

Impact of the electroplating regime on the chemical composition of Ni-Co-P based coatings in non-complexing acidic electrolyte

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Abstract: *The conditions appropriated for electrodeposition of Ni-Co-P based coatings on copper substrates were determined by acquisition and systematic analysis of potentiodynamic curves. The experiments were performed in acidic non-complex sulfate electrolyte (pH = 2), and by variation of the sodium hypophosphite concentration. As main result, it was established that the overall cathodic polarization rises with increase of the NaH_2PO_2 content, and the potentials corresponding to the deposition of the triple NiCoP alloy shift towards more positive values. The obtained coatings were subsequently submitted to Atomic Absorption Spectroscopy in order to analyze the dependence of the composition of the obtained coatings from the hypophosphite content, and the electrical regime applied. In this sense, a comparison is done between stationary and square wave impulse deposition regimes.*

Key words: Ni-Co-P system, coatings, electrochemical regime, square wave impulses

INTRODUCTION

The impressive strength and durability typical for the Ni-P coatings make them an interesting object of intensive worldwide investigations during the recent 5 decades, as an efficient alternative to the widely used Ni primer coatings [1-3]. A large variety of mechanisms are proposed for involvement of phosphorus in the nickel matrix during the electrochemical Ni-P film deposition at both stationary and impulse regimes [2]. Besides by electroplating, [2-6], spontaneous regimes for deposition of Co-Ni-P, Ni-P and/or Co-P coatings are also widely investigated [1], especially for the needs of the modern micro- and nanotechnology. Both kinds of electrolytes without complex forming agents [4], and complex based ones [2,3], based on metallic sulfamates are suitable for NiP and NiCoP film deposition. In accordance to the phosphorus content in the electrolyte, its concentration in the resulting coatings can achieve up to 20% [4].

The aim of the present brief research work is to investigate the NiCoP deposition kinetics in acidic sulfate electrolyte in accordance to the NaH_2PO_2 content, and to establish the most suitable electroplating regime

EXPERIMENTAL

All electrochemical experiments were carried out in three-electrode cell, at room temperature, without stirring. The cell with a total volume 150 dm^3 includes a working electrode from copper (Merck, 99.97 wt% Cu), a platinum counter electrode arranged concentrically around the working electrode, and as reference electrode - saturated calomel electrode in a special pan with Lugin's capillary (E versus SCE = 0.241V). Prior to each experiment the surfaces of the copper cathodes are fully cleaned from oxides by etching in the especially prepared solution for copper then the cathodes are rinsed several times with distilled water and then dried. All the deposition and electrochemical measurement procedures were performed by potentiostating device, type WENKING (Germany).

Three electrolyte compositions, described in Table 1 were investigated. Their pH was corrected towards pH = 2 by addition of suitable quantities of H_2SO_4 or NaOH.

Table 1. Composition of the investigated solutions

Component	Electrolyte (A-Ni-Co) [gmol dm^{-3}]	Electrolyte (B-NiCoP(0,8)) [gmol dm^{-3}]	Electrolyte (C-NiCoP(1,3)) [gmol dm^{-3}]
NiSO ₄ 6H ₂ O	0,5	0,5	0,5
NiCl ₂ 6H ₂ O	0,1	0,1	0,1
CoSO ₄ 7H ₂ O	0,3	0,3	0,3
NaH ₂ PO ₂ H ₂ O	-	0,8	1,3
Na ₂ CO ₃	0,2	0,2	0,2

The coating depositions were performed at potentiostatic regime at stationary regime (i.e. without agitation). The impulse coating electrodepositions were carried out using rectangular potentiostatic pulses generated by pulse generator, connected to the input of the potentiostat especially designed for the purpose. In turn, the potentiostat was connected to the three-electrode cell. The average values of potential \bar{E} and current \bar{I} were measured using digital voltmeter with high input resistance and ammeter, respectively, and the amplitude values of potential E_p were measured using oscilloscope.

The potentiodynamic curves were acquired by at potential sweep rate, equal to 30 mV s⁻¹. The compositions of the obtained coatings were analysed by Atomic Adsorption Spectroscopy in the Central Scientific Research Laboratory (CSRL), UCTM (Sofia).

RESULTS AND DISCUSSION

Definition of the coating deposition kinetics and the conditions – It was performed by systematical acquisition and subsequent analysis of the cathodic potentiodynamic curves, for Ni (i.e. NiP), Co (i.e. CoP) or mixtures of them, according to Table 1. The data acquired confirm the results published in previous our research works [7,8], that the individual electroplating of only Ni and NiP always proceeds by extended initial polarization, without of transition through a steady state. Thus, the corresponding curves do not have any plateau of limiting diffusion current (Figs. 1, and 2, curve 1). However, the Co (CoP), depositions at the same conditions of extended initial polarization proceed by appearance of a plateau, related to the occurrence of limiting diffusion current (Figs. 1, and 2, curve 2). In the electrolytes used, the molar ratio Ni/Co equals to 5, with strong predominance of nickel. Thus, the Ni predominance causes lower polarization and quicker deposition from the mixed solution, in comparison these of the cobalt solution, at the same cathodic potential. However, the data obtained for the composition of the coating obtained from Ni/Co mixed electrolyte (Table 2), the cobalt is the predominant element. This contradiction between the Ni/Co electrolyte composition and the content of the resulting Ni/Co coating is an evidence for anomalous type of deposition. It happens when preferable deposition of less noble metal is observed, as it is established for the cobalt [7]. Indeed, in all the investigated solutions, the curves of the coincident Ni/Co deposition from phosphorous containing electrolytes possess typical plateau, which can be ascribed to presence of limiting diffusion current, corresponding to this of individual cobalt deposition (Figs. 1, 2 curve 3).

