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# Electrodeposition and structure of Co coatings (CoCu, NiCo and CoNiCu) in potentiostatic and pulse potential modes

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The kinetics of the individual deposition of Cu, Co and Ni as well as the alloy deposition of CoCu, NiCo and NiCoCu in the slightly acidic citrate electrolyte (pH= 5,5) was investigated. Data about the alloy deposition in pulse potentiostatic mode at different pulse frequencies was received also. The morphology and the elemental composition of the coatings (using SEM and EDSA analysis) at stationary and pulse mode were compared. At potentiostatic conditions the produced coatings have average grain size of 250 to 500 nm and Co content up to 85 wt.%. Using the pulse mode of deposition decreases the grain size and the Co content was up to 76 wt.% for the three alloys. Applying the pulse frequencies up to 500 Hz for CoCu alloy lowers the grain size under 100nm (60-70 wt.% Co). At the same conditions the coatings of CoNi and CoNiCu have rounded grains with average grain size about 200-300 nm. The X-ray analysis show that the binary alloys CoCu and NiCo are two-phased, composed from Co, Cu (in CoCu) and Ni and Co (in NiCo) with face centred cubic lattice (f.c.c.). Only in the ternary alloy coating of Co-Ni-Cu, a presence of cobalt-containing phase with hexagonal crystal lattice (h.p.c.) was ascertained also together with the cubic phases.

**Key words**: constant and pulse potential modes, nano-structured alloys, morphology, phase composition.

## INTRODUCTION

Due to their high hardness, wear resistance, endurance and corrosion resistance, the cobalt alloys are widely used in medicine, in nuclear-power systems, chemical- and oil industry etc. The particular interest towards nano-sized Co alloys is due to their increasing application in magnetosensor technologies and magnetoelectronics where miniaturization of items is the underlying purpose [1-6].

Presence of Cu in Co crystallities makes the spectra of electrical resistance of the deposits wider and as result widening of their magnetic properties [4]. Recently, electrodeposits of Co and CoCu alloys have attracted intensive interest because of their wide use as magnetic materials in electronic devices for data saving, as electrical resistance devices and in semiconductor technologies but the electrocrystallization of CoCu alloy has been considered little so far [11]. Low amounts of Ni in CoCu alloy system can improve the properties of the thin films and can favour the segregations of small ferromagnetic particles and increase the magnetoresistance of the ternary CoNiCu coatings; decreases the stress in the copper/ ferromagnetic interface and can improve the corrosion resistance of the deposits [6]. The possibility for deposition of CoNiCu alloy coatings is proposed as alternative to Cu-Co -Ni/Cu multilayer preparation [12].

Recently, pulse electrodeposition has received considerable attention for synthesis of nanocrystalline and amorphous alloy coatings [7]. The advantage of the pulse over stationary electrodeposition is that the properties of the deposit could be improved by control of pulse parameters, which gives a possibility for producing of nanostructured coatings [8]. Pulse electrodeposition can be used as a means for producing the coatings with properties unachievable by stationary deposition. Plating at extremely high amplitude polarization gives conditions for non-equilibrium growth of the coating, which may results in changes of the alloy phase composition and formation of unusual (anomal) metastable structures [8-10].

The electrodeposition of Co and Co-Cu coatings was studied using sulphate [8, 11, 12], citrate [13-15] and sulfamate [16] baths. Several authors studied the pulse plating of CoCu alloys [10]. The CoNi coatings were deposited mainly from sulphate [17] and citrate [6, 18, 19] electrolytes.

The growing interest in using citrate electrolyte in recent years was determined because of its ability to serve as buffer, to form complexes, and to add coating lustre, thus avoiding the need of introduction of special organic additives in the

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electrolyte [18]. The difficulties in using citrate electrolytes come from its stability, which depend strongly on pH.

The magnetic properties of electrodeposited Co films can be correlated with their structure and plating conditions [7]. The electroplating parameters effect on the structure and growth modes of Co, CoCu [12] and CoNi [2, 4, 5] that is why a great interest exists to investigate the relation between the plate parameters, coatings structure and coating properties [11, 14, 21-24]. Anomalous galvanostatic deposition in gluconate bath of CoNi [20] and potentiostatic deposition of CoNi and CoNiCu [14] in citrate bath were performed. It was established formation of CoNi solid solution with hexagonal close packed lattice (hcp) [5] and solid solution of NiCoCu with face centred cubic lattice (fcc) [14].

