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EFFECT OF ORGANIC ADDITIVES IN CITRATE ELECTROLYTE ON THE PROPERTIES OF Ni-Co ALLOY

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ABSTRACT

The kinetics of independent and joined deposition of Ni and Co in citrate electrolyte in the presence of three types of additives: saccharine (SCH), urotropine (URT) and gelatine (GLT), is examined. Comparison is made between the chemical composition, the current cathodic efficiency (CCE) and the morphology of Ni-Co alloys depending on the type of the additive, both in constant potential mode (CPM) and in pulse potental mode (PPM). The study specifies the effect of GLT and SCH for formation of smooth, shiny, nanostructured Ni-Co coatings with average crystallite size less than 100 nm with a high CCE (about 80 % for SCH, and over 90 % for GLT), in both potential modes. The presence of SCH in the electrolyte with simultaneous application of PPM increases the content of Ni in the alloy to 25-30 mass % Ni. The optimum additive of SCH containing 0.5 - 1.0 g dm^{-3} is specified, wherein the electrolyte remains stable during continuous operation.

Keywords: nanostructured Ni-Co alloys, organic additives, citrate electrolyte, pulse potential mode, morphology, chemical composition.

INTRODUCTION

There is an increasing interest recently in obtaining nanostructured Ni-Co alloys mainly because of their application in microsystems, e.g. magnetic sensors, microrelays, and inductors [1 - 3, 6]. Due to their high hardness, wear resistance and anti-corrosion protection, Ni-Co alloys are also widely used in medicine, nuclear power systems, chemical and oil industry [4, 5]. During the deposition of very thin films via electrolysis, an increase of the internal tensions of the coatings is observed in most cases [7]. In order to decrease them, as well as to improve the other properties of the coatings, some organic additives are often applied to the electrolyte [8 - 18]. In [10] the data from EDS analysis are summarized, according to which, in presence of saccharine the contents of C and S in the Ni-Co coatings increases and the coatings are homogeneous not only along the outer surface, but throughout the entire cross section. There is evidence that the addition of 1 g dm^{-3} saccharine in the electrolyte results in decrease of the internal tension and tensile strength of Ni and Ni-Mn coatings [8] and has a positive impact on the structure and the hardness of Ni-Co alloy coatings [9, 11]. The additions of gelatine, as well as of glycerol, have a similar effect on the structure of Zn-Ni alloy [12]. It is also found that in presence of gelatine the rate of deposition of Ni and the cathode current usability increases in case of deposition of Zn-Ni alloy [13]. Although urothropine is often used as a corrosion inhibitor, there is an evidence in the reference sources that urothropine, as well as monoetanolamine, leads to formation of shiny Cr and Cr-Co alloy coatings in sulphate electrolyte [14, 15]. Additions of cysteine and sodium gluconate significantly influence the phase content and the properties of Ni-Co alloys [16] and the brighteners, as serine and vanillin, increase the corrosion resistance of Zn-Ni alloys [17]. During the examination of electrodeposition of Cu-Co multilayers in presence of two different organic additives, sodium dodecylsulphate (SDS) and saccharine, it is found that saccharine strongly inhibits the discharge of cobalt ions, and SDS has depolarizing effect [18]. Obviously the choice of the tested additives is very important since the effect of the organic additives is strongly dependent on their chemical nature and structure. Thus the shine additives, as thiocarbamide and Triton X100, have disastrous effect on the structural properties and the magnetic resistance of Cu-Co multilayers [19].

The application of pulse mode simultaneously with introduction of organic additives in the solution may significantly enhance the effect of additives [8, 14]. Additionally, there is data evidencing that the pulse deposition has several advantages over the conventional deposition of Ni-Co alloy coating [20 - 22]. The possibility to apply very high values of the current or the polarization during the delay in application of pulse mode significantly influences the nuclei formation, and thus improves the physical and mechanical properties of the coatings [21]. The presence of pauses between the pulses, on the other hand, allows additional adsorption of organic molecules or the products of a chemical reaction that may change the conditions of alloy formation and/or inhibit the crystal growth process [22].

The system Ni-Co belongs to the so-called “anomalous” type of deposition [23, 24]. There is an evidence that the anomalous type of deposition is observed after either introduction of organic additives in the electrolyte [8], or an application of pulsed current mode [22].

This article aims to clarify the influence of three types of additives, saccharine (SCH), urotropine (URT) and gelatine (GLT), on the kinetics of both independent and joined deposition of Ni and Co in citrate electrolyte and to compare the chemical content, the cathode current usability and the morphology of Ni-Co alloys in both constant and pulse potential mode for each additive.

EXPERIMENTAL

Composition of the electrolyte

The composition of the low acidic citrate electrolyte, which is the object of the examnations is as follows: 0.2 M Ni as $NiSO_4.2H_2O$; 0.2 M Co as $CoSO_4.7H_2O$; 0.485 M H_3BO_3 and 0.4 M Na_3citrat. The pH of the solution was adjusted to 5.5 using citric acid or sodium hydroxide. Herein we examine the influence of three types of organic additives: saccharine (SCH); urothropine (URT), and gelatine (GLT) in the range of concentrations from 0 to 1.5 g dm^{-3}. Among the three additives, only GLT has low solubility parameters and needs preliminary soaking in water to swell for a few minutes and subsequent dissolving with gentle warming (40 - 50°C) and stirring. All solutions are freshly prepared with analytically pure chemical agents and double-distilled water.

