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Electrodeposition and structure of Ni-Co-P alloy coatings in stationary and pulse potentiostatic mode

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The rate of growth, composition, morphology and microstructure of Ni-Co-P coatings, deposited at Constant Potential Mode (CPM) and at Pulse Potential Mode (PPM) were investigated depending on the content of NaH_2PO_2 in the electrolyte, temperature, cathodic polarization and the pulse frequencies.
It was established, that with the rising of NaH_2PO_2 content (from 0.189 M up to 0.5 M), the rate of growth and the phosphorous content in the Ni-Co-P coatings in both modes of deposition increase. Maximum phosphorous content in the coatings are received in pulse mode at pulse frequencies 100 Hz at a temperature of the electrolyte 20°C (9.7 mass.% P) and at 80ºC (14.8 mass. % P) at cathodic polarization ΔE = -1.15 V. With the raising of pulse frequencies the rate of growth of the coating and the phosphorous content decrease. The pulse potential mode (PPM) of deposition results in weaker manifestation of the phenomenon "anomalous" deposition of cobalt in the alloy and this being explained by stabilizing the pH of the solution in the pulse mode. The different conditions of electrocrystallization in the both mode of deposition reflect in formation of different type structures. Ni-Co-P coatings, deposited at stationary mode are monophasic and polycrystalline. The identified phase of the type NiCoP has a hexagonal symmetry. The coatings, deposited at pulse mode (PPM) are typical amorphous.

Key words: Ni-Co-P coatings,electrodeposition, pulse mode,alloy coatings, morphology, phase structure

INTRODUCTION

The ternary Ni-Co-P alloy coatings combine by unique way the high wear- resistance, corrosion resistivity and hardness of Ni-P alloys with the magnetic and lubricant properties of Co-reach Ni-Co coatings [1]. That is why they are used as anticorrosion coating (as alternative of the hard chromium coatings) [1-3] and as layers in magnetic recorders [4, 5].

The deposition of Ni-P and Ni-Co-P coatings can be carried out by two methods: electroless deposition [6] and electrodeposition [3, 7-12] using sulphate electrolytes [10], modified Watts electrolytes [11, 12], chloride [7] and sulphamate solutions [8].

It was established, that Co-P [12] and Ni-P [13] alloys are possible to be deposited at room temperature, which is an important contribution to the searching of the ways for the raising of the efficiency of the electrodeposition method.

Recently, a bigger attention is payd to the pulse methods of electrodeposition, and the most common being square-wave pulsed direct current and pulsed reverse current [14-19]. The possibility to receive fine-crystal and nano-structured coatings by pulse mode of deposition can be explain by creating of conditions of electrocrystallization in thinner diffusion layer [14-17]. According to [18], applying the pulse mode give Ni-P coatings with higher phosphorous content and higher cathodic current efficiency. This effect of the pulse electrodeposition is strongly manifested at lower pulse filling (θ = 0.1), which is explained by the mechanism of deposition of Ni-P coating. The mechanism of deposition can be direct [11, 12] or indirect [22], and the possible reactionsare given in Table 1. In the case of deposition of Ni-Co-P coatingto the reactions for Ni-P have to be added two other possible reactions: (5) and (10) [1, 21].

Independent of the mechanism of deposition, the presence of the high concentrations of H^+ and the formation of conditions for adsorbtion of atomic hydrogen on the surface of the rising coating (which is observed at bigger pauses) are the necessity condition for phosphorous incorporation [1,3,18]. pH of the solution is an important factor not only for the mechanism of Ni-P deposition [18], but also for the appearance of the phenomenon of "anomalous" deposition of cobalt in Ni-Co [15-17] and in Ni-Co-P alloys [1, 3].