In our previous study [25] some preliminary results concerning the possibility for codeposition of CoNi and CoNiCu alloy coatings in slightly acid citrate electrolyte were presented.

The present paper resumes the conditions of electrodeposition of the CoCu, CoNi and CoNiCu coatings and the effect of the mode of deposition (potentiostatic and pulse potentiostatic modes) on the structure (morphology, elemental and phase composition) of the alloy coatings.

## EXPERIMENTAL

The experimental setup consisted of a three-electrode cell (total volume 150 $dm^3$) with disk-shaped cathode (surface area 1$cm^2$) from pure electrolytic copper and Pt plate anode. The surface area ratio anode: cathode was 30:1. The reference electrode was saturated calomel electrode (SCE). The experiments were conducted at room temperature (20°C ±1). Before the experiment the cathode surface was etched in acid etching solution and washed with distilled water. The anode was cleaned in hot 1n $HNO_3$ and washed with distilled water.

The experiments were conducted in slightly acid citrate baths with composition as follows: 0.025M Cu (as $CuSO_4$ $5H_2O$); 0.32M Co (as $CoSO_4$ $7H_2O$); 0,38M Ni (as $NiSO_4$ $H_2O$); 0.2M $Na_3$ citrate ($Na_3C_6H_5O_7$); pH = 5,3-5,5. The pH was adjusted using NaOH and $H_2SO_4$ and measured using pH-meter.

The kinetics of deposition was studied using a method of potentiodynamic polarization curves (potential sweep rate 30 $mVs^{-1}$) using a potentioscan Wenking. The pulse electrodeposition of the coatings was carried out using pulse potential with rectangular shape, generated by pulse generator, connected to the input of a specially designed potentiostat, connected to the three-electrode cell. The average values of the polarization, $\Delta\bar{E}$, (calculated as a difference between the potential at the current and the equilibrium potential) and the average current, $I_{av}$, were measured using digital voltmeter with high input resistance and miliammeter. The amplitude values of the polarization, $\Delta E_p$, were controlled using an oscilloscope.

The relation between the average ($\overline{\Delta E}$) and amplitude ($\Delta E_p$) polarization values at potentiostatic rectangular pulse conditions is: $\Delta\overline{E} = \theta.\Delta E_p$ , where $\theta = \frac{\tau_p}{\tau_p + \tau_z}$ , $\tau_p$ - pulse time, and $\tau_z$ – time between the pulses. At each pulse frequency ( $f = \frac{1}{T}, Hz, T = \tau_p + \tau_z$ ), and $\theta = 0{,}5$ the relations $\Delta\overline{E} - I_{av}$ and $\Delta E_p - I_{av}$ were calculated. Data about the average polarization ($\overline{\Delta E}$) and the amplitude values of the polarization ($\Delta E_p$) as a function of applied pulse frequencies for the same value of the average current density were compared.

The morphology and the elemental composition (in wt %) of the coatings were determined using scanning electron microscope (SEM) with Energy Dispersive Spectral Analysis (EDSA) - equipment of Oxford Instruments JSM-6390 – Jeol.

The phase and crystal structure of the coatings were investigated using automatic Philips PW 1050 X-Ray diffractometer, equipped with secondary graphite monochromator for Cu K$\alpha$ radiation, and scintillation counter. The diffractograms were recorded in 2θ range from 10° to 100° with a step length 0.04° and a counting time of 1s per step.

## RESULTTS AND DISCUSSION

### *Individual deposition of Cu, Ni and Co at potentiostatic mode.*

The dependences of the individual deposition of Cu (curve 2), Ni (curve 3) and Co (curve 4) onto Cu surface (S= 1$cm^2$), compared to the polarization dependence in background electrolyte (0,2m $Na_3$citrat, curve 1), are presented in Fig.1.

The polarization curve, received in the background electrolyte shows wide polarization up to potential -1,4V; the following current growing is due to the hydrogen evolution on the electrode. When 0,025m Cu was introduced in the electrolyte the increasing of the current begins at potential -

0,96V and the polarization curve has two steps. The processes in the bath for Cu deposition include two stages of electrons transfer, the second one is the real copper deposition (at -1,35 V). Between the two, a chemical stage exists, related to the reaction of disproportion of the copper. This mechanism was proved in Cu deposition from ammonium-nitrate electrolyte [26], as well as in other Cu electrolytes [27].

The polarization curves for individual electrodeposition of Ni and of Co have only one plateau of the limiting current, related to the reduction of the metallic ions. The voltammerograms at different potential sweep rate [25] have shown that in both cases a part of the polarization has a diffusion reason, but in the Ni electrolyte the activation part is prevailed.