Methodology of the examination

All experiments were performed in a thermostated three electrode cell at normal conditions (20°C). The cell with a total volume150 dm^3 includes a cathode made of electrolytic copper (Merck, 99.97 mass % Cu), a platinum anode arranged concentrically around the working electrode, and saturated reference calomel electrode arranged in a special pan with Lugin’s capillary ($E_{SCE} = 0.241 \pm 0.003$ V). For the purpose of kinetic examinations the electrodes are shaped as 1 cm^2 discs and cast in epoxy resin. The kinetics of deposition is examined through the method of potentiodynamic polarization dependencies using potentioscan type Wenking (Germany). The applied rate of potential scanning of 10 mV s^{-1} is so selected that it was possible to measure the effects of adsorption of the additives tested on the electrodeposition of metals. For the purpose of electrodeposition of Ni-Co alloys coatings, copper cathode plates with dimensions 1.5 - 4 cm, are prepared. 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. The anodes are cleaned in hot 1 N HNO_3, rinsed with distilled water and dried.

The Ni-Co alloys are deposited for 4 min, considering the mass of the coating (Δm_t) by mass measurements of the cathode before and after theelectrolysis, as well as the amount of the current flown by $Q = I_m t [C]$. The data from atomic absorption spectrometry (AAS) is used to determine the chemical composition of the coatings, which are the basis for calculating the current cathodic efficiency (CCE) upon Faraday’s law of electrolysis: $CCE = \frac{m_{pr}}{q_{NiCo}\ Q}\ 100, \%$, where q_{NiCo} [geq C^{-1}]

is the electrochemical equivalent of the alloy and is also determined by using the data for chemical content of the alloy, and $q_{NiCo}\ Q = m_t$ is the theoretically determined mass of Ni-Co alloy.

The pulse deposition of coatings is carried out through potentiostatic pulses with rectangular shape of the potential. The applied pulse frequency is 500 Hz at filling the pulses $\theta = 0,5$

($\theta = \frac{\tau_p}{\tau_p + \tau_z}$, where τ_p is pulse time, and τ_z is pause time).

For the purpose a pulse generator is used connected to the input of the purpose-built potentiostat from which the signal is fed directly to the three electrode cell. The values of deposition potentials of Ni-Co alloys in pulse mode are selected similarly as for constant potential mode - from kinetic data and they are corresponding to the same cathodic current densities, determined from polarization dependencies for actual deposition of metals.

The data for the morphology of Ni-Co alloys were also obtained by the SEM images taken with JSM-6390-Jeol, Oxford Instruments. This instrument enables the obtaining of EDS spectra for each sample, allowing to evaluate the chemical composition of the alloy (in mass %). The data for the chemical composition are also obtained through atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

Effect of organic additives on the kinetics of self-deposition of Ni and Co

Figs. 1-3 show the effect of the content of additive imported on the kinetics of self-deposition of Co (Fig. 1-3, a) and Ni (Fig. 1-3, b) from the working citrate electrolyte. As it is seen from the curves, each of the organic additives influences in a specific way the kinetics of self-deposition of metals.

In previous research we have examined the kinetics of self- and joined deposition of Co and Ni in low acidic citrate electrolyte in absence of additives [25]. It was found that in both cases a long initial polarization is observed, more typical for Ni deposition. The deposition of Co occurs through combined control with predominantly diffusion polarization, and the deposition of Ni occurs mostly through activation control.

The influence of the content of SCH on the kinetics of self-deposition of metals is shown in Fig. 1 (a, b).

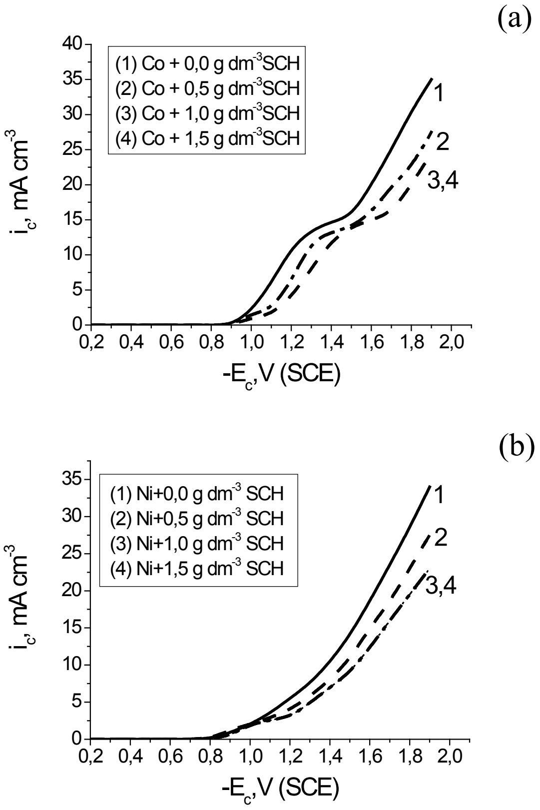


Fig. 1. Effect of the concentration of saccharin (SCH) on the cathodic polarization dependencies of deposition of Co (a) and Ni (b) in 0.2 M Co (0,2 M Ni, respectively); 0.485 M H_3BO_3 and 0.4 M Na_3citrat, pH 5,5.

