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INFLUENCE OF NaH_2PO_2 CONTENT ON THE COMPOSITIONAL AND MORPHOLOGICAL CHARACTERISTICS OF NiCoP COATINGS DEPOSITED AT ROOM TEMPERATURE AND POTENTIOSTATIC CONDITIONS

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Abstract: *The object of the presented paper is to determine the optimal conditions for NiCoP alloys deposition, and to evaluate the influence of NaH_2PO_2 on the resulting NiCoP coatings, their chemical composition and morphology. Besides, the deposition cathodic current efficiency was determined, at potentiostatic regime, as well. It is demonstrated that the higher content of NaH_2PO_2 in the deposition electrolyte results in phosphorous content from 3.2% to 7.0%, and the apparent cathodic current efficiency is superior to 100%. It passes through a maximum at 0,35M NaH_2PO_2, and the resulting coatings possess fine grain structure with grain size below 100 nm.*

Key words: *NiCoP alloy coatings, potentiostatic mode, electrodeposition, morphology*

INTRODUCTION

Nickel-phosphorus (Ni-P) alloys have been extensively used as protective coatings because of their high hardness degree, wear resistance, low friction coefficient and catalytic activity [1-4]. During the recent years, an increasing interest appeared on CoP alloys electrodeposition due to their excellent properties as soft magnetic materials [6-7], as well. According to recent reports, NiP, CoP and NiCoP coatings serve very well as reliable diffusion barriers for copper interconnects [8]. Deposited on and SiO_2 substrates, these alloy coatings can be successfully applied in electronics for integral sensors and inductors [5, 9, 10], whereas deposited on Al and its alloys these films can be used in memory disks and solar cells [11, 12].

The NiCoP coatings deposition [9] is relatively new field in the electroplating technology branch. Sulphate-chloride, chloride [11] and sulfamate electrolytes [12] are proposed for NiCoP coating deposition. The electrolysis is being usually performed at low pH values (2 to 4) and high temperatures. Djukic [8] reported for the possibility for CoP deposition at room temperature and Suzuki [2] show that it is possible also for NiP, which opens new possibilities for deposition and application of these coatings.

The object of the presented paper is to determine the optimal conditions for NiCoP alloy deposition and to investigate the influence of sodium hypochlorite occurrence on the chemical composition and the morphological characteristics of NiCoP coatings obtained at potentiostatic regime.

EXPERIMENTAL

All electrochemical experiments were conducted in three-electrode thermostated cell without stirring. The cell, with total volume 150 dm^3, contains as working electrode disk-shaped copper electrode (Merck, 99.97 wt% Cu) with 1 cm^2 of surface area; Pt counter electrode, concentrically located around the working electrode and saturated calomel electrode (SCE) as reference electrode, placed in a separate cell with Luggin-capillary. Before each experiment the cathodic surface was degreased in alkaline solution of sodium bicarbonate, etched in solution and washed with distilled water. The electrolyte composition used is: 0.2M $NiSO_4.6H_2O$; 0,1M $CoSO_4$ $7H_2O$; 0.125M H_3PO_4; 0.189M ÷ 0.5M $NaH_2PO_2.H_2O$; 0,1M KCl, pH = 2. pH of the solutions was 2 and it was corrected by H_2SO_4 or NaOH addition.

The deposition kinetics was studied through recording of cyclic voltammograms with scan rate of 30 $mV.s^{-1}$ at room temperature (~20 ^oC), using Wenking Electrochemical Analysis System (Germany).

The content of phosphorus in the coatings (in mass %) was determined with a photocolorimetric method in length of 880 nm. Nickel and cobalt were determined by atomic emission spectral analysis (in mass %) with ICP-OES (High Dispersion ICP) using "Prodigy" equipment (Teledyne Leeman Labs). Based on the data for the chemical content, the corresponding values for the cathodic current efficiency (CCE) of electrodeposition of NiCo alloy were calculated following the law of Faraday: $CCE = \frac{\Delta m_{pr}}{\Delta m_{th}}.100,\%$, where: Δm_{pr} is the practically mass of the Ni-Co coating, (g); $\Delta m_{th} = q_{Ni\text{-}Co\text{-}P} I.t$ is the theoretically determined mass of NiCoP alloy, (g). The obtained alloy layers morphology was observed by Scanning Electron Mictroscopy, performed by JSM-6390- Jeol of „Oxford Instruments" (U.K.).