The electrodeposition of Ni begins at potential -1,1V and of Co at -1,2V (Fig.1).

In the studied electrolyte the continuity of the electrodeposition of the metals under applying of sufficiently high cathodic potential is Ni – Co – Cu (Fig.1).

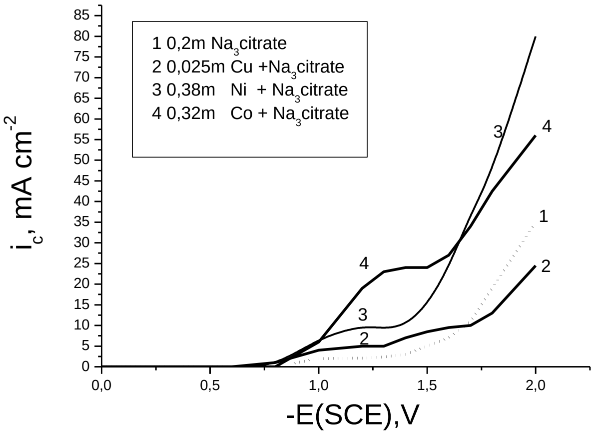


**Fig.1** Polarization curves in background electrolyte (0,2m Na$_3$citrat, pH=5,5) – (1); of individual deposition of Cu (2), Ni (3) and Co (4) in electrolytes with content: 0,025M Cu(1); 0,38M Ni(2) and 0,32M Co(3) all with 0,2M Na$_3$citrat; v = 30 mV.s$^{-1}$.

### *Electrodeposition of CuCo, NiCo CoNiCu alloys at potentiostatic mode*

Fig.2 represents voltammograms (potential sweep rate 30 mVs$^{-1}$) of deposition of Co-Cu (2), Co-Ni (3) and Co-Ni-Cu (4) alloys. With the aim of comparison, the dependence in the background electrolyte is shown as a curve 1.

The lowest values of the limiting current were established for the electrolyte, containing simultaneously Co and Cu (2). In all studied electrolytes for alloy deposition, the range of potentials was overlapped with this one for the pure metal deposition. The alloy coatings of Co-Cu, Co-Ni and Co-Ni-Cu with high quality in the studied electrolyte can be deposited in the range of potentials respectively -1,13V ÷ -1,3V (SCE);-1,2V ÷ -1,4V (SCE) and -1,25V ÷ -1,35V (SCE).

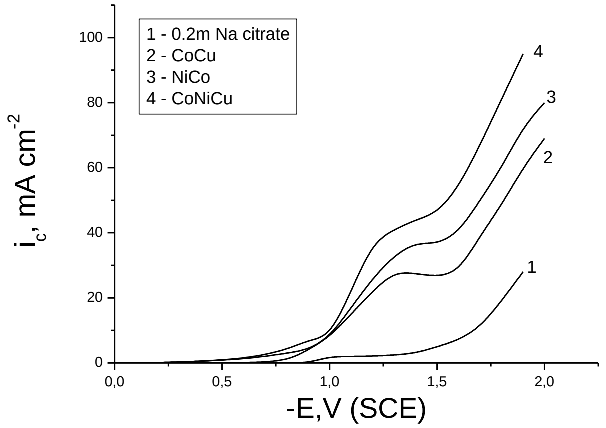


**Fig. 2.** Polarization curves in background electrolyte (0,2M Na$_3$citrat, pH=5,5) – (1) and in electrolytes for deposition of CoCu (2); NiCo (3) and NiCoCu (4). Content of electrolytes: 0,025M Cu(2,4); 0,38M Ni(3) and 0,32M Co(2-4) all with 0,2M Na$_3$Citrat; v = 30 mV.s$^{-1}$.

### *Pulse deposition*

In the values of the average and amplitude polarization the ohmic drop in the solution (between Lugin capillary and working electrode), as well as polarization, used for Double Electrode Layer (DEL) charging are included. While the first goes to negligible values as the polarization increase, the second one is significant and is about 1/3 of the total polarization, especially at frequencies over 1 000 Hz. At these frequencies the pulse time is of the same order as the time for DEL charging ($\tau_p << 0,5ms$), that is why an assumption exists that at frequencies over 1 000Hz the plating is no effective. Nevertheless, frequencies of 5 000Hz and even 10 000Hz were applied with the aim the change in the structure of the Co alloys at these unusual conditions to be established.