As can be seen, SCH strongly displaces the polarization of deposition of Co (Fig. 1a) and Ni (Fig. 1b) in negative direction, exactly in the area of potentials and currents, which has been found to deposit dense coatings of metals.

At the same time, the curves recorded in presence of SCH in the area of potentials from -1.0 to -1,15 V, outline the further retention of current, i.e. a plateau, most probably with adsorption nature. The introduction of SCH with concentration more than 1.0 g dm-3has no significant effect on the polarization dependencies since the state of surface saturation is reached.

The influence of URT addition is shown in Fig. 2 a,b. As can be seen from the self-deposition curves of Co (Fig. 2a) and Ni (Fig. 2b), the curves have also plateaus of current, right after the initial polarization, associated with the adsorption of additive. The curves evidence that the presence of URT additive causes a slight displacement of the polarization deposition of Co in negative

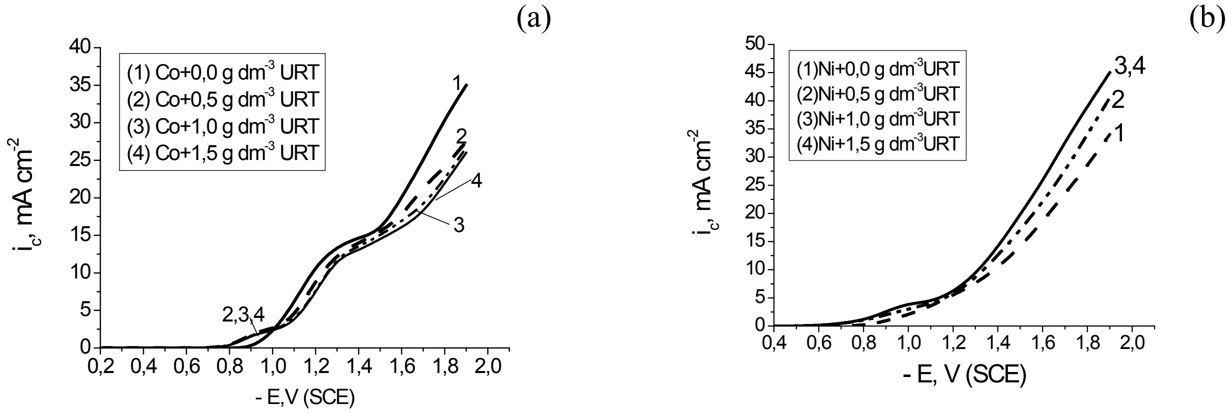


Fig. 2. Effect of the concentration of urothropine (URT) on the cathodic polarization dependencies of deposition of Co (a) and Ni (b) in 0.2 M Co (0,2 M Ni, respectively); 0.485 M H_3BO_3 and 0.4 M Na3citrat, pH 5,5.

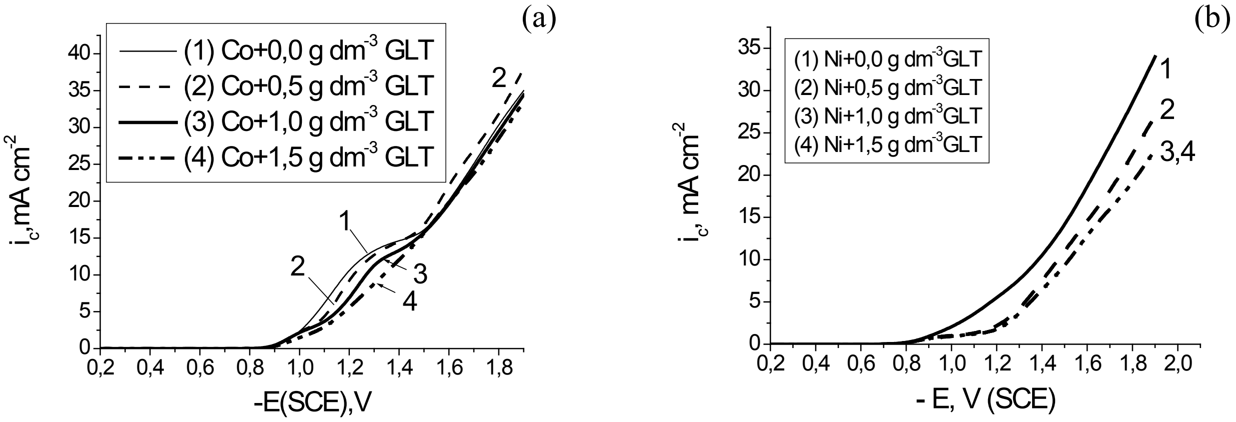


Fig. 3. Effect of the concentration of gelatine (GLT) on the cathodic polarization dependencies of deposition of Co (a) and Ni (b) in 0.2 M Co (0,2 M Ni, respectively); 0.485 M H_3BO_3 and 0.4 M Na_3citrat, pH 5,5.

direction compared to the one without additive in the area of metal electrodeposition (Fig. 2a, curves 2 - 4).The presence of URT in the electrolyte for self-deposition of Ni has depolarizing effect within the entire potential area at all concentrations of the additive (Fig. 2 b, curves 2 and 3). It might be said that the presence of URT in the solution facilitates the deposition of Ni and the accompanying process of hydrogen evolution since it decreases the polarization as a whole.