RESULTS AND DISCUSSION

- Deposition Kinetics – The comparison of the cyclic voltammograms recorded during deposition of NiP, CoP and NiCoP coatings in electrolyte with 0.2 M NaH_2PO_2 addition is shown in Fig.1.

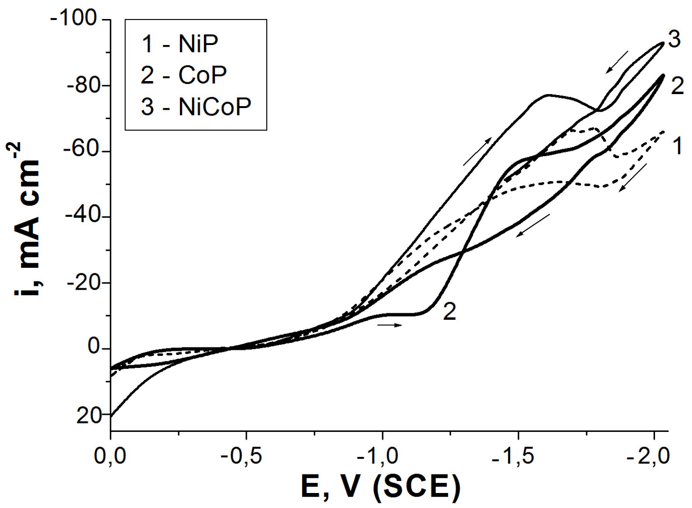

Fig. 1 Cyclic voltamograms:
(1) in electrolyte for NiP: 0.2M $NiSO_4.6H_2O$; 0.125M H_3PO_4; 0.189M $NaH_2PO_2.H_2O$; 0,1M KCl, pH = 2; (2) in electrolyte for CoP: 0.1M $CoSO_4.7H_2O$; 0.125M H_3PO_4; 0.189M $NaH_2PO_2.H_2O$; 0,1M KCl, pH = 2; (3) in electrolyte for NiCoP: 0.2M $NiSO_4.6H_2O$; 0.1M $CoSO_4.7H_2O$; 0.125M H_3PO_4; 0.189M $NaH_2PO_2.H_2O$; 0,1M KCl, pH = 2.

This comparison shows that the deposition of NiCoP alloy (Fig.1, cv.3) proceeds with a lower polarization compared to that of NiP alloy deposition (Fig.1, cv.1) and CoP alloys (Fig.1, cv.2). Characteristic maximum at higher cathodic potentials exists for each one of the cases mentioned above. In order to obtain uniform NiCoP alloy coatings at potentiostatic mode, the deposition potentials should match to the area of the curves before the cathodic peaks. So, the NiCoP alloy electrodeposition requires potential range from -1.10 to -1.35 V (SCE).

- Dependence of the NaH_2PO_2 content on the cathodic current efficiency and the obtained NiCoP-coatings growth rate and composition

The impact of the electrolyte content on the deposition resulting current density and the resulting coating growth rate are shown in Fig. 2.

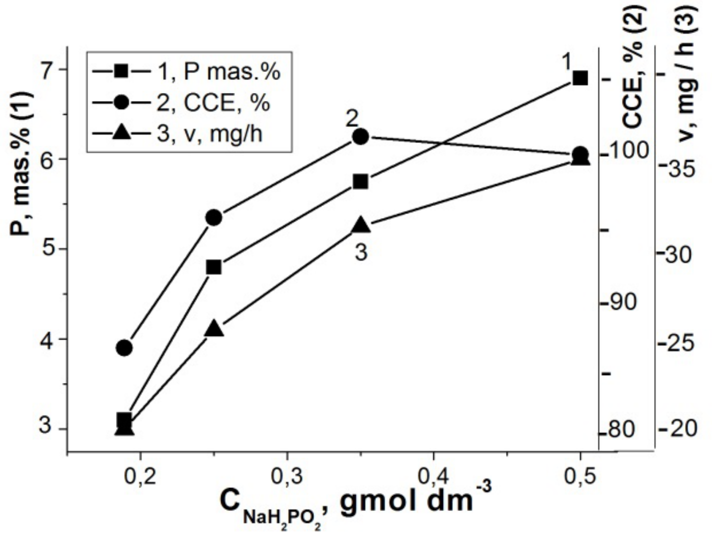

Fig.2. Dependence of the NaH_2PO_2 content on the content of phosphorous in NiCoP coatings (in mas.%)-(1); cathodic current efficiency (CCE) for their deposition-(2) and the growth rate (in mg/h)-(3) of the electrodeposited NiCoP-coatings.