Data about the average polarization ($\overline{\Delta E}$) and the amplitude values of the polarization ($\Delta E_p$) as a function of applied pulse frequencies (from 100 Hz to 2500 Hz at $\theta = 0,5$), are shown in fig. 3. Data was read in the three electrolytes for deposition of CoNiCu (curves 1,1*), CoNi (curves 2,2*), CoCu (curves 3,3*) for the same value of the average current density (30 mAcm-2). The same dependence was established at each value of the cathodic current density, higher than the showed. On the same figure the value of the polarization at the same current density in the stationary conditions is given.

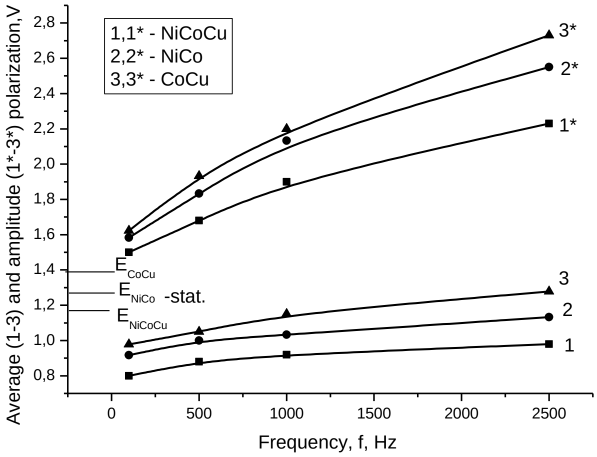


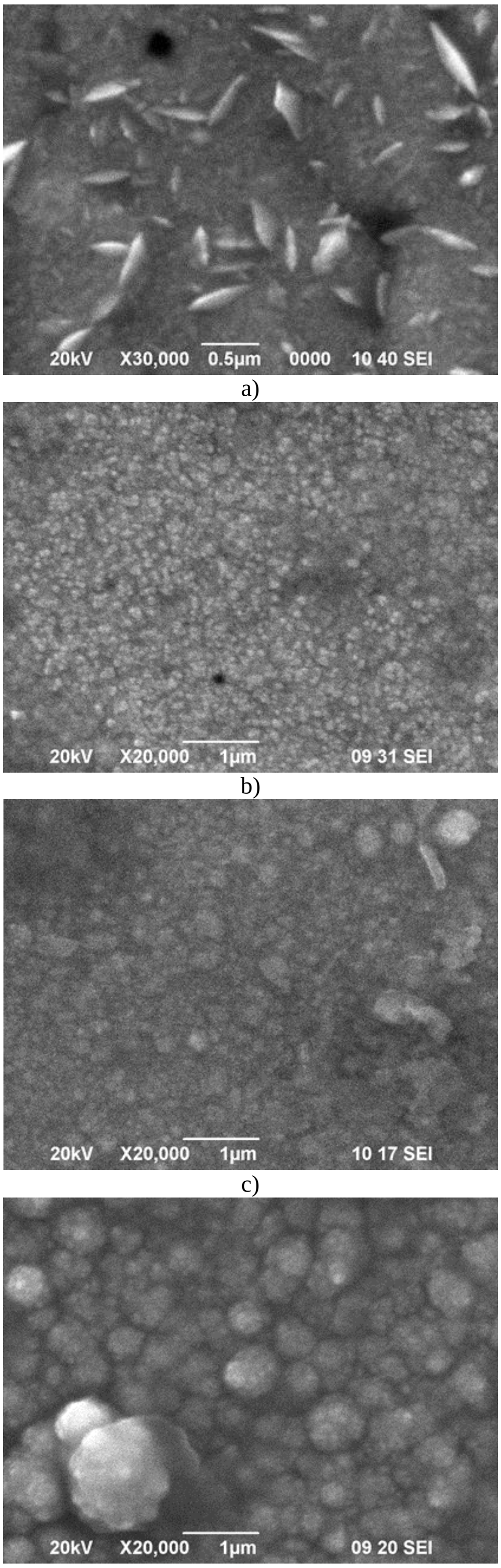
**Fig. 3.** Current densities reached at different vertex potentials on Pt cathode in electrolytes, containing: 1) $Cu^{2+}$ - 1 g/L and $Zn^{2+}$ - 50 g/L, 2) $Cu^{2+}$ - 1 g/L, $Zn^{2+}$ - 50 g/L and Ferasine 1 mL/L, 3) $Cu^{2+}$ - 1 g/L, $Zn^{2+}$ - 50 g/L and $H_2SO_4$ – 130 g/L, 4) $Cu^{2+}$ - 1 g/L, $Zn^{2+}$ - 50 g/L, $H_2SO_4$ – 130 g/L and Ferasine - 1 mL/L.

