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Effect of H_3BO_3 and Na_3citrate on the conditions of electrodeposition of Ni-Co alloy from citrate electrolyte

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The article reports the results from the examination on the effect of background additive (H_3BO_3) and complexation agent Na_3citrate on the type of Ni and Co complexes at either pH=5.0 or pH=7.0. It is found that at pH=5.0 in an electrolyte containing both additives, $NiCit^-$ and $CoCit^-$ prevail (lg $K_{inst(Ni)}$ = -5,379; lg $K_{inst(Co)}$.= -4,38). At pH=7.0, simultaneously with $NiCit^-$, complexes of the type $NiCit_2^{4-}$ and $CoCit_2^{4-}$ with a lower constant of unsteadiness are also formed (lg $K_{inst(Ni)}$ = -8,193; lg $K_{inst(Co)}$.= -7,103).

It was found that the simultaneous presence of H_3BO_3 and Na_3citrate results in increased buffer capacity of the electrolyte compared to that containing the complexation agent (Na_3citrate) only and increases the rate of deposition of Ni and decreases that of Co, which is beneficial for alloy formation. It is proved through SEM images that the addition of H_3BO_3 results in formation of needle-shaped crystals up to 500 nm, as the share of crystals of dimensions below 100 nm increases above 50%. This additive also leads to an increase in the Ni content in the Ni-Co alloy at comparable conditions.

Key words: buffer capacity, potentiometry, cyclic voltammetry, morphology of alloys.

INTRODUCTION

The Ni-Co alloys have been examined for several decades for their unique properties: hardness, wear resistance, heat conductivity [1], electrocatalytic activity [2], as well as for their magnetic properties, whence they are widely used in production of sensors, inductors, recording devices [3].

The choice of electrolyte depends on the intended use of the coating and the associated requirements for its properties. The more important electrolytes for deposition of high quality Ni-Co coatings are sulfamate electrolyte [4] and sulfate electrolyte, chloride electrolyte [3, 5], Watts-type bath [6]. The latter includes boric acid as additive and is recommended for preparation of coatings with low internal tensions.

Both the citrate electrolytes and phosphate electrolytes have a lot of advantages for preparation of coatings with good quality, high content of Ni and high usability of current [7]. Although some disadvantages of those electrolytes are indicated in the reference sources, i.e. low conductance and low stability [7, 15, 19], their obvious advantages in terms of quality of the obtained coatings support the interest in them [8-14]. The citrate electrolytes exhibit complex properties of bleaching [8], structure-defining [9], and buffering [10] agents. The buffering and complexation impacts of the citrate ions are applied in electroless deposition of nickel [11], as well as in electrodeposition of Fe-alloys [12], Ni-W [13] and Cu-Ni alloys [14]. The issue with the use of citrate electrolyte is its instability [15]. It is found in case of electrodeposition of Cu-Ni alloy that the electrolytes with pH<4 are unstable. In an electrolyte with $pH \approx 6$, soluble $NiCit^-$complexes are formed (lg K_{inst} = -5.35), as the solution remains stable for a few weeks and can be used for deposition of Cu-Ni alloys at almost 100% usability of current [15]. Some authors have obtained very helpful results for the values of the stability constants of nickel [16] and cobalt [17] with the citrate ions. Thus, according to [16], at pH<4.5 the forms Ni^{2+} and NiHCit prevail in citrate solutions, correspondingly the forms being Co^{2+} and CoHCit [17] in the case of cobalt. When pH increases to 5÷6,5, ions of the type $NiCit^-$ (lgK_{st}= 5.35) are present, correspondingly $CoCit^-$ (lgK_{st}= 4.63) [17]. According to another source [15], when pH increases to about and above 7, complexes of the type $NiCit_2^{4-}$ (lgK_{st}= 8.11) are formed, as increasing the share of less soluble forms like $Ni(OH)SO_4^-$ is also possible.

The conclusion from the review of the literature suggests that the electrodeposition of Ni-Co alloy in

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presence of each of H_3BO_3 and Na_3 citrate is widely investigated and discussed in the literature but there are fewer and incomplete data for their joint influence on the electrodeposition of Ni-Co. That is why we set the goal in this paper to investigate the joint effect of H_3BO_3 and Na_3 citrate on the complexation of Ni and Co, as well as their buffer effect on the kinetics of deposition of the metals.

