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Composition and structure of Ni-Co coating depending on the ratio of Ni and Co in a citrate electrolyte

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This paper reports the effect of the Ni/Co ratio in a citrate electrolyte (with an optimum content of Na_3 citrate) on the deposition kinetics, chemical and phase composition of the Ni-Co alloy coating, current cathodic efficiency of the electrodeposition, and morphology of the coating. It was established that by increasing the Co content in the solution, the deposition potentials of the Ni-Co alloy were shifted towards the values where Co reaches a plateau of limited diffusion current. When the Co content in the solution increases and the applied cathodic potential gets more positive values, the Co content in the alloy increases (up to max 85%), and so does the cathodic current efficiency (in respect to electrodeposition of the alloy). The Co content in the alloys deposited in all studied electrolytes was over 60 mass % and the phenomenon of “anomalous” co-deposition of Ni and Co in the alloys was identified.

The SEM images of the alloy coatings deposited at potentiostatic conditions show that when the Co content in the alloy increases, the dimension of the crystals increases from about 100 nm up to about 300 nm. The alloy coatings have mixed structure of face-centered cubic (fcc) and hexagonal closed packed (hcp) lattice, which was proven by the XRD results.

Key words: kinetics of deposition, morphology, chemical composition, Ni-Co alloys, phase structure

INTRODUCTION

Recently, there is an increasing interest to nanostructured Co alloys which are mostly applied in magnetic sensor technologies and magnetic electronics [1-5]. The metals from the iron group and their alloys, including Ni-Co, exhibit high hardness, wear resistance and anti-corrosion protection. Ni-Co alloys are widely used in medicine, nuclear power systems, chemical and oil industry [6-8]. In addition to their excellent ferromagnetic and super hydrophobic properties, the nanostructured Co, Ni, and Ni-Co coatings also exhibit valuable catalytic properties [9-11]. The studies of electrodeposited Ni-Co alloys have shown that their microstructure and properties strongly depend on the Co content which can be controlled by the experimental parameters, such as bath composition, temperature, pH value, current density, etc. [2, 12-20].

According to the binary phase diagram of Ni and Co [26] and their similar atomic diameters, the Ni-Co alloy forms a substitution solid solution. Myung and Nobe [20] and Golodnitsky et al. [13] found three different crystal structures of Ni-Co alloy controlled by the Co-content. At low cobalt content (<40-50%) pure face-centered cubic (fcc) lattice (which would exist for pure nickel) was identified. As the content of cobalt increased, both fcc and hexagonal close packed lattice (hcp) appeared, and for Co-rich alloy (>80%), pure hcp was observed. Similar conclusions were proposed by Tury [19] and El-Feky Hesham [16] in the case of pulse deposition of Ni-Co alloys. The differences in the results about the phase composition of the Ni-Co alloys [15-20] are not very significant and are related to differences in the electrolyte composition and deposition conditions.

In previous works [27, 28] the effect of $Na_3C_6H_5O_7.2H_2O$ (Na_3 citrate) and H_3BO_3 concentrations on the electrolyte stability and deposition kinetics of Ni-Co alloys [27] as well as on the chemical composition, morphology and the phase composition [28] was studied. It was established that with increasing the concentration of Na_3 citrate in the solution (0.2-0.6 M), the deposition of Ni-Co alloy took place with lower cathodic current efficiency and bigger crystal dimensions; the Ni deposition was more difficult. As an optimum Na_3 citrate concentration in the electrolyte the lowest one (0.2M) was assumed.

The object of this paper is to study the effect of the ratio of the main components Ni and Co in a low-acidic citrate electrolyte (optimized in respect to Na_3 citrate concentration) on the deposition kinetics of Ni-Co alloys, chemical composition, current efficiency of the electrodeposition, morphology and phase composition of the Ni-Co coatings.

EXPERIMENTAL

The study was carried out in three electrolytes with compositions given in Table 1. All solutions were freshly prepared with distilled water and

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analytical grade chemicals. The pH was adjusted through addition of H_2SO_4 and NaOH.