With the raise of pulse frequency from 100Hz to 2500 Hz the measured average polarization in the three electrolytes (Fig.3, curves 1-3) is lower than this one in stationary condition, which may be explain with a possible decreasing of the diffusion limitations as a result of diffusion gradient relax during the time of pauses – effect, more important at low frequencies. At the same time, with the rise of the pulse frequency in the studied range, the amplitude values of the polarization increase almost twice (Fig.3, curves 1* -3*). As the polarization may be used as a measure for oversaturation, it is awaited to reach more fine-structured coatings when apply higher frequencies especially in the range 100Hz to 1 000Hz.

At the frequencies over 2 500Hz the tendency towards lower average polarization than this one in stationary condition was kept, but the "useful" part of the measured total polarization (used for the alloy deposition) decrease and the part for DEL charging increase.

### *Morphology and elemental composition of CoCu, NiCo and CoNiCu coatings.*

Fig.4-6 show the SEM images of the CoCu (Fig.4), CoNi (Fig.5) and CoNiCu (Fig.6) coatings. The applied potentials, respectively polarizations, correspond to the same value of current density, which however is different for each type of coating (28 mA.cm$^{-2}$ for CoCu, 35 mA.cm$^{-2}$ for NiCo and



a)
b)
c)
d)

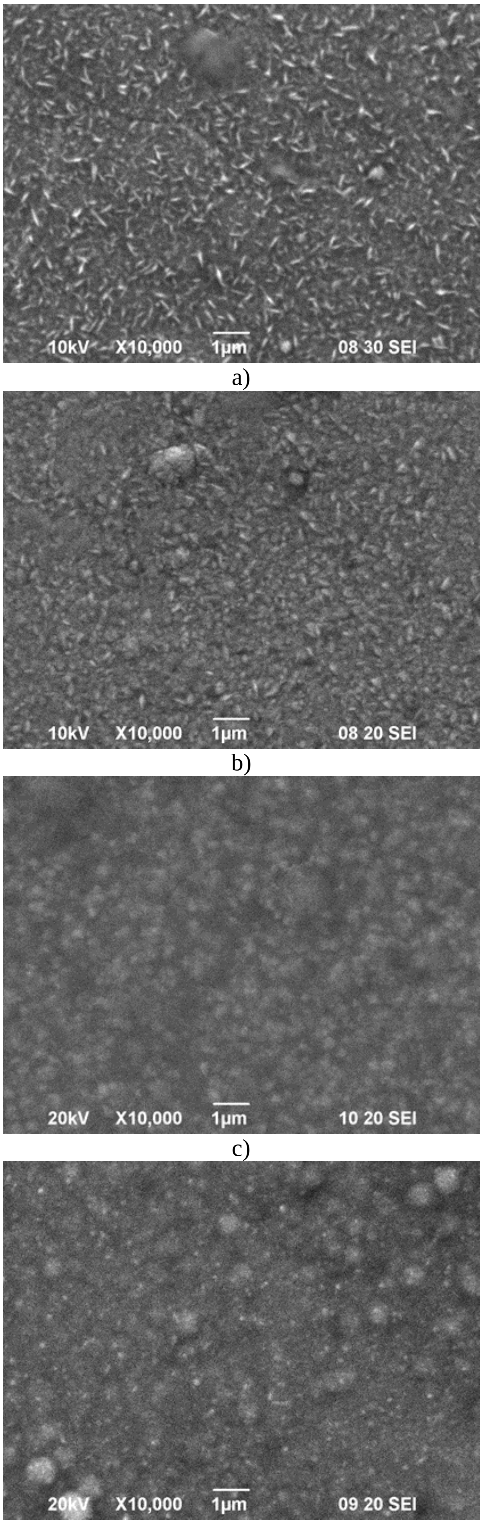
**Fig.4.** SEM images of CoCu coatings, deposited at potentiostatic mode (a) and at pulse frequencies: 500 Hz (b); 1000 Hz (c); 10000 Hz (d) in bath: 0,32M Co, 0,0,25M Cu and 0,2M $Na_3$citrat. The applied deposition polarization corresponds to the same average current $I_{av}$=28 mA (S=1 cm$^2$) in the polarization curve. Coating composition (in wt.%): (a) 73%Co-27%Cu; (b) 35%Co-75%Cu; (c) 38%Co-55%Cu (7%O); (d) 64%Co-32%Cu (4%O)

45 mA.cm$^{-2}$ for CoNiCu). Current density chosen corresponds to the same point of each polarization curve, close to and before the plateau, thus ensuring realization of identical kinetic conditions for the deposition of each alloy. EDSA results for elemental composition (wt. %) of the coatings are given in the text captions.