The addition of SCH and URT influences the initial stages of the electrodeposition of Co and Ni, but in the area of actual deposition of metals for both additives the rate of deposition of Ni remains lower than that of cobalt at a particular potential. This should be considered in the preparation of cobalt-enriched alloys, regardless of the commensurate concentrations of the two metals in the solution, both in presence and in absence of additives, defined as depostion of „anomalous” type.

Fig. 3a,b shows the effect of GLT on the kinetics of self-deposition of Ni and Co. The sequential increase of the gelatine content results in a gradual displacement of the deposition polarization of Co and Ni in negative direction, as in the case of Co the plateau of boundary diffusion current disappears, but a more clearly outlined plateau is formed at lower potentials as a result of the adsorption of GLT molecules. Both self-depositions of Co and Ni would be strongly impeded in presence of GLT. In this case, the kinetic data also indicate an „anomalous“ deposition with regard to the comparison of the rates of actual deposition of metals.

Effect of organic additives upon the kinetics of joined deposition of Ni and Co

Fig. 4 shows a comparison between the curves of joined deposition of Ni and Co in absence (Fig. 4, curve 1) and in presence of 0.5 g dm^{-3} of the additives. This concentration is optimal for all three additives, since in this case the electrolyte remains stable, and the effect on the cathode polarization is maximal. In the case of GLT compared to the other additives, the increase of concentration above 0.5 g dm^{-3} significantly decreases the stability of the solution.

The comparison between the curves of joined deposition of metals (Fig. 4) in presence of additives shows an increased polarization within the entire operative potentials window. The strongest increase of cathode polarization in the area of deposition of dense coating of Ni-Co was observed in presence of SCH (Fig. 4, curve 2). The URT additive (Fig. 4, curve 3) has depolarizing effect on the joined deposition of Ni and Co. Since polarization is the measure for the difficulties in electrochemistry, it is expected that SCH and GLT additives have stronger impact on the morphology and structure of Ni-Co coatings compared to URT.

Chemical composition and cathode current efficiency of Ni-Co coatings in constant (CPM) and pulse potential mode(PPM)

The kinetic studies carried out proved that the comparison of the chemical content and the cathode efficiency of current in both potential modes, as well as the structure of the Ni-Co coatings obtained in presence of various additives in the solution can be done at potentials values, which corresponding to the same cathodic current density i = 7,5 mA cm^2 (E = - 1.180V ÷ -1.290V for different conditions). The data are shown in Fig. 5a for the chemical content (% mass Co) and in Fig. 5b for the current cathodic efficiency (CCE, %) depending on the concentration of additives and the used potential mode.

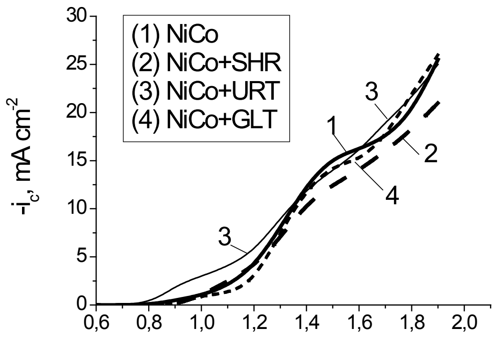


Fig. 4. Effect of presence of additives (C = 1,0 g dm^{-3}) on the co-deposition of Ni and Co in electrolyte with composition: 0.2 M Ni; 0.2 M Co; 0.485 M H_3BO_3 and 0.4 M Na_3citrat; pH 5,5.

The analysis of the data obtained proves that both in constant (Fig. 5, curves 1 - 3) and in pulse mode (Fig. 5, curves 1* - 3*) the content of Co (mass %) increases with the increase of the content of organic additives, and achieves maximum at 0.5 - 1.0 g dm^{-3} in presence of GLT and URT but decreases with the increase of SCH content (Fig. 5a). Accordingly, the content of Co in Ni-Co coatings is higher in pulse mode (Fig. 5, curves 1* - 3*).

The discussed kinetic results show that in presence of URT a certain effect of "depolarization" occurs for self-deposition of Ni. The data presented in Fig. 5 demonstrate that the addition of URT to the solution does not lead to increase in Ni content in the coatings, compared to the other two additives. Most probably the URT additive facilitates the hydrogen release simultaneously with Ni, and this result is proved by the data for CCE, shown in Fig. 5b. It also proves that the CCE decreases with the increase of the content of organic additive; it reaches the lowest value (about 60 %) in presence of URT, and the highest value in presence of GLT (about 95 %).