The electrolyte compositions differ in the Ni/Co ratio within the range 1-3 through a change in the Co concentration at constant content of Ni (0.3M) and of the other electrolyte components (Table 1).

Table 1. Electrolyte compositions

Electrolyte (pH = 5.5)	Co [mol.dm^{-3}]	Ni [mol.dm^{-3}]	H_3BO_3 [mol.dm^{-3}]	Na_3citrate [mol.dm^{-3}]	Ni/Co ratio in the electrolyte
I	0.1	0.3	0.485	0.2	3
II	0.2	0.3	0.485	0.2	1.5
III	0.3	0.3	0.485	0.2	1

The deposition of the Ni-Co alloy coatings was examined using the method of potentiodynamic polarization curves with a scan rate of 30 mV.s^{-1} at room temperature using the Wenking Electrochemical Analysis System (Germany). A conventional three-electrode cell (total volume of 150 dm^3) equipped with a platinum foil counter electrode and saturated calomel electrode (SCE) as reference electrode was used. The working electrode was a disk-shaped copper electrode with surface area of 1 cm^2. All potentials are quoted with respect to the SCE.

The coatings intended for analysis were deposited for 6 min on rectangular copper plates with dimensions of 1.5×4 cm at constant potentials, determined from the polarization curves in the studied electrolytes. After electrodeposition the coatings were dissolved in 3.0 M HNO_3 and analyzed.

Prior to electrodeposition, the surface of the copper cathodes was rinsed with distilled water, cleaned in an etching solution $(H_2SO_4 : HNO_3 = 1:1;\ +10\%\ HCl)$, rinsed several times with distilled water and dried.

Elemental analyses of the coatings (in mass %) were performed by means of atomic emission spectral analysis, ICP-OES (high-dispersion ICP) using a 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 the Ni-Co alloy were calculated following the law of Faraday: $CCE = \frac{\Delta m_{pr}}{\Delta m_{th}}.100,\%$ where: Δm_{pr} is the practical mass of the Ni-Co coating, [g]; $\Delta m_{th} = q_{Ni\text{-}Co} I.t$ is the theoretically determined mass of the Ni-Co alloy [g]; **I** is the current during deposition [A]; t - the time of deposition [s]; $q_{Ni\text{-}Co} = \frac{q_{Ni}.q_{Co}}{N_{Co}q_{Ni} + N_{Ni}q_{Co}}$ [eq.C^{-1}] is the electrochemical equivalent of the alloy, calculated using the data about the chemical content of the alloy (N_{Ni} and N_{Co} are the molar parts of Ni and Co in the alloy).

The morphology of the coatings was examined through scanning electron microscopy (SEM) using the JSM-6390 Jeol equipment (Oxford Instruments). The phase composition of the coatings was identified using X-ray analysis with a powder diffractometer Philips PW 1050, CuKα radiation and operating voltage of 20.0 kV.

RESULTS AND DISCUSSION

Kinetics of deposition of the Ni-Co alloy

Comparisons between the potentiodynamic curves of deposition of Ni, Co and Ni-Co alloy coatings in the studied electrolytes are shown in Fig.1 (a-c).

As can be seen, the curves for the Ni deposition (curves 1) in all studied electrolytes have no plateau of limited diffusion current. An activation nature of the polarization was established [29, 30]. In the deposition curves of Co (curves 2), as well as the curves for the Ni-Co alloy deposition sharply expressed plateaus can be seen, which can be related to diffusion limitations. When the concentration of Co in the solution increases, the plateau of the limited current density in the curves of Co and CoNi deposition is shifted to more negative potentials, while the potentials for Ni deposition (-1.1V to -1.3V) stay the same. This phenomenon shows that the potentials for the Ni-Co alloy deposition (-1.0V to -1.3V) in the electrolytes with compositions II and III will correspond to conditions, where Co deposition will take place with diffusion limitations, which would worsen the structural characteristics of the alloy.

For all studied Ni/Co ratios in the solution co-deposition of Ni and Co in the Ni-Co alloy is possible. The kinetic peculiarity of the deposition of each metal will affect the structure of the alloy coatings.