Co-Cu (Fig.4): The deposited at stationary conditions CoCu coatings are with numerous needle-shaped crystals (Fig.4a) and bigger spherical crystals. Small negative shift of the applied potential makes the coating more fine-crystal with average grain size of about 250-500 nm. The coating composition is ranging within wide limits - from 2% Co to about 82%Co.

Using the pulse mode changes significantly the coating structure (Fig.4,b-d). The structure becomes more homogeneous, with more levelled surface compared to this one in stationary condition. At pulse conditions the structure is levelled and with round to spherical shaped crystals. Applying frequencies up to 500 Hz (Fig.4,b), the coatings are fine-crystal, with nano – measurements (grain size less than 100 nm), with low Co content (35% Co). With the increase of pulse frequency the content of Co in coatings grow up (up to 64%) and the average grain size increases up to 300 nm, in the same time the coatings become smoother (Fig.4,c,d). This result is in good correlation with the pulse mode results which showed, that at frequencies over 1000 Hz the average polarization and the part of amplitude polarization, responsible for the Faraday reaction, are close to these in potentiostatic condition.

Ni-Co (Fig.5): Compared to the coatings obtained in stationary mode (Fig.5,a), the ones obtained in pulse mode (Fig.5, b-d) have low Ni content (up to 12%). Judging on the weight % of oxygen, the presence of oxides was found in the coating at high frequencies. The application of pulse mode in general and the higher frequencies of pulses result in increased share of the more oval crystals compared to the needle-shaped ones, their size decreases reaching 200-400 nm and the surface smoothes as a whole. The increase of frequency of pulses above 1 000 Hz results in obtaining alloys enriched in cobalt (about 90% Co). The blurred SEM images at increased frequencies are explained with obtaining of nano-size structure and smoothing the surface.



a)

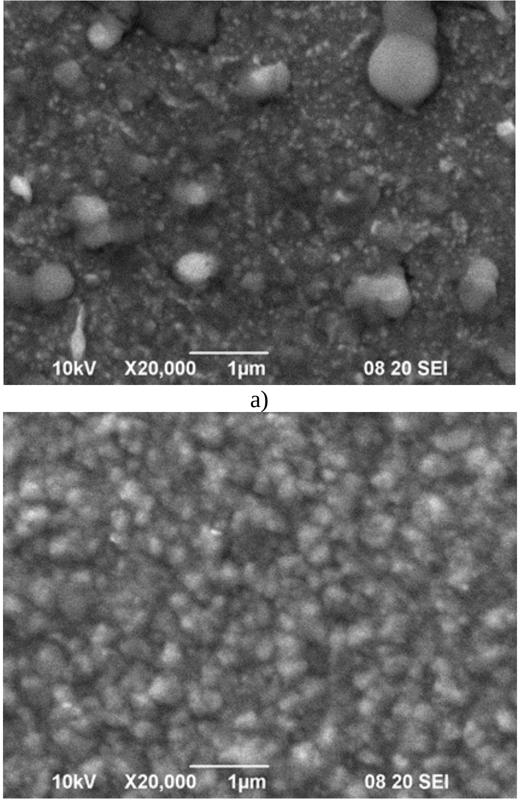
b)

c)

d)

**Fig.5** SEM images and EDSA data of NiCo coatings deposited at stationary mode (a) and at pulse frequencies: (b) 500 Hz; (c) 1000 Hz; (d) 10000 Hz in electrolyte with composition: 0,32M Co, 0,38M Ni and 0,2M Na$_3$citrat. The applied deposition polarizations correspond to the average current $I_{av}$ =45 mA (S=1 cm$^2$) in the polarization curves. Coating composition (in wt.%): (a) 76%Co-21%Ni (3%O); (b) 88%Co -12% Ni (c) 96%Co- 4%Ni, (d) 90%Co-5%Ni (5%O)

CuNiCo (Fig.6): It was found that in the case of deposition of the triple alloy CuNiCo, the coatings obtained at frequency 500 Hz have larger crystals and are more inhomogeneous compared to CoNi coatings (Fig. 5,c and Fig.6,a). The increase of the pulse frequency up to 1000 Hz results in obtaining of rounded, more uniform, and finer crystals of average diameter 400-500 nm (Fig.6, b). Moreover, the percentage of nickel in the alloys increases (up to 27% Ni). The percentage of cobalt, however, does not change significantly and remains about 71-76 %, and the content of copper decreases from 8% to less than 5% at the applied potentials.