EXPERIMENTAL DETAILS

The experimental research is carried out in a three-electrode cell of total volume 150 dm^3 at room temperature (18-20^o C). In order to examine the kinetics of deposition, we used disk-shaped cathodes of electrolytic copper (by kinetics examination), Ni-plated and Co-plated copper (by the potentiometric method) with surface area of 1 cm^2. The surface of the platinum anode is ≈ 30 times larger than that of the working electrode. Saturated calomel electrode (SCE) is used as a comparative electrode (E_{SCE} = 0.241 V). The surfaces of the copper cathodes are prepared beforehand through polishing, etching in especially prepared etching solution for copper, and washing with double distilled water. Prior to each experiment, the anode is cleaned in hot 1M HNO_3 and then is washed with water. The impact of H_3BO_3 and Na_3citrate on the kinetics of deposition of Ni and Co is examined on the following compositions of electrolytes:

For cobalt: **1:** 0.2M Co (as $CoSO_4.7H_2O$), background of 0.2 M Na_3citrate (as Na_3 citrate. H_2O) and 0.485M H_3BO_3; **2:** 0.2M Co,background of 0.2M Na_3citrate; **3:** 0.2M Co, background of 0.485M H_3BO_3.

For nickel: **1*:** 0.2M Ni (as $NiSO_4.2H_2O$), background of 0.2 Na_3citrate, M and 0.485M H_3BO_3; **2*:** 0.2M Co, background of 0.2M Na_3 citrate; **3*:** 0.2 M Co, background of 0.485M H_3BO_3.

The data for the buffering behavior of each solution were obtained through pH-metric titration and building the dependencies pH-$V_{0,5MNaOH}$.

The constants of instability of the citrate complexes of Ni and Co were determined through application of a potentiometric method, whilst having in mind that this method does not yield precise data regarding the internal mechanism of building complexes. The potentiometric method is based on measurement of equilibrium potentials of the working electrodes (Ni-plated copper for Ni-electrolytes and Co-plated copper for Co-electrolytes, thickness of 4-5 µm) both in presence and in absence of complexation agent, i.e. citrate ion introduced as Na_3 citrate with increasing concentration (0.0M; 0.1M; 0.2M; 0.3M and 0.4M). The difference ΔE^{k-o} between the potentials in presence and in absence of complexation agent at i=0 is related to the constant of instability of the complex $Me_x[Cit]_y$ upon the equation:

$$\Delta E^{k-o} = E^k - E^o = \frac{0,058}{n}.\lg K_{inst} - y.\frac{0,058}{n}.\lg C_{cit}, (1)$$

After building the dependencies ΔE^{k-o}– $\lg C_{cit}$ according to equation (1), we obtain the constant of instability, K_{inst} , from the segment at $\lg C_{cit}$= 0.

The kinetics of deposition was examined by linear and cyclic chronovoltammetry using the Wenking Electrochemical Analysis System (Germany). The rates of potential scanning applied are v=30mV s^{-1}.

The morphology of Ni-Co alloys was examined by means of a Scanning Electron Microscope (SEM) with equipment of Oxford Instruments, JSM-6390-Jeol.

RESULTS AND DISCUSSION

Potentiometric determination of the type and stability of the complexes of Ni and Co

With the increase in Na_3 citrate concentration from 0.0 to 0.4M (with a step of 0.1M), the equilibrium potentials of the Ni-plated copper electrode for Ni-electrolytes and Co-plated copper electrode for Co-electrolytes and the differences in electrolytes containing only Ni or only Co at pH=5.0 and pH=7.0 were measured.

The dependencies ΔE^{k-o}– $\lg C_{cit}$ are displayed in Fig. 1. The constants of instability of the complexes of Ni and Co were computed from the segments of the obtained straight lines at lg C_{cit}=0 and after comparing the values obtained with the reference data [15-17] we can make a suggestion about their possible structure. The final results are displayed in Table 1.

As is seen from the results in Table 1, at pH=5.0 the prevailing complex in the electrolyte for deposition of Ni is $NiCit^-$ $(\lg K_{inst} = -5,379, K_{inst} = 4,18.10^{-6})$; and at pH=7.0 the complexes of the type $NiCit_2^{4-}$ with lower constant of instability lg K_{inst} = -8,193; $K_{inst(Co)}$.= 6,0.10^{-9} prevail. These results agree well with the reference data [15, 16]. The latter also suggest that with the increase in pH, it is possible that the complexes turn into insoluble forms of the type $Ni(OH)SO_4^-$, thus decreasing the stability of the solutions. The data obtained for cobalt indicate the formation of the same complexes as is the case with nickel, as a certain difference between the values of the constants of instability is observed (Table 1).