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Table 1. Possible reactions during the deposition of Ni-P and Ni-Co-P coatings by direct and indirect mechanism

Direct mechanism	Indirect mechanism
(1) $Ni^{2+} + 2e^- \rightarrow Ni$	(6) $6H^+ + 6e^- \rightarrow 6H_{ads}$
(2) $H^+ + e^- \rightarrow H_{ads}$ and $H_{ads} + H_{ads} \rightarrow H_2$	(7) $H_3PO_3 + 6H_{ads} \rightarrow PH_3 + 3H_2O$
(3) $H_3PO_3 + 3H^+ + 3e^- \rightarrow P(wh) + 3H_2O$	(8) $2PH_3 + 3Ni^{2+} \rightarrow 3Ni + 3P + 6H^+$
(4) $H_2PO_2^- + 2H^+ + e^- \rightarrow P(red) + 2H_2O$	(9) $H_2PO_2^- + 5H^+ + 4e^- \rightarrow PH_3(g) + 2H_2O$
(5) $Co^{2+} + 2e^- \rightarrow Co$	(10) $2PH_3 + 3Co^{2+} \rightarrow 3Co + 3P + 6H^+$

In the case of electroless deposition of Ni-P, the most commonly used phosphorus-producing agent is $NaH_2PO_2$and the main reaction in this case is as follows [6]:

$$Me^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Me + 2H_2PO_3^- + 2H^+ + H_2 \quad (11)$$

There is not a common opinion in the literature about what phosphorous – producing agent to be used in electrolytes for electrodeposition of Ni-P [11], Co-P [5] or Ni-Co-P coatings [1, 6]. According to most of the authors, most frequently this is only sodium hypophosphite [1]. Its influence on the phosphorous content and on the structure of Ni-Co-P alloy coating in the presence of the two phosphorous oxyacids (H_3PO_4, H_3PO_3) is not sufficiently discussed in the literature. Data about the use of pulse potentiostatic mode for deposition of Ni-Co-P alloy coating was not found.

The aim of the presented paper was to investigate the influence of the sodium hypophosphite during the stationary and pulse potentiostatic mode of deposition, as well as the effect of the pulse frequency and electrolyte temperature on the rate of growth, composition, morphology and microstructure of Ni-Co-P coatings.

EXPERIMENTAL

The electrolyte for Ni-Co-P alloy deposition was with composition: 0.2M $NiSO_4.6H_2O$; 0.1M $CoSO_4.7H_2O$; 0.1M KCl; 0.125M H_3PO_4; 0.2M H_3PO_3; 0.32 M H_3BO_3 and NaH_2PO_2 (0.189 M ÷ 0.5 M) with pH = 2. The pH correction was done using diluted solutions of NaOH and H_2SO_4. The potentiodynamic voltammograms (sweep rate 30 mV s^{-1}) and coating deposition at constant potentiostatic mode (CPM) were realized using Potentioscan type Wenking (Germany).

Tree-electrode thermostated electrochemical cell was used with total volume 150 dm^3. The working electrode for the voltammograms was cylindrical, disk-shaped with surface area 1 cm^2, made from copper foil (Merck, 99.97%).The counter electrode was Pt foil with surface, ten times bigger than this one of the working electrode(=>10 cm^2). The reference electrode was commercial saturated calomel electrode (SCE). The alloy coatings were deposited on copper foil (Merck, 99.97%) with work area 4 cm^2 (2x2 cm). Before the deposition, the work electrode was etched, rinsed with distilled water and drying [19]. The mass of the coating was calculated by the difference of the cathodic masse before and after the deposition, using analytical balance (accuracy 0.0001g). By calculation, the masse of the coating, deposited on the unity of surface during the unity of time (i.e. the rate of growth), G [$mgcm^{-2}$ h^{-1}], was determined.

The realization of the pulse potentiostatic mode (PPM) with rectangular form of pulses of the potential is described in details in [20]. The frequency of pulses are changed from 100 up to 500 Hz at constant pulse filling $\theta = 0{,}5$. The theoretical relation between the average and amplitude value of the polarization ΔE_m (calculated as difference between the potential at a given current and the equilibrium potential), and the amplitude value (ΔE_p) of the polarization is $\Delta E_m = \theta.\Delta E_p$. The coatings are deposited with the aim of comparison at the same value of the cathodic polarization in both modes of deposition (ΔE for CPM and ΔE_m for PPM).