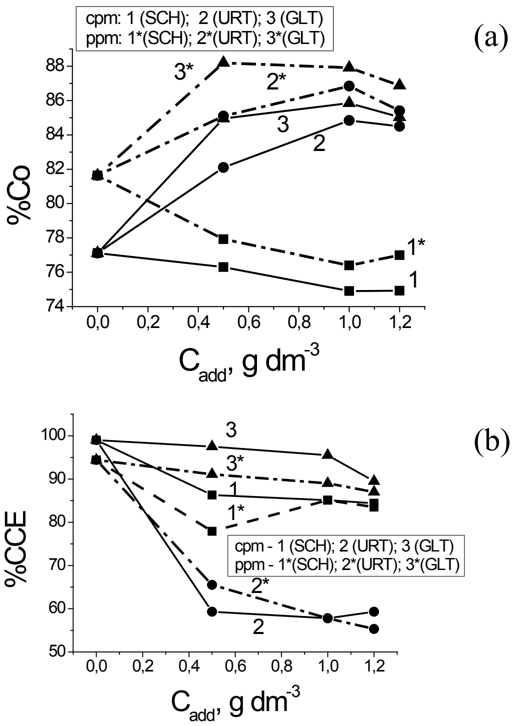


Fig. 5. Effect of the additives (C = 1,0 g dm^{-3}) on the chemical composition, mass %Co (a) and on the CCE, % (b) of Ni-Co alloy in constant potential mode (CPM) and in pulse potential mode (PPM) in 0.2 M Ni; 0.2 M Co; 0.485 M H_3BO_3 and 0.4 M Na_3citrat; pH 5,5.
Curves 1-3 for CPM; Curves 1*-3* - for PPM.

Moreover Fig. 5b evidences that the application of pulse mode under comparable conditions leads to lower CCE for additions of SCH and GLT. One possible explanation of this result is the presence of pauses between pulses in pulse potential mode, in which additional adsorption of the additives possibly occurs. This may lead to a lower total cathode active surface and therefore to a decrease in CCE. It is possible that the pauses relieve the reaction of removal of the hydrogen-gas released simultaneously with metals, which could also reduce the CCE for deposition of Ni-Co alloy.

Joined influence of organic additives and application of pulse mode on the morphology of Ni-Co coatings

The data for the morphology (Figs. 6 and 7) and the composition of coatings (Fig. 8) are obtained through SEM images and EDS analysis.

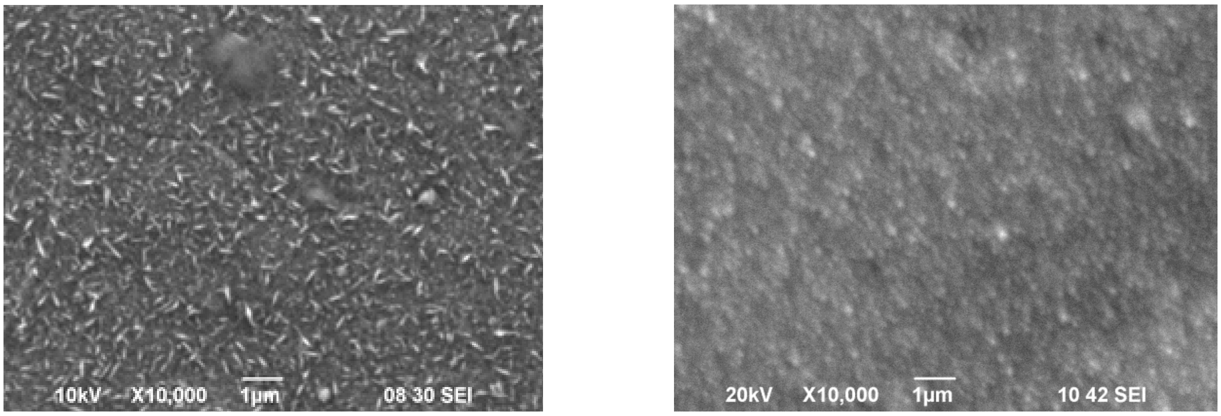
Fig. 6a,b shows SEM images of Ni-Co coatings deposited without additive in CPM, Fig. 6a and in PPM, Fig. 6b. This comparison indicates that the application of PPM results in formation of more fine crystalline Ni-Co alloys. While in stationary mode (CPM) the deposited coatings present clearly shaped needle-like crystallites with an average size of about 300 nm, in pulse mode (PPM) a more fine crystalline structure is observed as well as the tendency to rounded crystallites with size of about 100 - 150 nm and a general smoothing out of the relief. This is evidenced by the more obscure SEM-image at a comparable magnification.

Fig. 7a-c compares SEM-pictures of Ni-Co coatings prepared in citrate electrolyte in presence of additives in pulse mode only, at two magnifications. Our observations and the data obtained show that in the presence of SCH (Fig. 7a,a*) and GLT (Fig. 7c,c*) combined with application of pulse mode, lead to formation of very smooth, shiny Ni-Co coatings, as the amount of the crystallites observed is very close to and below 80 nm size.

In presence of URT (Fig. 7b,b*) the Ni-Co coatings have very clearly shaped crystalline structure with lenticular shape of crystals. It is evident that the addition of URT has no positive effect on the morphology of the deposited Ni-Co coatings compared to the other two additives - the size of the crystals formed remains less than 250 nm.