Based on the results obtained we can draw the important conclusion that at pH=5.0 and pH=7.0 the complexes of Ni exhibit higher stability compared to those of Co, although the difference is not very large. This can be one of the reasons leading to greater difficulties in the deposition of Ni compared to that of Co and consequently to the anomalous co-deposition of both metals in the alloy that we found. As a basis for these conclusions not only the voltammograms, but also the data for the chemical content of the Ni-Co alloy [20] are used.

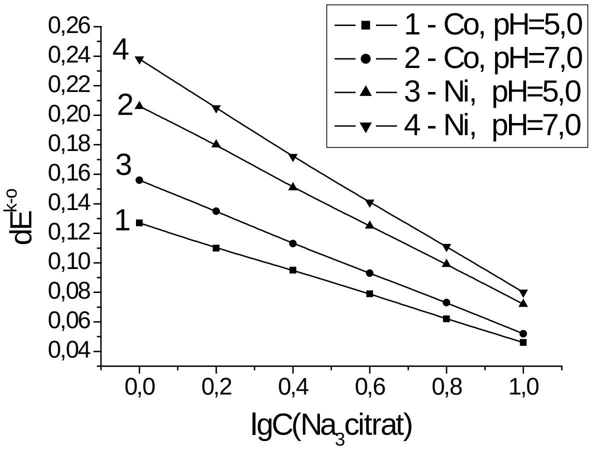


Fig. 1. Dependence $\Delta E^{k\text{-}o}$– lgC_{cit} in electrolytes of compositions: **0.2M Co**; 0.485M H_3BO_3 (curve 1 for pH=5 and curve 2 for pH=7), and **0.2M Ni**; 0.485M H_3BO_3 (curve 3 for pH=5 and curve 4 for pH=7).

The results obtained are in accordance with the data given by Golodnitsky [4] for the difference between the electronic structures of Co(II) and Ni(II) and the instability of their aqueous complexes based on the ligand field theory. This is also consistent with the conclusions made by Vazquez-Arenas and Pritzker [18] regarding the rate constants for aqueous phase exchange and substitution reactions of complexes containing Fe(II), Co(II), and Ni (II).

Effect of the background additive (H_3BO_3) and Na_3 citrate on the buffer capacity of the electrolyte

In order to ascertain the buffer capacity of the background additive H_3BO_3 and the complexation agent Na_3 citrate, the electrolytes for self-deposition of Co (1-3) and Ni (1*-3*) with contents presented in Section 2 were subjected to pH-metric titration with 0.5M NaOH. The dependencies obtained are presented in Fig. 2. The data indicate that when only H_3BO_3 is present in the electrolyte (Fig. 2, curves 3,3*), the buffer capacity of the Co- and Ni-solutions is insignificant and pH increases rapidly after addition of small quantities of NaOH. In the electrolyte with addition of 0.2M Na_3citrate only (curve 2 for Co and curve 2* for Ni), the buffer capacity rapidly increases, which is more pronounced in the case of Co (Fig. 2, curve 2). In this case pH remains constant at values about 5.0 and in the range 5.5-6.0. There is a slight retention of pH about 5.5, and 6.0, and at 6.5.

The behavior of the electrolytes for deposition of Ni and Co in presence of the two additives (Fig.2: curve 1 for Co and curve 1* for Ni) is also of interest. In this case, the solutions exhibit maximum buffer capacity, which is demonstrated by the slight increase of pH with addition of 0.5M NaOH.

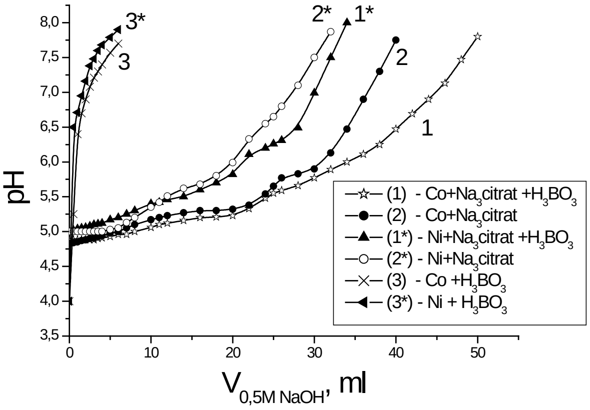


Fig. 2. pH - $V_{0,5M\,NaOH}$ dependencies in electrolytes for self-deposition of Co (**1-3** electrolytes) and Ni (**1*-3***electrolytes).