The morphology and the elemental composition of the coatings were investigated through SEM and Energy Dispersive Spectral Analysis (EDSA) methods using equipment of Oxford Instruments, JSM-6390- Jeol. The phases, presented in the deposited coatings, were identified by XRD analysis using vertical automatic diffractometer Philips PW 1050 with secondary graphitemonochromator, operating with CuKα radiation and scintillation counter. The diffraction curves were recorded in angular interval from 10 to 100 degrees, 2θ with step 0.04 degrees and exposure 1 sec.

RESULTS AND DISCUSSIONS

At Fig. 1 are compared the cathodic voltammograms in electrolytes for deposition of Ni-Co-P alloys without (curve 1) and with 0.5M NaH_2PO_2(curve 2) at room temperature (20^0C) at constant composition of the rest of solution.

As can be seen, in the presence only of the phosphorous – containing acids (cv.1),

the current reach to very high values at high cathodic polarizations and at the potential of E = -1.75V (SCE) passes through maximum.

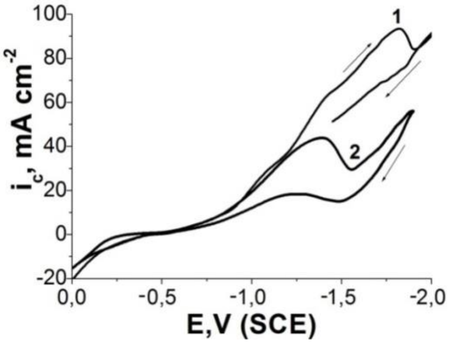

Fig. 1 Cathodic voltammograms in electrolytes for deposition of Ni-Co-P coating without NaH_2PO_2 (curve 1) and with 0.5M NaH_2PO_2 (curve 2) in the bath at 20^0C.

Supplementing to the bath of 0.5M NaH_2PO_2 (curve 2) results in strong decrease of the current and to displacement of the potential, corresponding to the maximum, in a more positive direction.

The two opposite effects, observed in the presence of NaH_2PO_2 – its depolarization effect and the lowering of the rate of the process of deposition, could be explained using the chemical mechanism of deposition. According to this mechanism, NaH_2PO_2 is a reducing agent regarding to nickel and cobalt ions and its presence at high concentrations can result in reduction of these ions not only by the electrochemical but also by chemical mechanism [6, 19] according to the reaction (11).

Data about the rate of grow of the mass G (Fig. 2a) and the phosphorous content in the coating (Fig. 2b) depending on NaH_2PO_2 content in the solution at stationary (curve 1) and pulse (curves 2-4) mode of deposition at pulse frequencies 100 up to 500 Hz is presented at Fig. 2.

The coatings of Ni-Co-P are deposited at room temperature at the same cathodic polarization in CPM and PPM at -1.15V (ΔE and ΔE_m resp.).

Data, presented in Fig. 2 show, that when stationary mode is applied, with the rise of NaH_2PO_2 content up to 0.4 M the coating mass rise with bigger rate, almost linearly. At bigger concentration the rate decrease (Fig. 2a, cv. 1). Applying the pulse mode, the mass of the coating rise slowly with the increasing of NaH_2PO_2 concentration (Fig. 2a, cvs 2-4) compared to the stationary mode (Fig. 2a, cv. 1) especially at frequencies, higher than 500 Hz (Fig. 2a, cv. 4). At a given average value of the polarization, according to the relation $\Delta E_m = \theta.\Delta E_p$, during the pulse time, almost twice bigger values of the amplitude values of the polarization (respectively of the current density) are achieved. It can be assumed, that at this conditions, the part of the current, used for hydrogen evolution is bigger, compared to the stationary conditions [18]. At pulse frequencies, higher than 250 Hz, the time for nuclei creation and growth, as well as for the recovery of the concentration gradient of the deposited ions, is smaller than this one at lower frequencies, which results in lowering of the rate of coating deposition (Fig. 2a, cv. 4).