Chemical composition of the Ni-Co alloy and current efficiency

The data about the percent content of the coating depending on the deposition potential (in the range of -1.1V to -1.3V) and on the Ni/Co ratio in the electrolyte are shown in Fig. 2.

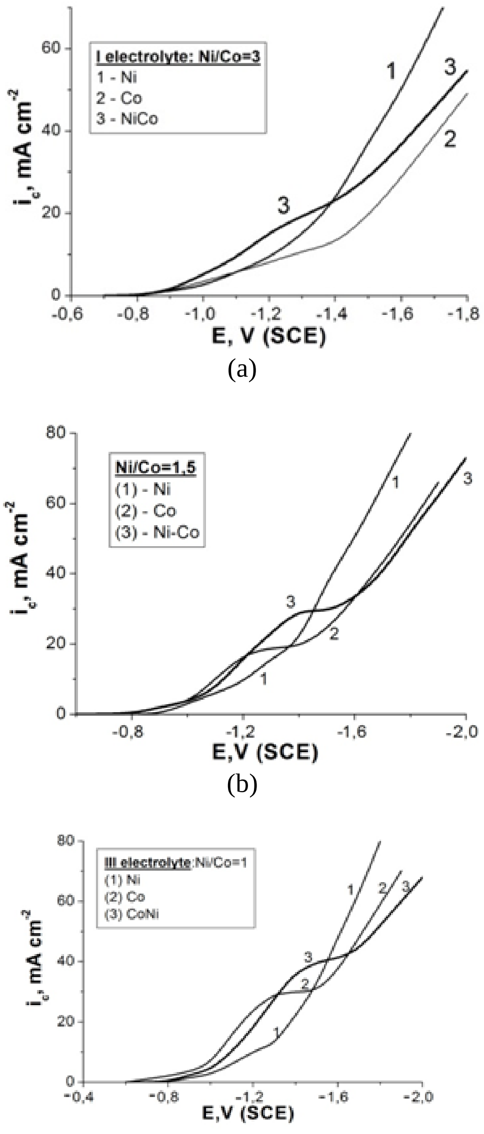


Fig. 1. Comparison of the polarization curves of deposition of Ni (1), Co (2) and the Ni-Co alloy (3) in electrolytes with composition I (a); II (b) and III (c).

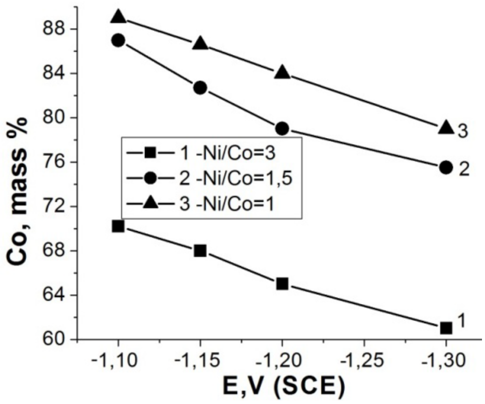


Fig. 2. Chemical content (in mass % of Co) of Ni-Co alloys depending on the cathodic potential and on the Ni/Co ratio in the electrolytes with composition I (1); II (2) and III(3).

For all studied Ni/Co ratios in the solution, the Co content in the alloy coatings is over 60% even though the Co content in the electrolytes is 50 and under 50% (Table 1). This result proves that Co is deposited preferentially in the Ni-Co alloy and for all electrolyte compositions the phenomenon "anomalous deposition" exists.

This phenomenon was also established by other authors [6-8, 21, 22]. According to Brenner [22], it consists in preferential deposition of the less noble metal in the alloy at comparable conditions for both metals. There are attempts to explain this phenomenon with formation of solid solutions [6], inclusion of oxides of metals with higher extent of oxidation associated with the presence of oxygen in the solution [23, 24] or formation of complexes [25].