The results obtained evidence that the addition of 0.485M boric acid to the citrate electrolyte enhances the buffer capacity of the electrolyte.

Our observations also indicate that in case of continuous operation, the electrolytes containing boric acid remain stable longer (up to 4-5 weeks) than in the case without boric acid (up to 1-2 weeks).

Table 1. Constants of instability determined from the experimental data and from the references.

pH	$\lg K_{unst}(Co_xCit_y)$	$\lg K_{unst}(Ni_xCit_y)$	Reference
5.0	-4.38	-5.379	[17](Co)
Complex →	$CoCit^-$	$NiCit^-$	[15,16] (Ni)
7.0	-7.103	-8.193	[17](Co)
Complex →	$CoCit_2^{4-}$	$NiCit_2^{4-}$	[15,16] (Ni)

This is valid especially for the electrolyte for Co deposition without boric acid in which sediment is formed within less than 2 weeks after preparation. The reason for such behavior of the solution can be justified by comparing the obtained data to the type and stability of the complexes of nickel and cobalt ions with citrate ions (Table 1) and the curves in Figure 1.

Introduction of boric acid in the citrate solution more reliably maintains the pH within the range where the soluble complexes of the metals prevail: at pH=5.0 they are CoCit^- and NiCit^-. In case of continuous operation, pH within the space around the electrode increases due to the parallel reaction of hydrogen evolution on the cathode. In absence of boric acid, a more rapid increase of pH is possible, as it reaching values about and above 7.0 leads to formation of not only soluble complexes of the metals CoCit_2^{4-} and NiCit_2^{4-}, but also to formation of less soluble forms of the type $\mathrm{Co(OH)SO_4}^-$ or $\mathrm{Ni(OH)SO_4}^-$, as [15,16] indicate. That justifies the necessity of working with citrate electrolytes with addition of boric acid, which is an important circumstance that we have to consider during the final optimization of the electrolyte.

Effect of the background additive (H_3BO_3) and Na_3 citrate on the kinetics of self-deposition of Ni and Co

The influence of the presence of H_3BO_3 and Na_3 citrate on the kinetics of self-deposition of Ni and Co in the citrate electrolyte was examined. The cyclic voltammograms in the range of potentials from 0.6 V to -2.0 V in electrolytes for deposition of Ni (Fig. 3) and Co (Fig. 4) with addition of boric acid only (Figs. 3,4 curve 3); Na_3citrate only (Figs. 3,4 curve 2); and with both H_3BO_3 and Na_3citrate (Figs. 3,4 curve 1) are shown. The voltammograms obtained indicate a characteristic impact of each background additive on the kinetics of self-deposition of the metals.

Self-deposition of Ni

In the case of Ni (Fig. 3) in presence of boric acid only (curve 3), a long initial polarization is observed. Then the current increases slightly and reaches a plateau at about -1,5V (SCE). In presence of Na_3 citrate only (curve 2), the curve passes through two cathode peaks, i.e. at about -0.300 V and -1.150 V. The first cathode peak is associated with the induction of copper ions obtained at high anode potentials. This peak is reproduced even after a few cycles of the curve (4-5), which is not typical for the rest compositions of the electrolyte. The second cathodic peak at 1.150V is associated with the reduction of the nickel complex ions to nickel. The deposition of nickel proceeds at low rate andaccording to our observations at those high enough cathodic potentials, the coating on the cathode has low density and adhesion and is virtually almost absent. The copper electrode remains active within almost the whole range of potentials. There are two consecutive retentions occurring in anode direction: at -0.200 V and at 0.100 V, that might be associated with the solution of nickel and copper correspondingly. As a whole, in the electrolyte containing no H_3BO_3 but only Na_3 citrate, the surface is active and sufficiently dense Ni coatings are not formed.