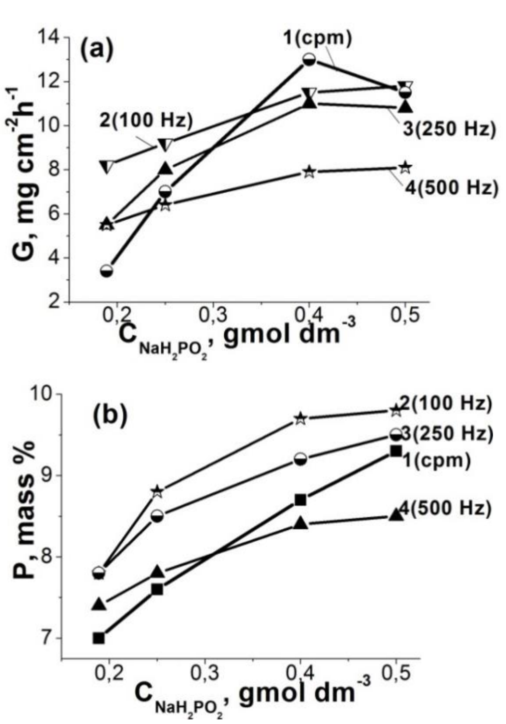

Fig. 2. Effect of NaH_2PO_2 concentration in the solution on the rate of growth G of the coating (a) and the content of P, mass.% (b) of the Ni-Co-P alloys in CPM (curve 1) and in PPM (curves 2-4); ΔE, resp. ΔE_m = - 1.15V (SCE)): (2) 100 Hz; (3) 250 Hz and (4) 500 Hz, $\theta = 0.5$.

At stationary mode, with the growing of NaH_2PO_2 content, the phosphorous content in Ni-Co-P coatings also grow (Fig. 2b, cv. 1), but it stay lower compared to this one at pulse mode at pulse frequencies from 100 up to 250 Hz (Fig. 2b, cvs 2,3). The maximum phosphorous content (up to about 9.7%) is achieved at pulse frequency 100 Hz and maximum NaH_2PO_2 content in the solution 0.5M. With the raising of pulse frequencies (Fig. 2b, cv. 4), the phosphorous content in the alloys going down under this one in stationary mode. The fact, that at lower pulse frequencies (100 and 250 Hz) the phosphorous content in the alloy is higher, can be explained with the time of pauses between the pulses, which in these conditions is higher. This give a possibility for adsorbtion of hydrogen ad-atoms on the cathodic surface, which facilitate the reactions (7) and (8) and (10) from Table 1, all chemical by nature, and resulting in producing of P, Ni and Co, combined in the ternary Ni-Co-P alloy.

Table 2 presents data from EDSA analysis about the composition of the coatings. It can be seen, that at all studied concentrations of NaH_2PO_2, the phenomenon of "anomalous" high cobalt concentration in the coatings (compared to this one in the solution in respect to the nickel concentration) is observed.The cobalt content, compared to this of the nickel, decrease notably at pulse mode (for example by 0.189 M NaH_2PO_2 from 70,6% at CPM to 66.3% in PPM).

Table 2 Chemical composition of Ni-Co-P coatings (in mass %), deposited in stationary mode (CPM) and in pulse mode at 250 Hz (PPM)depending on the NaH_2PO_2 content in the solution;Cathodic polarization ΔE, resp. ΔE_m= -1.15V (20º C)

Content, mass % →	**% P**	**% Ni**	**% Co**	**% P**	**% Ni**	**% Co**
$C_{NaH_2PO_2}$, M ↓	**CPM**	**CPM**	**CPM**	***PPM***	***PPM***	***PPM***
0.189	7.0	22.4	70.6	7.8	25.9	66.3
0.250	7.6	25.9	66.5	8.8	28.1	63.1
0.400	8.7	27.8	63.5	9.7	31.5	58.8
0.500	9.3	29.3	61.4	9.8	33.1	57.1

In pulse mode a supplementary rise of the phosphorous content (up to 14.8 % at 100 Hz) in the coatings and decreasing of the manifestation of the "anomalous" deposition is observed at rising the electrolyte temperature up to 80ºC at lower pulse frequencies (Table 3). The explanation can be related to the change in pH of the solution close to the electrode and its raising as a result of hydrogen evolution simultaneously with the main reactions (Table 1). According to many authors, the hydrogen evolution from Watts and sulphamate electrolytes begins at potentials, close to the potentials of deposition of nickel and cobalt [15, 16, 18].