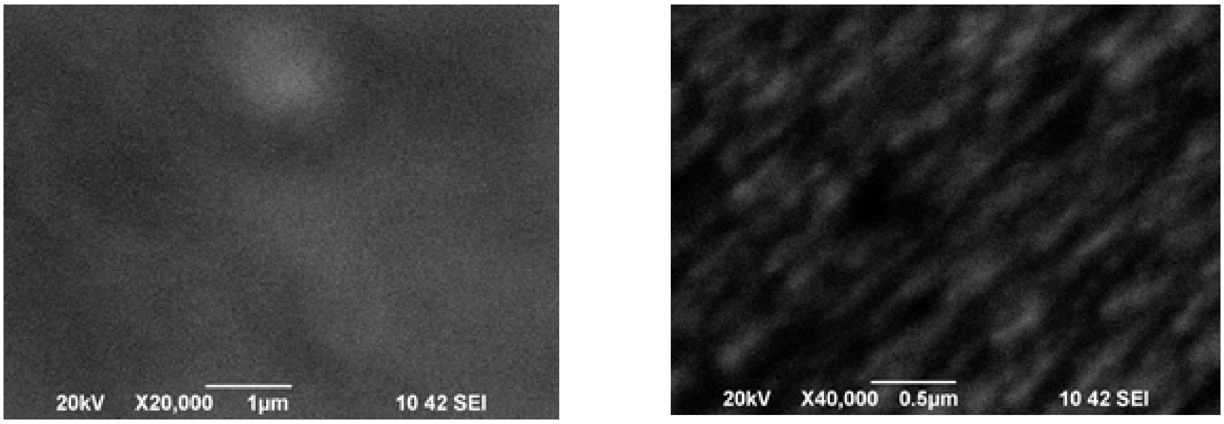
The established strong effect of SCH on the morphology of coatings and the fact that the addition of GLT leads to weaker effect on the increase of nickel content and the cathode current usability, and makes the electrolyte very unstable in the same time, allows indicating SCH with content about 0.5 - 1.0 g dm^{-3} as the optimal additive.

The EDS spectra obtained (Fig. 8a-d) provide a statistically averaged image of the ratio between the two metals in the alloy. The comparison between the spectra of Ni-Co alloys deposited during electrolysis for 2 min (Fig. 8c) and 4 min (Fig. 8d) indicates that in the beginning of deposition in presence of URT the average Ni content in the coatings is high, and over time it rapidly decreases compared to that of Co. No such effect is found for the other two additives. It is possible that during the initial stages of the electrodeposition the depolarizing influence of URT upon the deposition of Ni results in its prevalence in the alloy. However, the

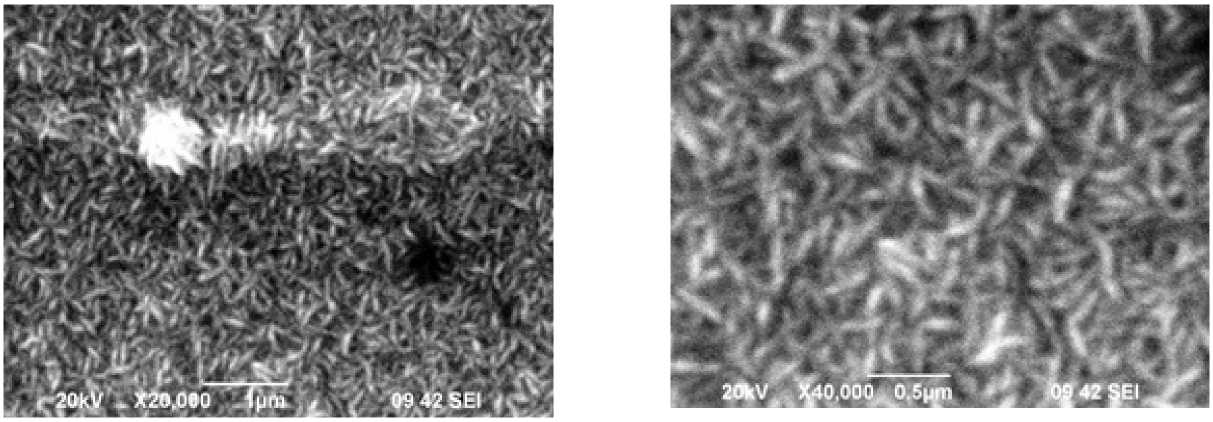


(a) CPM(86 % Co -14 % Ni) (b) (89 % Co – 11 % Ni)

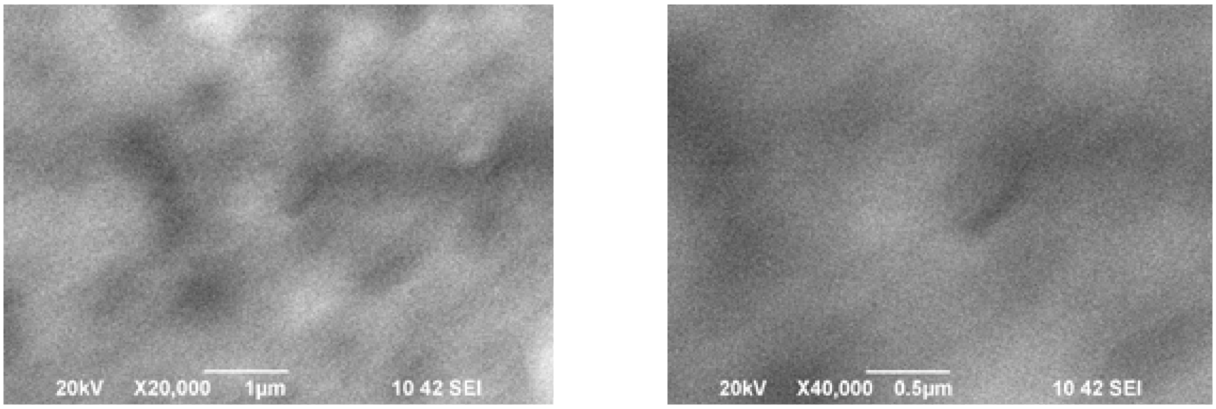
Fig. 6. SEM-images of Ni-Co alloys electrodeposited in CPM (a) and in PPM (b) in 0.2 M Ni; 0.2 M Co; 0.485 M H_3BO_3 and 0.4 M Na_3citrat; without additives, pH 5,5.