a)

b)

**Fig. 6** SEM images and EDSA data of CoNiCu coatings deposited in electrolyte: 0,32M Co, 0,38M Ni, 0,025M Cu and 0,2M $Na_3$citrat in pulse mode with pulse frequencies: (a) 500 Hz; (b) 1000 Hz. The applied deposition polarizations correspond to the average current $I_{av}$ =35 mA (S=1cm$^2$). Coating composition (in wt.%): (a)76%Co-9%Ni-8%Cu-(7%O); (b)71%Co-21%Ni-(5%Cu)-3%O

### *Phase composition of CoCu, NiCo u CoNiCu coatings*

The results from the X-Ray analysis show (Fig.7), that in the studied alloy coatings Cu, Co and Ni crystallize in cubic lattice (f.c.c.). Only in the ternary CoNiCu coating deposited at pulse frequency 1000 Hz (Fig.7, 4), a presence of Co both with face-centred cubic crystal lattice (f.c.c.) and with hexagonal crystal lattice (h.p.c.) was found. All diffraction images are characterized with relatively wide peaks due to their fine structure reaching nano-sizes. The clear Cu spectrum is due mainly to the fact, that the coatings have small thickness (about 3μm) and are deposited on copper.

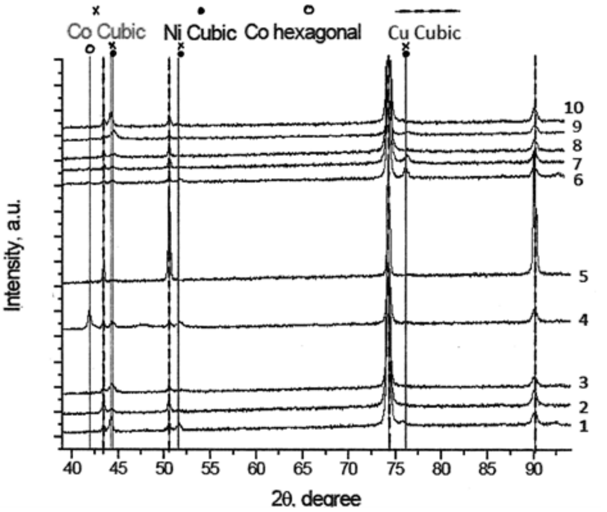


**Fig.7** X-Ray diffractograms of the **CoCu** coatings(1-3), deposited at pulse condition at frequencies: 500 Hz (1); 5000 Hz (2); 10000 Hz (3); of the **CoNiCu** coatings at pulse frequencies 1000 Hz (4) and of the **CoNi** coatings (5-10) deposited in stationary (5) and pulse mode at pulse frequencies: 500 Hz (6); 1 000 Hz (7); 5 000 Hz (8); 10 000 Hz (9,10) in bath with the same composition and at the same polarizations as these in Fig.4-6.

## CONCLUSION

The conditions for the electrodeposition of CuCo, CoNi and CoNiCu in potentiostatic and pulse potentiostatic modes in citrate solutions were determined. It was found that the applying of pulse potentiostatic mode and higher frequency of pulses significantly smoothes the surface and resulted in finer crystals with rounded shape and average size under 100 nm for CoCu coatings; up to 200-300 nm for CoNi and up to 500 nm for CoNiCu (wt.% Co up to 80%).

## REFERENCES

1. B. Y. C. Wu, P. J. Ferreira, and C. A. Schuh, *Metallurgical and Materials Transactions A*, **36A**, 1927 (2005)
2. J. Horkans, J. Chia, H. Chang, P. C. Andricacos and E.Chassing, *J. Electrochem. Soc.*, **138**, 441 (1991)
3. A. Bastos, S. Zaefferer, D. Raabe, *Advanced Materials Research*, **15-17**, 274 (2007)
4. A. Bastos, S. Zaefferer, D. Raabe, *J. of Microscopy*, **230**, pt3, 487 **(**2008)
5. A. Hiroki, I. Masanobu, *Papers of Technical Meeting on Magnetic*, IEE, Japan, **50-63**, 49 (2005)
6. M. Uhlemann, A. Gebert, M. Herrich, A. Krause, L. Shulz, *Electrochim. Acta*, **48**, 3005 (2003)
7. S. Armyanov, *Electrochim. Acta*, **45,** 3323 (2000)