With increase of the pH of the solution in the cathodic range, the appearance of hydroxide complex ions of the metals is observed. The constant of stability of $Co(OH)^+$ are lower than this of $Ni(OH)^+$ which means, that at conditions where the first ones are formed and adsorbed easier, a preferential deposition of Co in Ni-Co alloys is observed [15, 16]. As it is shown in [18] during the pulse mode of deposition the pH of the solution is stabilized, i.e. the low values of pH are supported, as a consequence of restoring of the concentration gradient, created during the pulses at hydrogen evolution. That is why at lower and middle pulse frequencies the possibility for formation of metal-hydroxide complex ions decreases and as a result the effect of "anomalous" Co deposition decrease.

Table 3. Composition of Ni-Co-P alloys depending on the parameters of the applied mode (ΔE for CPM and frenquency, ffor PPM, ΔE_m = -1.15 V) at 80ºC and 0.189 M NaH_2PO_2

CPM ΔE, V	**% P**	**% Ni**	**% Co**	**PPM** f, Hz	**% P**	**% Ni**	**% Co**
- 0.95	10.3	33.6	56.1	100	14.8	36.7	48.5
-1.15	9.5	31.1	59.4	250	13.7	34.2	52.1
-1.25	8.7	29.3	62.0	500	12.3	34.4	53.3

Morphology

At the Fig. 3, the SEM images are shown of the surfaces of the Ni-Co-P alloys, deposited at room temperature at stationary (Fig. 3 a,b) and pulse (Fig. 3 c,d) potentiostatic mode (ΔE и ΔE_m = -1.15V) and different content of NaH_2PO_2 in the solution: 0.189 M NaH_2PO_2 (a, c); 0.5 M NaH_2PO_2 (b, d). The SEM images show, that the mode of deposition has a strong effect on the character of the formed crystals.

The deposited at stationary mode coatings have a columnar structure. At lower concentration of NaH_2PO_2 the coatings are nano-dimensioned (Fig. 3a), and at higher concentration of NaH_2PO_2 simultaneously with the predominate nano-dimensional crystals, crystals with dimensions about and over 500 nm are formed (Fig. 3b).

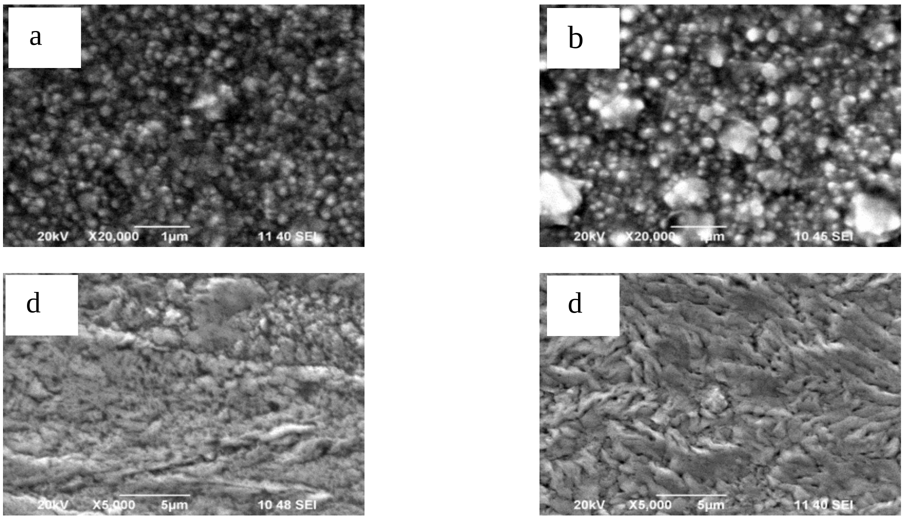

Fig.3. SEM images of Ni-Co-P alloys, deposited in CPM (a, b) and in PPM (c, d) (ΔE, resp. ΔE_m = -1.15V) at different content of NaH_2PO_2 in the solution: 0.189 M NaH_2PO_2 (a, c); 0.5 M NaH_2PO_2 (b, d)