As can be seen from Fig. 2, the NaH_2PO_2 concentration increment promotes the phosphorous content in the resulting alloy coating content from 3.2% to 7.0 % (curve 1) and the cathodic current efficiency passes through a maximum, situated at 0.35 M of NaH_2PO_2, reaching almost 100% at higher Na-salt content values, beyond the maximum. The increasing of the NaH_2PO_2 under constant other conditions (cathodic potential, a composition of the other components of the solution) leads to faster growth of the coatings (curve 3). The latter fact and that the values of the cathodic current efficiency exceeds 100% at high NaH_2PO_2 contents, allows to make the assumption that besides via purely electrochemical, NiCoP alloy is deposited also through a chemical mechanism - by reduction of Ni^{2+} from NaH_2PO_2 . This could affect the morphology and the other physical and mechanical properties of the alloy.

- Morphology

The SEM images shown in Fig. 3 reveal obvious difference of the average NiCoP grain size in accordance to the NaH_2PO_2 content.

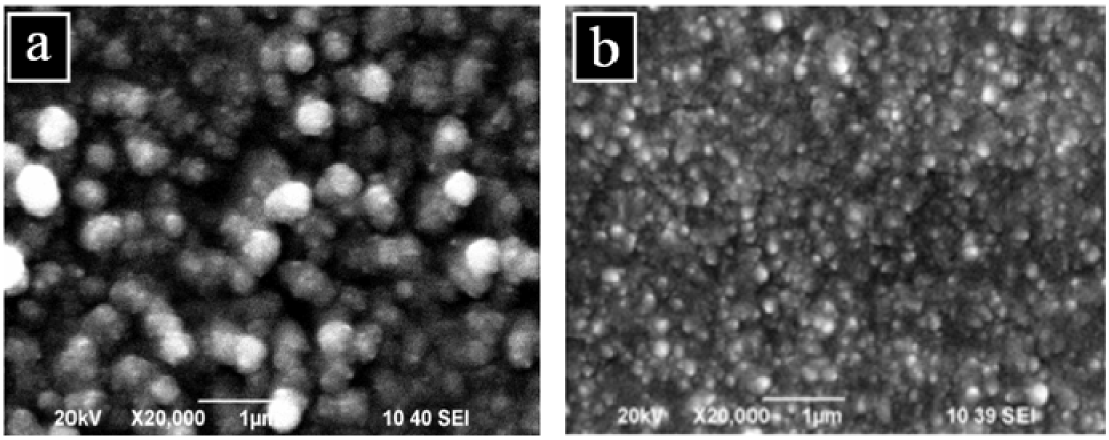

Fig.3. SEM images of NiCoP alloy films, deposited in potentiostatic conditions at presence of: 0.5M NaH_2PO_2 (a) and 0.189M NaH_2PO_2 (b) at applied potential E= -1.2 V (SCE).

For 6 minutes of electrodeposition duration, the film thickness reaches 3 μm and its structure is represented by oval grains with 400-500 nm of average size, when electrolyte with low NaH_2PO_2 content is used (Fig. 3a). The decrease of the content of sodium hypophosphite from 0.5 M to a concentration of 0,189M lead to fine crystal and nano-sized structure of the NiCoP alloys with grain size lower than 100 nm (Fig. 3b).

CONCLUSIONS

The results obtained during the present brief research work lead to the following inferences:

- The electrodeposition of reliable uniform NiCoP alloy films proceeds in potential range from -1.10 to -1.35 V (SCE).

- The increase of NaH_2PO_2 concentration promotes the phosphorous content in the resulting alloy coating content from 3.2 % to 7.0 %.

- The cathodic current efficiency passes through a maximum, situated at 0.35 M of NaH_2PO_2, reaching almost 100%. That fact allows to make the assumption that besides via purely electrochemical, NiCoP alloy is deposited also through a chemical mechanism - by reduction of Ni^{2+} from NaH_2PO_2.

- The decrease of the content of sodium hypophosphite from 0.5 M to a concentration of 0,189M lead to fine crystal and nano-sized structure of the NiCoP alloys with grain size lower than 100 nm

These conclusions can serve as a basis for further investigations regarding the electrochemical co-deposition of alloyed metal phosphate thin films and layers.

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