Figure 3 illustrates the influence of sodium hypophosphite NaH₂PO₂ in the electrolyte composition on the cathodic polarization curves of NiCo (NiCoP) deposition. As may be seen from the data obtained, the increase of the NaH₂PO₂ content in the solution suppresses the overall polarization and increases of the limiting diffusion current plateau. Nevertheless, the plateau of the limiting diffusion current remains almost the same, irrespectively the increase NaH₂PO₂ concentration from 0,8M to 1,3M (compositions B and C (curves 2 and 3 in Fig. 3). Thus, further and more detailed investigations are necessary for establishment of the phosphorous penetration in the NiCo, in order to obtain more detailed explications on the shape of the obtained curves.

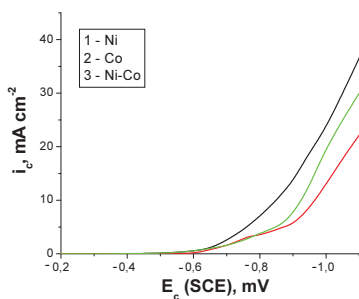


Fig. 1. Kinetic curves recorded during the deposition of Ni - 1, Co - 2 and NiCo - 3 from solution A.

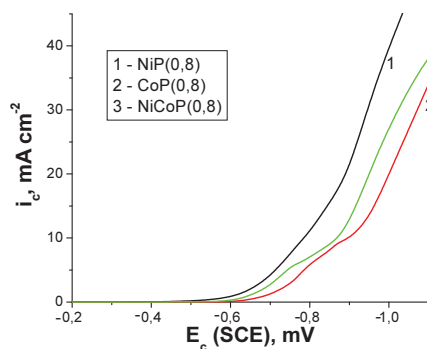


Fig. 2. Kinetic curves recorded during the deposition of NiP(0,8) - 1, CoP(0,8) - 2 and NiCoP(0,8) - 3 from solution B.

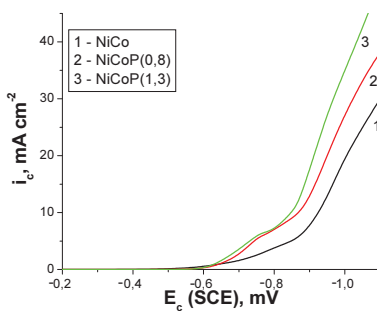


Fig. 3. Kinetic curves recorded during the deposition of: NiCo – 1, NiCoP(0,8) – 2 and NiCoP(1,3) – 3 from the respective solutions

From the kinetic data acquired, together with the visual observations on the coatings electroplated at different electrical potentials follows that the real electroplating of NiCoP films from solutions B and C becomes exactly at the respective limit diffusion current plateaus, in the range between -0.740V to -0.990 V versus Saturated Callomel

Electrode (SCE). Taking in account the correspondence of the polarization average values ($\Delta \bar{E}$) and its amplitude values (ΔE_p): $\Delta \bar{E} = \theta \cdot \Delta E_p$, where $\theta = \frac{\tau_p}{\tau_p + \tau_z}$ is pulse filling, τ_p is

the pulse time, and τ_z is interval between the pulses, the optimal electrodeposition conditions in impulse regime were determined for three different frequencies and filling rate $\theta = 0.5$.

Coating chemical composition definition – Table 2 resumes the data (in weight percentages) for the contents of each element in the coatings deposited at various regimes (i.e. stationary and impulse ones), with application of different impulse frequencies, and potentials.

Table 2. Exact chemical compositions of NiCo (NiCoP) based coatings in accordance to the applied electroplating conditions

Electrolyte	Current mode	Conditions*	Ni, wt%	Co, wt%	P, wt%
A	ppm	f=100 Hz	23.40	76.60	-
A	ppm	f=250 Hz	12.60	87.40	-
A	ppm	f=500 Hz	11.90	88.10	-
A	cpm	E = -0.80V	12.50	87.50	-
B	ppm	f=100 Hz	19.67	76.68	3.32
B	ppm	f=250 Hz	15.28	82.27	2.23
B	ppm	f=500 Hz	13.00	85.90	1.10
B	cpm	E = -0.80V	12.00	85.80	2.20
C	ppm	f=100 Hz	24.00	71.40	4.60
C	ppm	f=250 Hz	22.50	72.07	5.43
C	ppm	f=500 Hz	11.30	84.80	3.90
C	cpm	E ₁ = -0.80V	11.80	87.07	1.13
C	cpm	E ₂ = -0.98 V	13.00	81.30	5.70

cpm – constant potential mode; ppm – pulse potential mode

*The applied average potential values at impulse regime always correspond to average current density, equal to 9 mA per square centimeter.

As can be seen from the obtained data the phosphorus is included in the resulting coatings only at frequencies lower than 500 Hz, and its content is between 2 and 6 %_{wt}. Probably, the phosphorus inclusion is a result of purely chemical adsorption processes, during the pauses among the impulses. At potentiostatic electroplating regimes performed by applying of potentials between -0.8 V and -0.98 V, the phosphorus content increases almost 5 times, and for instance, it rises from 1.13 to 5.7 wt % for electrolyte "C".

CONCLUSIONS

The kinetics of NiCoP combined coating electroplating from acidic sulfate electrolyte with different NaH₂PO₂ additions is investigated. As a result, it was established that the real deposition process proceeds in the potential range between -0.740V and -0.990 V (SCE).

The phosphorous content in the obtained NiCoP coatings can be increased up to about 6 wt%, by increase of the applied electrical potential, at impulse electroplating regime with frequencies below 500 Hz.

The anomalous deposition of Cobalt will be an object of further investigations.

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This paper has been reviewed