At pulse mode of deposition, the dimensions and the form of the crystals are changed (Fig. 3c,d), which prove, that during this mode the conditions of electrocrystallization are changed. The coatings have prolonged crystals, arranged in networked structure, peculiar to the higher concentration of NaH_2PO_2 (Fig. 3d). In the both modes of deposition, the coating at lower content of NaH_2PO_2 have more fine-crystal structure (Fig. 3a,c).

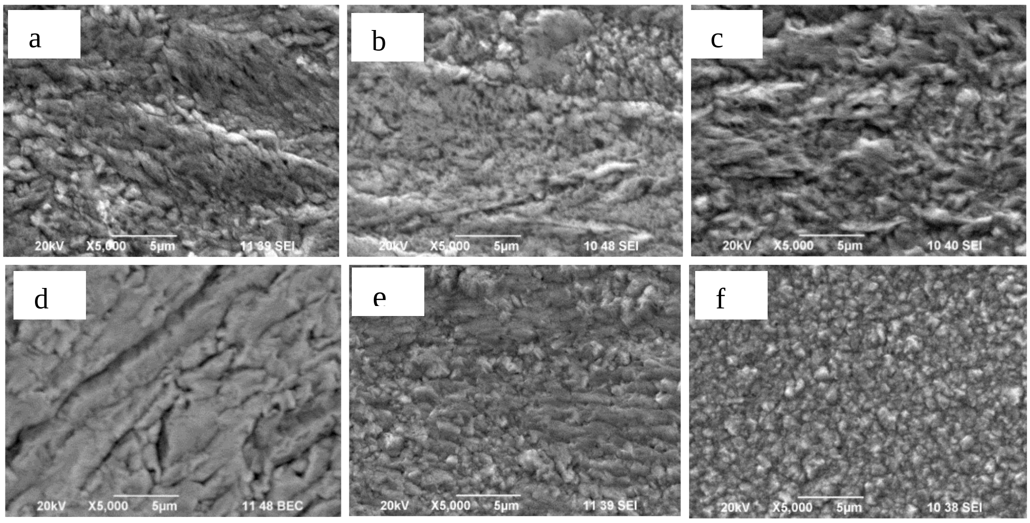

Fig. 4. SEM images of Ni-Co-P alloys, deposited in pulse mode at pulse frequencies 100 Hz (a, d); 250 Hz (b, e); 500 Hz (c, f) at 20ºC (a-c) and 80ºC (d-e); 0,189 M NaH_2PO_2 (ΔE, resp. ΔE_m = -1.15V).

Fig.4 shows the influence of the pulse frequencies and the temperature on the morphology of the Ni-Co-P alloys in pulse mode. The increase of the pulse frequency at room temperature does not change importantly the morphology of the coatings (Fig.4 a-c). The coatings are build up from crystals with filiform structure. In the coatings, deposited in pulse mode, at a temperature of the electrolyte 80ºC, the morphology of the Ni-Co-P coatings is changed (Fig.4, d-f). At low pulse frequency (100 Hz) a layered structure is seen with a maximum smoothing compared to other coatings (Fig. 4d). With the rising of pulse frequencies up to 500 Hz, the structure of the coatings begins to look like this one in stationary conditions (for comparison Fig.4 f and Fig. 4a) – it is fine-crystal, composed by separate grains. The established higher phosphorous content for the coatings, deposited at lower pulse frequency compared to these, deposited at 500 Hz (Fig. 2b) is a possible reason for the smoother structure at 100 Hz.

