increased adsorptive capacity of cobalt hydro-oxy-compounds [2]. In Ni-Mo-P-S alloy generated from citrate electrolyte the greatest content (14 at %) of a nonmetallic component (phosphorus) in coating has been observed. It could be due to the increased catalytic activity of nickel during chemical reduction of hypophosphite ion in the cathode zone, which could dominate when depositing an alloy in the conditions of complicated reduction of molybdate ions on deposited coating surface.

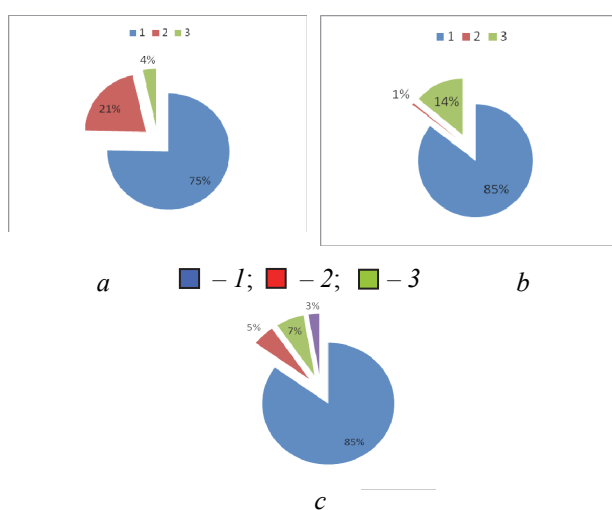


Fig. 3. Chemical composition of electrodeposited alloys Ni-Co-P (a), Ni-Mo-P-S (b), Co-Mo-P-S (c): 1 – basic metal (Ni for a and b; Co for c); 2 – codeposited metal (Co for a; Mo for b and c); 3 – codeposited nonmetal P; 4 – codeposited nonmetal S

In order to analyze the nature of codeposition of different components into alloy coating, values of ratio of incorporation were used, they being calculated as

$$K = \omega_c / \omega_{el}$$

where ω_c – proportion of i-component in an alloy, at. %; ω_{el} – proportion of the corresponding source of the component in electrolyte, mole %.

In analyzing values of ratios of incorporation of separate components in an alloy it is necessary to consider both values of balance electrode potentials of the corresponding processes and features of polarization phenomena in the electrolytes applied. From the practical point of view the typical value for controlled deposition of alloys is $K = 1$, which is the best for providing the given alloy composition. In the experiments performed the pulsing ratio close to 1 (Tab. 3), is recorded for

the basic metal in Co-Mo-P-S alloys (citrate electrolyte) and Ni-Co-P (malate electrolyte). In the researches concerned the theory of anomalous codeposition of nickel - cobalt alloys [5], according to which less precious metal, i.e. cobalt, is mainly deposited in the alloy has not been confirmed. The lowered ratio of incorporation of cobalt in Ni-Co-P alloy is probably caused by the influence of parallel codeposition of phosphorus for which the ratio of incorporation has exceeded the value of 1. Data on incorporation of a nonmetallic component, phosphorus being an example, are indicative of facilitated reduction of the hypophosphite ion in citrate electrolyte for which the relative amount of phosphorus in an alloy have exceeded many times its content in electrolyte irrespective of the nature of the basic metal.

Table 3
Ratios of incorporation of components in electrodeposited alloys

Nature of alloy	Ratio of incorporation			
	Ni	Co	Mo	P
Co-Mo-P-S	-	1.01	0.59	8.51
Ni-Mo-P-S	0.75	-	0.05	12.62
Ni-Co-P	0.97	0.83	-	1.13

Analyzing a set of data on the ratios of incorporation of components into alloys, using various electrolytes, it is necessary to take into account that, on the one hand, more precious metal (in our case, nickel) usually forms stronger complexes, and, on the other hand, citrate complexes are more stable than malate ones. In our experiments these features have been confirmed by the data obtained for the basic metal in citrate electrolytes (Tab. 4), and also by data for nickel in different electrolytes (marked cells of Tab. 4).

Table 4
Data on the nature of incorporation of components into an alloy, different ligands being used

Coating component	Nature of electrolyte	
	citrate	malate
Ni	<1	>1
Co	>1	<1
P	>1	<1

Conclusion. Investigation of electrodeposition of multicomponent alloys based on nickel and/or cobalt with the inclusion of nonmetallic components from electrolytes containing citric or malic acid as the complexing and buffering additive, has allowed to determine conditions of deposition of Co-Mo-P-S, Ni-Mo-P-S, Ni-Co-P coatings 2–3 microns thick at lowered current density and rather low temperature 20–30 °C.

It has been confirmed that the decrease in stability of depositing metals complexes formed

causes an increase in metal components current efficiency. The use of malate complex electrolytes makes it possible to avoid anomalous codeposition of nickel and cobalt in an alloy.

Electrodeposition of multicomponent nickel or cobalt alloys from citrate electrolytes is accompanied by over-stoichiometric codeposition of non-metallic components, phosphorus in particular.

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