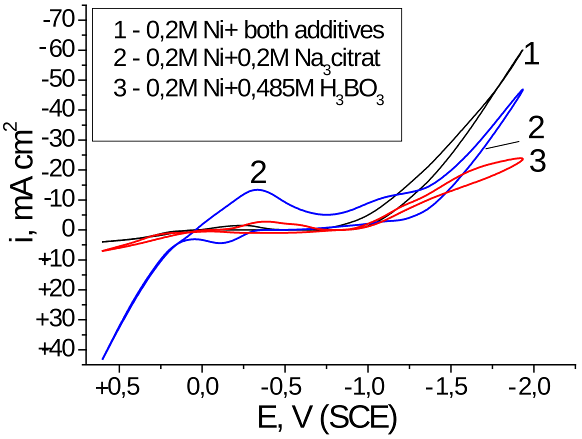


Fig. 3. Voltammograms (v=30 mV/s) in electrolyte for self-deposition of Ni in presence of the different background additives (1 – electrolyte 1*; 2 – electrolyte 2*; 3 – electrolyte 3*).

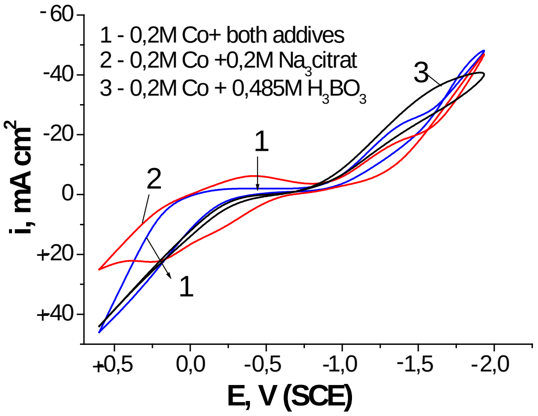


Fig. 4. Voltammograms (v=30 mV s^{-1}) in the electrolyte for self-deposition of Co in presence of the different background additives (1 – electrolyte **1**; 2 – electrolyte **2**; 3 – electrolyte **3).**

In presence of both H_3BO_3 and Na_3 citrate simultaneously in the electrolyte for deposition of Ni (Fig. 3, curve 1), the dependence features long cathodic and anodic polarization, and absence of cathodic and anodic peaks, which most probably suggests a completely different control of deposition, and most probably an activation one. There is a decrease of the total polarization observed, which is also associated with the evolution of hydrogen together with nickel. Visually, a dense nickel coating with high adhesion is observed on the cathode in case of retention of the cathodic potential at high values above -1,250 V (SCE).

Self-deposition of Co

In an electrolyte for self-deposition of cobalt (Fig.4), the typical impact of each additive is also observed. In presence of boric acid only (Fig. 4 curve 3), the lowest total and initial polarization and the highest currents are achieved. This impact is completely opposite to that of boric acid on deposition of Ni (Fig. 3, curve 3). In presence of Na_3 citrate only (Fig. 4, curve 2) the curve passes through two cathodic peaks at about -0,300 V and -1,150 V, like in the case with the nickel electrolyte (Fig. 3, curve 2). In case of cobalt, the first plateau is the result of reduction of copper ions obtained at the high anodic potentials and the second is the result of deposition of cobalt. In the anodic direction, two subsequent retentions of the current are obtained at -0.300 V and at 0.100 V, which might be associated with the solution of cobalt and copper, correspondingly. In the electrolyte containing Na_3 citrate only, the cobalt coatings deposited at high cathodic potentials, unlike the nickel coatings deposited in the same conditions, are dense and have a very good adhesion which is demonstrated in their difficult dissolution through etching.

In presence of H_3BO_3 and Na_3citrate (Fig. 4, curve 1) in the Co solution, the curve passes through a long initial polarization and a plateau at -1,250V, as the rate of the process of cobalt deposition is lower in comparison with that in presence of boric acid only. This is an evidence for the formation of stable citrate complexes of Co with a rate of reduction lower than that of the single cobalt ions only.

These difficulties in the deposition of cobalt associated with the complex formation in presence of citrate ions could result in formation of a fine grain structure of the coatings in presence of the total background (with both additives).

Determination of the conditions for deposition of Ni-Co alloy

Based on the data above proving the advantages of the simultaneous presence of H_3BO_3 and Na_3 citrate, the conditions for co-deposition of the two metals are determined in this electrolyte. For this purpose, the voltammograms in electrolytes for self- and co-deposition of Ni and Co are taken in comparable conditions and the deposition potentials of the metals are registered in both cases.