Phase composition

Fig.5 (a, b) show the diffractograms of the deposited at stationary and at pulse mode Ni-Co-P alloys at temperature 80ºC at the same cathodic polarization and the same content of NaH_2PO_2 (0.189 M) in the solution. In the stationary mode of deposition a monophasic polycrystalline Ni-Co-P coating is forming. The compound is of the type NiCoP and it is well distinguished by the diffraction peaks. It has a hexagonal symmetry (according ICSDref 98-062-4449).

The Ni-Co-P coating, deposited in pulse mode at frequency about 250 Hz, is amorphous. The deposited coating is thin (under 10 μm), as the peaks of the substrate is seen (Fig.5, b).

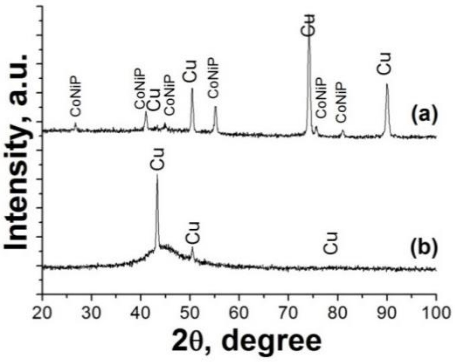

Fig. 5. Diffractograms of Ni-Co-P alloy coatings, deposited at temperature 80ºC in stationary, CPM (a) and pulse mode, PPM (250 Hz) (b) at the same cathodic polarization ΔE (CPM), resp. ΔE_m (PPM) = -1.15V.

CONCLUSIONS

1. With the increase of the NaH_2PO_2 content in the solution the mass of the deposited Ni-Co-P coating and the phosphorous content grow up faster in stationary mode compared to the pulse mode. Using the pulse mode with frequencies between 100 and 250 Hz results in higher phosphorous content in the coatings;

2. When the temperature of the electrolyte rise and the polarization is lower, in stationary mode and at lower pulse frequencies in pulse, the content of phosphorous in the coatings grow (up to 14.8% P at 100 Hz, 80^0C); the manifestation of the phenomenon of “anomalous” cobalt deposition and of the fine-crystal structure going down.

3.Ni-Co-P coatings, deposited in stationary mode, are monophasic and polycrystalline and the identified phase has hexagonal symmetry. The coatings, deposited in pulse mode are typical amorphous.

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ЕЛЕКТРООТЛАГАНЕ И СТРУКТУРА НА NI-Co-P СПЛАВНИ ПОКРИТИЯ В СТАЦИОНАРЕН И ИМПУЛСЕН ПОТЕНЦИОСТАТИЧЕН РЕЖИМ

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(Резюме)

Изследвани са скоростта на нарастване, състава, морфологията и микростуктурата на Ni-Co-P покрития, отложени в стационарен и в импулсен потенциостатичен режим в зависимост от съдържанието на NaH_2PO_2 в електролита, температурата, катодния потенциал и честотата на импулсите. Установено е, че с нарастване на съдържанието на NaH_2PO_2 (от 0.189 M до 0.5 M), скоростта на нарастване на масата на покритието и съдържанието на фосфор в Ni-Co-P покрития и при двата токови режима нараства. Максимално съдържание на фосфор в покритията е получено при честота на импулсите 100 Hz при температура на разтвора 20°C (9.7 mass.% P) и при 80ºC (14.8 mass. % P) при катодна поляризация $\Delta E = -1.15$ V. С нарастване на честотата на импулсите скоростта на нарастване на масата на покритието и съдържанието на фосфор намаляват. В импулсен потенциостатичен режим се наблюдава по-слабо проявление на феномена „аномално“ отлагане на кобалт в сплавта и това е обяснено със стабилизиране на pHна разтвора в този режим. Различните условия на електрокристализация в двата режима се отразяват във формиране на различни типове структури. Ni-Co-P покрития, отложени в стационарен режим, са еднофазни и поликистални. Идентифицираната фаза е от типа NiCoP с хексагонална симетрия. Покритията, отложени при импулсен режим са типично аморфни.

Ключови думи: електроотлагане, импулсен режим, сплавни покрития, морфология, фазова структура