Data presented on Fig. 2 show that the Co content in the coatings of Ni-Co alloy increases when the Ni/Co ratio in the solution increases and when the cathodic potential has positive values. In electrolyte I (with the lowest Co concentration) the Co content in the alloys increases from 62% at -1.3 V to 70% at –1.1V (respectively Ni decreases from 43% to 30%). In the case of electrolyte III the Co content is about 79-90% depending on the deposition potential value.

The cathodic current efficiency, CCE (in mass %) decreases when the deposition potential goes in negative direction for all Ni/Co ratios in the solution (Fig.3). This result can be explained with the increasing part of the reaction of hydrogen evolution at more negative potentials.

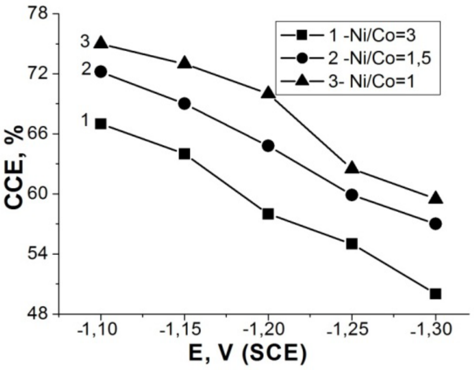


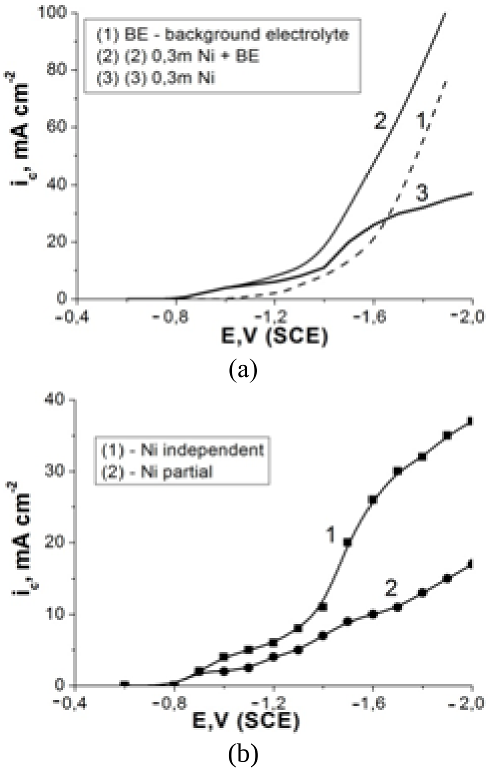
Fig. 3. Cathodic current efficiency (CCE, %) during Ni-Co alloy deposition depending on the deposition potential E, V (SCE) and on the Ni/Co ratio in electrolytes with composition I (1); II (2) and III (3).

At a given potential, as the Co concentration in the solution increases (composition III), the cathodic efficiency of the current also increases (Fig.3, 3).This effect can be related to the coating morphology. During hydrogen evolution, the electrolyte in the cathodic space is getting alkaline and complexes Ni(OH)$^+$ and Co(OH)$^+$are formed [19]. Because of higher adsorption ability, Co(OH)$^+$

are accumulated on the peaks of the rising crystals to a higher extent, which is a reason for the increase in Co content in the alloy and also for the growing dimensions of the crystals (Fig. 6). When the Ni content in the alloy increases (resp. the Co content decreases) the cathodic current efficiency decreases, which can be explained by the increase in the electrocatalytic activity of the coatings in respect to the reaction of hydrogen evolution because of the higher Ni content and finer crystal structure.

Effects of depolarization and overpolarization during deposition of Ni-Co alloys

The effects of depolarization and overpolarization during the deposition of Ni and Co in the Ni-Co alloy in electrolyte III were investigated. The results for the electrolytes with compositions I and II were similar.