The cyclic voltammograms in electrolytes at the same rate of potential scanning v= 30 mv s^{-1} are presented in Fig. 5 (c.1 for Ni; c.2 for Co; c.3 for Ni-Co).

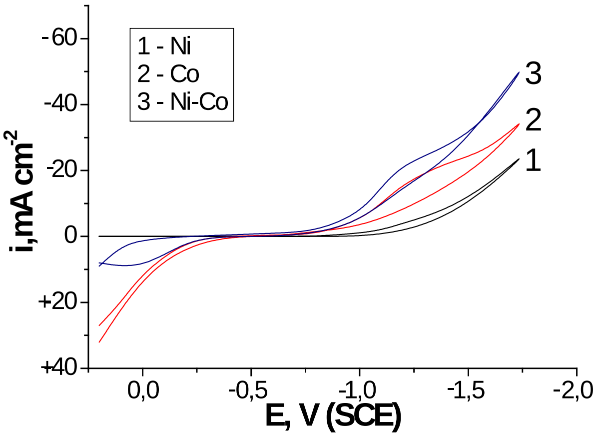
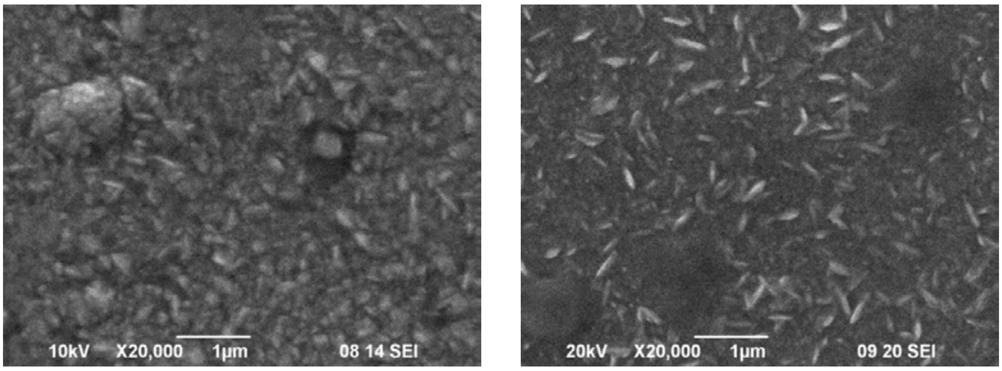


Fig. 5. Voltammograms in electrolytes for self-deposition of Ni in electrolyte **1*** (1); of Co in electrolyte **1** (2); and of Ni-Co in electrolyte composition: 0,2M Ni; 0,2M Co; 0.2M Na_3citrate and 0.485M boric acid, pH=5÷5,5 (v= 30 mV s^{-1}).

The comparison of the dependencies obtained indicates that in the electrolyte for self-deposition of Ni (Fig. 5, curve 1), long initial cathodic and anodic polarizations are observed; however in the case of cobalt both polarizations are lower and the current begins to increase in anodic direction at -0,250V (SCE), which is associated with its anodic increase (Fig.5, curve 2). In the curve for co-deposition of the two metals (Fig.5, curve 3), the anodic current increases at the same potential which means that Co first begins dissolving from the two metals deposited in the alloy. The initial increase of the current associated with the beginning of deposition of the metals points to anomalous deposition, which is characteristic for both electrolytes examined [14] and the alloys from the iron group as a whole [12-14]. Thus the potential for beginning the deposition of Ni is about -1,150V (SCE), while that of deposition of Co is about -0,980 V(SCE), i.e. more positive than the dynamically predetermined potential of Ni. The reasons might be associated with the larger difficulties for deposition of Ni in the composition examined related to the determined higher stability constants. The reasons for the long initial polarization in case of Ni compared to that of cobalt are the possible adsorption processes of the citrate complexes of Ni and even of hydrocitrate nickel compounds with low solubility.



(a) (b)

Fig. 6. SEM images of Ni-Co coatings in an electrolyte containing: 0.2M Ni, 0.2M Co, 0.2M Na_3 citrate: (a) in absence of H_3BO_3 and (b) in presence of 0.485M H_3BO_3 , pH=5÷5.5 at E=-1.250 V (SCE); Elemental composition of Ni-Co alloys: (a) 86.79wt% Co-13.21wt% Ni; (b) and (b) 81.15wt% Co-18.85wt% Ni.