(a) SCH (a*) SCH



(b) URT (b*) URT



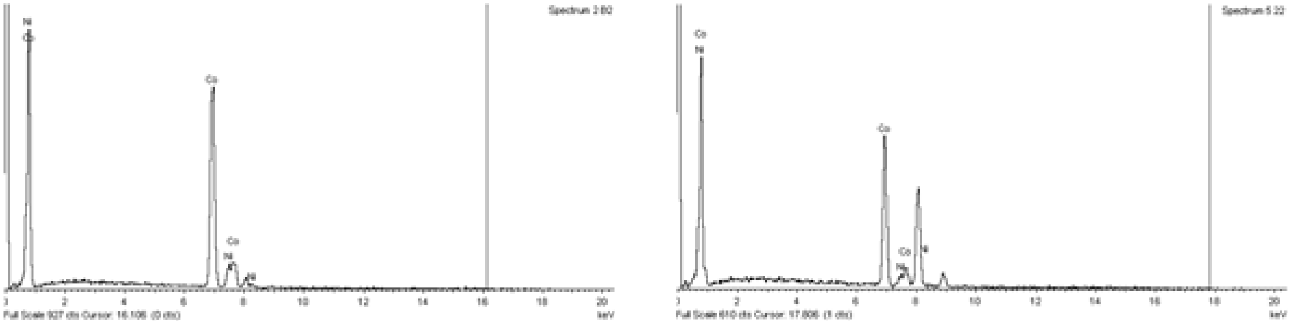
(c) GLT (c*) GLT

Fig. 7. SEM -images of Ni-Co alloys, electrodeposited in PPM in 0.2 M Ni; 0.2 M Co; 0.485 M H_3BO_3 and 0.4 M Na_3citrat; pH 5,5, with 1,0 g dm^{-3} SCH (a, a*); 1,0 g dm^{-3}URT (b, b*); 1,0 g dm^{-3}GLT (c, c*) at two magnifications: x20000 (a - c) and x40000 (a* - c*).

emission of hydrogen begins with the time, which is known to occur with a lower overvoltage over Ni than over Co - the CCE decreases and the content of Ni in the alloy is also reduced compared to Co.

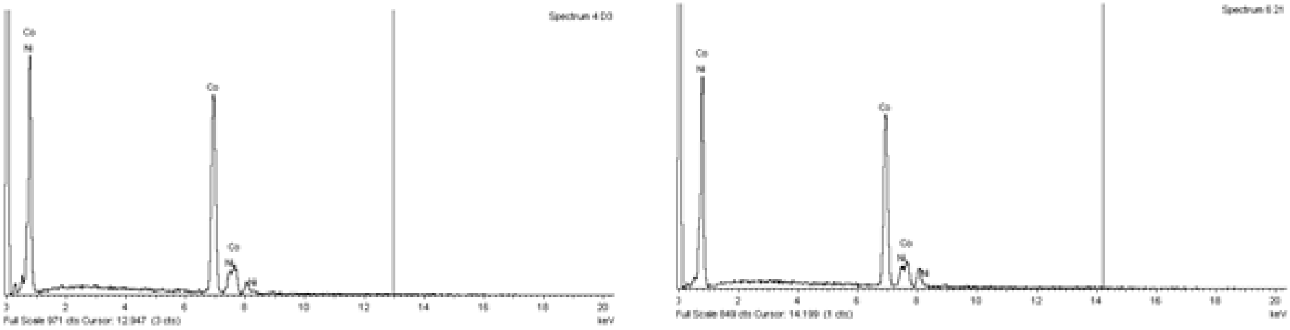
CONCLUSIONS

Based on the examinations with the addition of three organic additives (saccharine (SCH), urotropine (URT), and gelatine (GLT)), the conclusion for the ef-



(a) ppm+SCH, 4 min

(c) ppm +URT, 2 min



(b)ppm+GLT, 4 min

(d) ppm+URT, 4 min

Fig. 8. EDSA-spectra of Ni-Co alloys, electrodeposited in 0.2 M Ni; 0.2 M Co; 0.485 M H_3BO_3 and 0.4 M Na_3citrat; pH 5,5: (a) with 1,0 g dm^{-3} SCH and t = 4 min; (b) with 1,0 g dm^{-3} GLT and t = 4 min; (c) with 1,0 g dm^{-3} URT and t = 2 min; (d) with 1,0 g dm^{-3} URT and t = 4 min.

fect of GLT and SCH for formation of smooth, shiny nanostructured Ni-Co coatings with average crystallite size less than 100 nm, high cathode current efficiency (80 - 90 %) and higher content of Ni (20 - 30 mass % Ni) was demonstrated. It can be appointed as optimal additive SCH with content of 0.5 - 1.0 g dm^{-3}, wherein the electrolyte remains stable during continuous operation, unlike the case with addition of GLT.