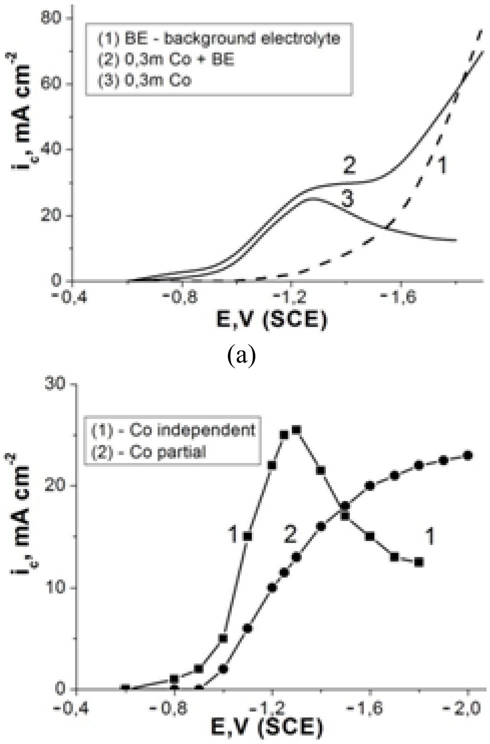
(a)

(b)

Fig. 4. (a) Partial curve of Ni deposition in alloy (3) obtained from the curves of Ni deposition in an electrolyte with composition 0.3M Ni+0.485M H_3BO_3 and 0.2M Na_3 citrate (2) and the curve in the background electrolyte (BE) (1); (b) Comparison of the curve of individual deposition of Ni (1) with the partial curve of deposition of Ni in the Ni-Co alloy (2).

In Figs. 4 (a,b) and 5 (a,b) the curves for individual deposition of Ni and Co are compared to the curves, obtained in a solution containing boric acid and Na_3 citrate (in concentrations given in Table 1), serving as a background to the electrolyte for deposition. This comparison was made with the aim to extract from the total current corresponding to each cathodic potential, the current due to the reactions related to background electrolyte and mainly to the reaction of cathodic evolution of hydrogen. The partial curves for deposition of metals in the alloy are obtained by decomposition of the deposition curves of Ni and Co in the alloy. The decomposition was performed by subtracting the current for the pursuing reactions (using data for the cathodic efficiency of current, Fig. 3) and the current for deposition of the second metal from the total current corresponding to each cathodic potential.

The comparison of the curves on Figs. 4 and 5 shows that the polarization during Ni and Co co-deposition in the alloy is higher than those of their individual deposition, i.e. Ni and Co are deposited in the alloy with overpolarization. This result shows difficulties in the co-deposition of the two metals, which are often related to thermodynamic difficulties during electrocrystallization [31, 32].



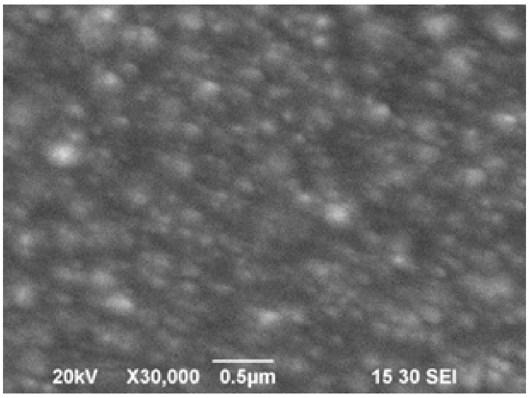
(a)

(b)

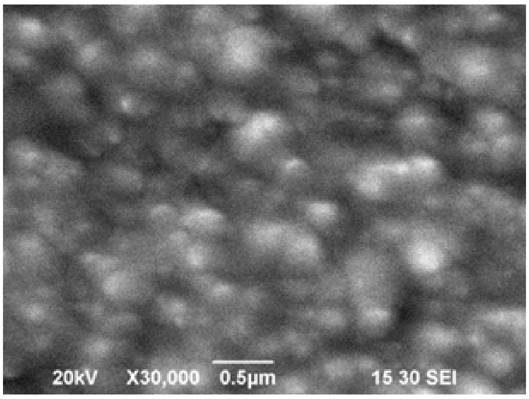
Fig. 5. (a) Partial curve of Co deposition in alloy (3) obtained from the curves of Co deposition in an electrolyte with composition 0.3M Ni+0.485M H_3BO_3 and 0.2M Na_3 citrate (2) and the curve in the background electrolyte (BE) (1); (b) Comparison of the curve of individual deposition of Co (1) with the partial curve of deposition of Co in the Ni-Co alloy (2).