The greater difficulties during the deposition of nickel compared to cobalt and the conditions when that difference was the largest constituted the base for optimization of the content of citrate electrolyte. It was found in the course of the examinations that the ratio of concentrations of Na_3 citrate and each metal ($C_{Na_3citrat}/C_{Me^{z+}}$) should not exceed 1 in order to allow their deposition in coatings. In case $C_{Na_3citrat}/C_{Me^{z+}} > 1$, the deposition of the metals and especially the deposition of Ni is extremely difficult and practically does not occur. The increase in concentration of the components up to 0.3M and maintaining the concentration 0.2M for the sodium citrate is beneficial for both the stability of the electrolyte and the deposition of metal itself. The positive influence of boric acid on the stability of the electrolyte and the quality of coatings proven during the examination point to the following optimal content: 0.2÷0.3M Ni; 0.1÷0.3M Co; 0.485M H_3BO_3 and 0.2M Na_3citrate, pH=5÷5.5.

Effect of boric acid on the morphology of the Ni-Co coatings

In Fig. 6 the SEM images of Ni-Co coatings deposited in stationary potentiostatic mode at potential E= -1,250 V (SCE) in electrolyte in absence of boric acid (Fig. 6,a) and in presence of 0.485M boric acid are shown (Fig. 6,b). The images taken indicate that the presence of boric acid leads to formation of a more fine-grain structure, as the share of smaller size crystals greatly increases (Fig. 6,b). The higher density of distribution of crystals in the presence of boric acid can explain the resistance of the coatings against etching, i.e. their better adhesion.

CONCLUSIONS

The type and stability of the citrate complexes of Ni and Co at two values of pH are determined. It is found that the simultaneous presence of H_3BO_3 and Na_3citrate increases both the buffer capacity of the electrolyte and its stability during extended operation. It is shown that each additive has a characteristic impact on the kinetics of deposition. The presence of H_3BO_3 in the citrate electrolyte increases the rate of deposition of Ni and Co, which has beneficial effect on the alloy formation. It is found through SEM images that the addition of H_3BO_3 leads to more than 50% increase of the share of crystals with dimensions less than 100 nm. The addition of H_3BO_3 leads to about 6% increase of Ni content in comparable conditions.

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ЕФЕКТ НА H_3BO_3 И Na3 ЦИТРАТ ВЪРХУ УСЛОВИЯТА НА ЕЛЕКТРОЛИТНО ОТЛАГАНЕ НА Ni-Co СПЛАВИ ОТ ЦИТРАТЕН ЕЛЕКТРОЛИТ

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(Резюме)

В статията се докладват резултатите за влиянието на H_3BO_3 и комплексообразуващия агент Na_3цитрат върху вида на комплексите на Ni и Co при две стойности на pH (5,0 и 7,0). Установено е, че при pH=5,0 в електролит, в който присъстват и двете добавки преобладават комплекси от типа NiCit^- и CoCit^- $(\lg K_{unst(Ni)} = -5{,}379 \quad и \quad \lg K_{unst(Co)} = -4{,}38)$. При pH=7,0, заедно с NiCit^- се образуват комплекси от вида NiCit_2^{4-} и CoCit_2^{4-} с по-ниска константа на неустойчивост $(\lg K_{unst(Ni)} = -8{,}193 \quad и \quad \lg K_{unst(Co)} = -7{,}103)$.

Установено е, че присъствието на H_3BO_3 едновременно с Na_3цитрат повишава буферния капацитет на електролита в сравнение с електролит, в който присъства само Na_3цитрат. Особено силен е този ефект в електролит за самостоятелно отлагане на Co. Чрез снемане на циклични хроноволтамперометрични зависимости е показано, че присъствието на H_3BO_3 едновременно с Na_3цитрат повишава скоростта на отлагане на Ni в по-висока степен, отколкото на Co, което има за ефект повишаване на процента на никел в сплавта. Чрез SEM е установено, че добавката от H_3BO_3 води до формиране на кристали с игловидна форма с размери до 500 nm. Делът на кристалите с размери под 100nm нараства до над 50%. Добавката на H_3BO_3 води и до нарастване съдържанието на Ni с около 5 % при съпоставими условия.