8. Q. Huang, D. Davis, E. J. Podlaha, *J. Appl. Electrochem.*, **36,** 871 (2006)
9. P. Neufeld, A. T. Kuhn, H. A. Skinner, *Inst. Chem. Eng. Symp. Proc.*, **69**, 1 (1983)
10. A. E. Mohamed, S. M. Rashwan, S. M. Abdel-Wahaab, M. M. Kamel, *J. Appl. Electrochem.*, **33,** 1085 (2003)
11. M. Gu, *Electrochimica Acta*, **52**, 4443 (2007)
12. J. J. Kelly, M. Cantoni, D. Landolt, *J. Electrochem. Soc.*, **148,** C620 (2001)
13. G. R. Pattanaik, D. K. Pandya, S. C. Kashyap, *J. Electrochem Soc*, **149,** C363 (2002)
14. C. P. Singh, R. K. Shukla, S. C. Srivastava, *Surface Technology*, **16,** 219 (1982)
15. S. Pané, E. Cómez**,** E. Vallés, *J. Electroanalytical Chem.*, **596,** 87 (2006)
16. D. Golodnitski, N. V. Gudin, G. A. Volyanuk, *J. Electrochem. Soc.*, **147**, 4156 (2000)
17. N. J. Petch, *J. Iron Steel Inst.*, **174**, 25
18. E. Chassaing, *J. Electrochem. Soc.*, **148,** C690 (2001)
19. A. M. El-Sherik, PhD.Thesis, Queen’s University, Kingston, Canada, 1993
20. T. A. Green, A. E. Russel, S. Roy, *J. Electrochem. Soc.*, **145**,.875 (1998)
21. T. Ohgai, X. Hoffer, L.G ravier, J.-Ph. Anseremet, *J. Appl. Electrochem.*, **34,** 1007 (2004)
22. S. K. Gupta, M. G. Gartley, *J.CPDS International Centre for Diffraction Data*, 688 (1999)
23. H. J. Blythe, V. M. Fedosyuk, O. I. Kasyutich, *Materials Letters*, **26,** 69 (1996)
24. R. Loloee, P. A. Schroeder, W. P. Pratt Jr., J. Brass, A. Fert, *Physica B: Condensed Matter*, **204,** 274 (1995)
25. K. Ignatova, Y. Marcheva, *Journal of the University of Chemical Technology and Metallurgy,* to be published (vol.2, 2013)
26. L. Petkov, K. Ignatova, *Bulgarian Chemical Communication,* **41,** 39 (2009)
27. D. Grujicic, B. Pesic, *Electrochimica Acta*, **50**, 4426 (2005)

# ЕЛЕКТРООТЛАГАНЕ И СТРУКТУРА НА Co ПОКРИТИЯ (CoCu, NiCo AND CoNiCu) В ПОТЕНЦИОСТАТИЧЕН И ИМПУЛСЕН РЕЖИМ

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(Резюме)

Изследвана е кинетиката на самостоятелно отлагане на Cu, Co и Ni както и на отлагането на сплавите CoCu, NiCo и NiCoCu в слабокисел цитратен електролит (pH= 5,5). Получени са и данни за отлагането на сплавите в импулсен потенциостатичен режим при различни честоти на импулсите. Съпоставени са морфологията и елементния състав (чрез SEM и EDSA анализи съответно) на получените в стационарен и в импулсен режим сплавни покрития от всеки вид.

Установено е, че докато отлаганите покрития в стационарен потенциостатичен режим са със среден размер на кристалитите от около 250 до средно 500 nm, а съдържанието на Co е над 85 wt.%, то в импулсен режим се наблюдава намаление на средния размер на кристалитите, а съдържанието на Co е под 76 wt.% за всички сплави. Прилагането на честоти на импулсите до 500 Hz при отлагане на CoCu сплави, води до понижение на размера на кристалитите под 100 nm (при 60-70 wt.% Co). В същите условия покритията от CoNi and CoNiCu се характеризират с окръглена структура на кристалитите, със среден размер около 200-300 nm. Данните от X-Ray анализа показват, че двойните сплави CoCu и NiCo са двуфазни и се състоят от фази на мед, кобалт и никел с кубична стенноцентрирана решетка (f.c.c.). Единствено в тройното покритие Cu-Co-Ni освен кубични фази на трите метала е установено и наличие на Co-съдържаща фаза в хексагонална сингония (h.p.c.).