Morphology and phase composition of Ni-Co alloys.

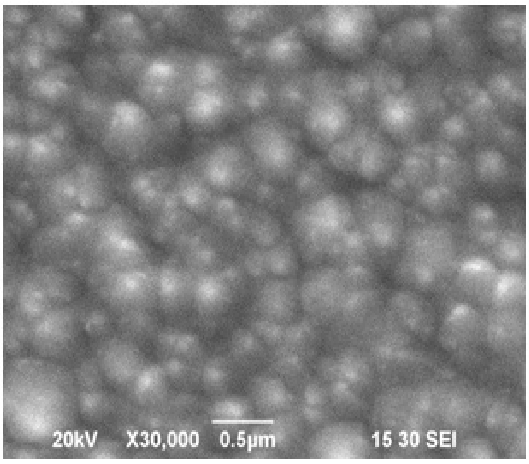
Fig. 6 presents SEM images of the Ni-Co coating deposited in electrolytes with composition I (Fig. 6,a), II (Fig. 6,b) and III (Fig. 6,c) at a deposition potential E= - 1.2 V (SCE). As can be seen, in the Ni-Co alloy coatings with higher Ni content deposited from electrolyte I (Fig. 6,a), the crystal dimensions are less than 100 nm, while by increasing the Co content, the dimensions gradually increase to about 150-250 nm in electrolyte II (Fig. 6,b) and to 300 nm in electrolyte III (Fig. 6,c). In the latter case the alloy coatings are characterized with formation of spheroidal crystals with uniform distribution by form and dimensions.



(a) 65% Co-35% Ni (electrolyte I)



(b) 79% Co- 21% Ni (electrolyte II)



(c) 85% Co-15% Ni (electrolyte III)

Fig. 6. SEM images of Ni-Co alloys deposited at a potential E = -1.2V (SCE) in electrolytes with compositions I (a) II (b) and III (c).

Fig.7 shows the XRD patterns of Ni-Co alloy electrodeposited from the three studied solutions at the deposition conditions for coatings used in SEM analysis. Ni-Co alloy coatings deposited from the three electrolytes are characterized by polycrystal structure. In the XRD patterns 4 peaks can be seen at 2θ values 44.4°, 51°, 76.5° and 92.5°, corresponding to reflexes by (111), (200), (220) and (311) faces for a face-centered cubic (fcc) lattice of a nickel-rich phase. The XRD patterns contain also 2θ values of 41.3°, 47.5° and 75° corresponding to reflexes by (100), hcp (101), hcp (110) from a hexagonal close packed (hcp) lattice of a Co-rich phase.