REFERENCIES

1. S. Armyanov, Crystallographic structure and magnetic properties of electrodeposited Co and Co alloys, Electrochim. Acta, 45, 2000, 3323-3335.
2. B. Lochel, A. Maciossek, H. Quenzer, B. Wagner, C. Engelmann, Magnetically driven microstructures fabricated with multilayer electroplating, Sensors&Actuators, A46, 1995, 98-104.
3. D. Golodnitsky, Yu. Rosenberg, A. Ulus, The role of anion additives in the electrodeposition of Ni-Co alloys from sulfamate electrolyte, Electrochem. Acta, 47, 2002, 2707-2714.
4. L. Wang, Y. Gao, Q. Xue, L.H. Huiwen, T. Xu, Microstructure and tribological properties of electrodeposited Ni-Co alloy deposit, Applied Surface Science, 242, 2005, 326-332.
5. R. Orinakova, A. Turonova, D. Kladekova, M. Galova, R. Smith, Recent developments in the electrodeposition of Ni and some Ni based alloys, J.Appl.Electrochem., 36, 2006, 957-972.
6. P.C. Andricacos, in: M.Paunovic (ed.), Electrochemically Deposited Thin Films II, PV94-31, The Electrochemical Society Priceedings Series, Pennington, NJ, 1995, 157.
7. S. Armyanov, G. Sotirova-Chakarova, Internal Stress in Electrodeposited Cobalt, Nickel and Their Alloys: Part II, Metal Finishing - New Jersey; 91, 3, 1993, 42.
8. S.H. Goods, J.J. Kelly, N.Y.K. Yang, Electrodeposited Ni-Mn: an alloy for microsystem applications, Microsystem Technologies, 10, 2004, 498-505.
9. Y.C. Wu, P.J. Ferreira, C.A. Schuh, Nanostructured NiCo alloys with tailorable grain size and twin density, Metallurgica and Materials Transactions, 36A, 7, 2005, 1927-1957.

10. C. Fan, D.L. Piron, Study of anomalous Ni-Co electrodeposition with different electrolytes and current densities, Electrochim.Acta, 41, 1996, 1714-1719.
11. E. Gomez, E. Valles, Electrodeposition of Ni-Co alloys on modified silicon substrates, J. Appl. Electrochemistry, 29, 1999, 805-812.
12. M.E. Soares, C.A.C. Souza, I.A. Kuri, Characteristics of a Zn-Ni electrodeposited alloy obtained from controlled electrolyte flux with gelatin, Mater. Sci. Eng. Ser A, 402, 2005, 16-21.
13. R.R. Vaishaka, A.Ch. Hegde, Role of Cd on corrosion resistance of ZnNi alloy coatings, Surf. Engineering and Appl. Electrochem., 50, 1, 2014, 63-71.
14. V.A. Spiridonov, Electrodeposition of Cr-Co alloy coatings from sulphate electrolytes, Applied electrochemistry and corrosion protection of metals, J.Applied Chemistry, 76, 1, 2003, 65-70, (in Russian).
15. A.A. Edigaryan, Yu.M. Polukarov, The electrodeposition of Co-Cr, ZastitaMetallov, 37, 2, 2001, 115-118, (in Russian).
16. El-F. Hesham, H. Mosaad, R. Sudipta, H. Nadia, A. Baraka, Electrodeposition of Ni and NiCo alloys using cysteine and conventional ultrasound waves, Science China Chemistry, 59, 10, 2013, 1446-1454.
17. S. Basavanna, Y.A. Naik, Study of the effect of new brightener on Zn-Ni alloy electrodeposition from acid sulphate bath, J. Appl. Electrochem., 41, 5, 2011, 535-541.
18. E. Chassaing, Effect of organic additive on the electrocrystallization and the magnetoresistance of Cu-Co Multilayers, J.Electrochem.Soc., 148, 10, 2001, C690-C694.
19. S.K.J. Lenczowski, C. Schonenberger, M.A.M. Gijs, W.J.M. Dejonge, Giant magnetoresistance of electrodeposited Co/Cu multilayers, J. Magn. Magn. Mater., 148, 1995, 455.
20. W. Hansal, B. Tury, M. Halmdienst, M. Versanyi, W. Kautek, Pulse plating of Ni-Co alloys: Deposition kinetic of Watts sulphamate and chloride electrolytes, Electrochim. Acta, 52, 2006, 1145-1151.
21. B. Turi, M. Lakatos-Varsanyi, S. Roy, Microstructure properties of pulse plated Ni-Co alloy, Surf. Coat. Techn., 200, 2006, 6713-6717.
22. G. Chung, W. Chang, Effect of pulse frequency and current density on anomalous composition and nanomechanical property of electrodeposited Ni-Co films, Thin Solid Films, 517, 2009, 4800-4804.
23. K.Y. Sasaki, B. Talbot, Electrodeposition of iron-Group metals and binary alloys from sulfate baths, J. Elecrochem. Soc., 145, 3, 1998, 981-990.
24. N. Zech, E.J. Podlaha, D. Landolt, Anomalous codeposition of iron group metals, I: Experimental results, J. Electrochem. Soc., 146, 8, 1999, 2886-2891.
25. K. Ignatova, Y.S. Marcheva, Electrodeposition and structure of Co coatings (CoCu, NiCo and CoNiCu) in potentiostatic and pulse potential modes, Bulg. Chem. Comm., 45, 2013, 53-59.