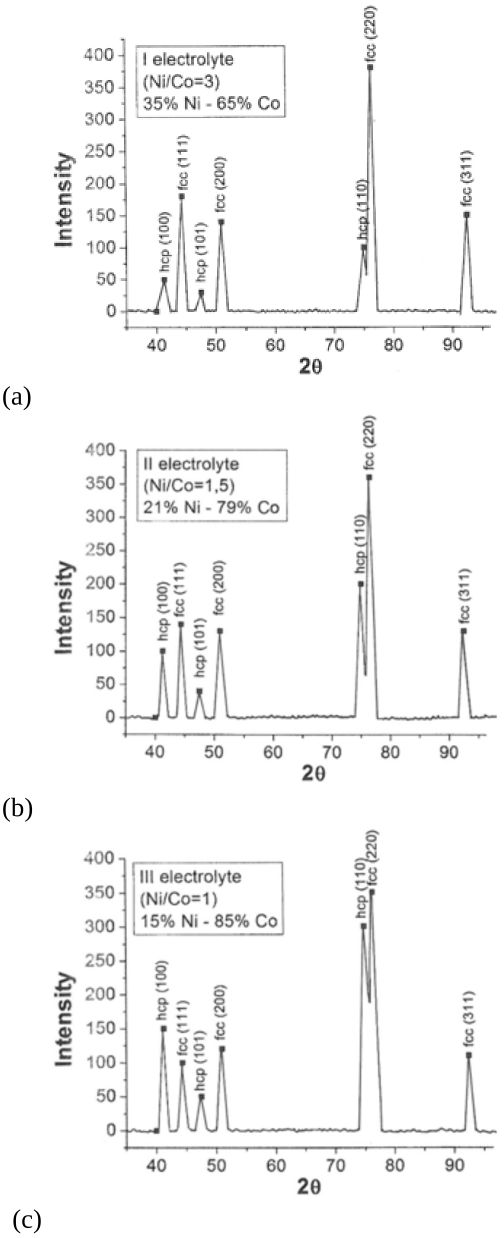


Fig. 7. XRD patterns of Ni-Co alloys deposited in electrolytes with composition I (a); II (b) and III (c) at E= -1.2V(SCE).

By rising the Co content in the alloys from 65% to 85% (Fig.7) the intensity of the peaks related to the hcp phase increases compared to those of the fcc phase. It can be concluded that the alloys deposited in the studied electrolytes are a mixture of fcc and hcp phases.

The obtained results support the conclusions made in [15,16,19]. In the case of nanostructured materials, the crystallographic structure may differ from the geometric structure of micro- or macro-structured materials. Based on this statement the formation of mixed structure is possible [33] in which either hexagonal Co contains cubic structured Ni or hexagonal Co is built in the cubic structured Ni. A theoretical model of the described crystal structure is given in [19].

CONCLUSIONS

The co-deposition of Ni and Co in Ni-Co alloy coatings in electrolytes with different Ni/Co ratio is possible in all electrolytes studied. Increasing the Co concentration in the solution, the potentials for Ni-Co alloy deposition are displaced towards conditions, at which Co is deposited with diffusion limitations, which could worsen the quality of the alloys, especially at more negative potentials.

At all investigated Ni/Co ratios in the solution, the Co content in the alloy coatings (in mass %) is over 60% and a conclusion was made about the phenomenon of “anomalous deposition” of Ni and Co**.**

The deposited Ni-Co alloys are with nano-dimensioned structure. When the Co content in the alloy decreases, the dimensions of the crystals decrease from about 300 nm to about and less than 100 nm.

The Ni-Co alloys are characterized with a mixed structure of face-centered cubic (fcc) and hexagonal closed packed (hcp) lattice, i.e. either hexagonal Co contains cubic structured Ni or hexagonal Co is built in the cubic structured Ni.

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СЪСТАВ И СТРУКТУРА НА Ni-Co ПОКРИТИЯ В ЗАВИСИМОСТ ОТ СЪОТНОШЕНИЕТО НА Ni И Co В ЦИТРАТЕН ЕЛЕКТРОЛИТ

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(Резюме)

В статията се докладва влиянието на съотношението Ni/Co в цитратен електролит (с оптимално съдържание на Na_3 citrat от 0,2М) върху кинетиката на отлагане, химичния и фазов състав на сплавното Ni-Co покритие, токовата използваемост за електроотлагане и морфологията на покритията. Установено е, че с нарастване на съдържанието на Co в разтвора, потенциалите на отлагане на Ni-Co сплав се изместват към стойности, при които кобалтът достига до плато на граничен дифузионен ток. При нарастване на съдържанието на Co в разтвора, катодният потенциал на отлагане на сплавта се измества в по-положителна посока, като при това съдържанието на кобалт в сплавта нараства (до максимум 85%), както и катодната използваемост на тока по отношение на отлагане на сплавта. Съдържанието на Co в сплавите, отложени във всички изследвани електролити, беше над 60 мас.% като беше установен ефект на „аномално“ съотлагане на Ni и Co в сплавите.

Резултатите от SEM анализа на сплавните покрития, отложени в потенциостатичен режим, показаха, че когато съдържанието на Co в сплавите нараства, размерът на кристалитите също нараства от около 100 nm до около 300 nm. Сплавните покрития представляват смес от фази със стенно-центрирана (fcc) и с хесагонална опаковка (hcp), доказано от резултатите на XRD анализа.