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# Electrodeposition of Co-Ni and Co-Ni-Cu systems in sulphate-citrate medium

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#### Abstract

Electrodeposition of Co–Ni and Co–Ni–Cu alloys was performed in a sulphate–citrate medium. Experimental electrodeposition parameters (pH, cobalt(II), nickel(II) and citrate concentrations) were varied in order to analyse their influence on the deposition. Anomalous Co–Ni codeposition occured in the citrate medium. High [Ni(II)]/[Co(II)] ratios (above 5) were suitable for the preparation of homogeneous magnetic Co-rich Co–Ni deposits of hexagonal close-packed (hcp) structure or face centred cubic (fcc) structure as a function of the deposition potential.

The presence of very low copper(II) concentrations ( $<10^{-2}$  mol dm<sup>-3</sup>) in the nickel–cobalt bath makes it possible to incorporate copper in the deposits in amounts ranging from 5 to 60% Cu, although uniform deposits are obtained only for low copper percentages. These ternary deposits are solid solutions with fcc structure and magnetic behaviour both dependent on the deposition potential. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Cobalt-nickel; Cobalt-nickel-copper; Magnetic alloy; Electrodeposition; Ternary alloy

## 1. Introduction

Electrodeposition has been shown to be a useful tool for preparation of alloys or heterogeneous films of different metals for several magnetic applications. Co-based binary alloys with magnetic or magnetoresistive properties were studied and prepared by electrodeposition in our laboratory: Co–Ni alloy was deposited from chloride and implemented in MEMS technology [1–4] and Co–Cu heterogeneous deposits [5–8] were obtained from a sulphate–citrate medium.

The functional properties of electrodeposited Co–Ni alloy depend greatly on their composition, which should be turn strongly affected by deposition parameters. A characteristic feature is that in the chloride medium studied, the Co/Co + Ni ratio in the alloy is considerably higher than in the bath, indicating the anomalous character of Co–Ni alloy electrode-

position in this medium, where the less noble constituent is deposited preferentially.

The aim of the present study is to test the possibilities of the electrodeposition to introduce copper on the Co–Ni system and to prepare ternary Co–Ni–Cu alloys from a sulphate–citrate bath without additives. Co–Ni–Cu alloys would be used as either magnetic or magnetoresistive materials with better corrosion resistance than Co–Cu system. For this ternary system, research works related to the codeposition from pyrophosphate or ammonium citrate media [9,10] are in the bibliography and recently, to the preparation of Co–Ni (Cu)/Cu multilayers [11–15]. A previous study of the behaviour of Co–Ni electrodeposition in the selected medium is necessary due to the controversy given in the literature about that Co–Ni anomalous codeposition occurs only in baths that contain simple cobalt and nickel salts [16].

The present paper shows the results of laboratory research centred both in the deposition of Co–Ni and Co–Ni–Cu alloys using sulphate–citrate solutions. The objective was to determine the way in which the composition of alloys, morphology and structure are dependent upon several variations

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of the electrolyte composition and electrolysis parameters as the concentration of cobalt and nickel ions, citrate concentration and applied potential.

## 2. Experimental

The electrochemical measurements were performed in a conventional three-electrode cell using a potentiostat/galvanostat Autolab with PGSTAT equipment and GPES software. The temperature was maintained at 25 °C. Chemicals used were  $CoSO_4 \cdot 7H_2O$ ,  $NiSO_4 \cdot 6H_2O$ ,  $CuSO_4 \cdot 5H_2O$ and  $Na_3C_6H_5O_7 \cdot 2H_2O$ , all of analytical grade. All solutions were freshly prepared with water which was doubly distilled and then treated with a Millipore Milli Q system. Before each experiment the solutions were de-aerated by argon bubbling and they were maintained under argon atmosphere during the experiment.

A working electrode of vitreous carbon (Metrohm) of  $0.0314 \text{ cm}^2$  was used. It was polished to a mirror finish using alumina of different grades "3.75 and 1.85  $\mu$ m" and cleaned ultrasonically for 2 min in water before each experiment. The reference electrode was Ag/AgCl/1 mol dm<sup>-3</sup> NaCl mounted in a Luggin capillary containing 0.5 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> solution. All potentials are referred to this electrode. The counter electrode was a 3 cm diameter platinum spiral located parallel to the working electrode in order to optimize current distribution.

Voltammetric experiments were carried out at 50 mV s<sup>-1</sup>, scanning initially towards negative potentials. Only one cycle was run in each voltammetric experiment. Chronoamperometric experiments were done from an initial potential at which no process occurred to a potential value at which reduction process occurred. Stripping experiments of deposits oxidation were recorded at  $10 \text{ mV s}^{-1}$ , from a potential value at which no current was detected.

Deposits were prepared with stirring ( $\omega = 100$  rpm, magnetic stirrer), since more uniform and reproducible deposits can be obtained under hydrodynamically controlled conditions specially at low [Cu(II)]/([Co(II)] + [Ni(II)]) ratios. The morphology of the deposits was examined with a Hitachi S-2300 Scanning Electron Microscope.

Film composition was determined by electron probe microanalysis (EPMA), performed on a Cameca SX-50 electron microprobe and/or inductively coupled plasma mass spectrometry (ICP-MS). For chemical analysis, the deposits were dissolved in 5 ml of 1% nitric acid solution and measurements were taken on a Perkin-Elmer spectrometer Elan 6000. Certified standard solutions were used to calibrate the instrument. The results of ICP-MS and EPMA analysis were in agreement in all cases. The efficiency of the deposition process was calculated by comparing the reduction charge deduced from chemical analysis and that involved in the preparation of the film.

XRD analysis was performed on a Philips MRD diffractometer. To avoid the vitreous carbon response, the films were separated from the electrode and mounted on silicon. Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) was selected by means of a diffracted-beam flat graphite monochromator crystal. Diffractograms were obtained with  $2\theta$  ranging from  $10^{\circ}$  to  $100^{\circ}$  with a step size of 0.05 and a measuring time of 5 s per step.

The magnetic measurements were taken at room temperature with a Manics DSM8 pendulum-type magnetometer and a SQUID magnetometer.

# 3. Results

#### 3.1. Co-Ni electrodeposition in sulphate-citrate bath

The preliminary study of the cobalt–nickel electrodeposition process in sulphate–citrate medium was performed using a total Ni(II) + Co(II) concentration of 0.2 mol dm<sup>-3</sup>, varying the [Ni(II)]/[Co(II)] ratio between 10 and 0.33, at different sodium citrate concentrations (0.2–0.5 mol dm<sup>-3</sup>) and solution pH (3–5).

Fig. 1A shows the voltammetric response of a  $0.175 \text{ mol dm}^{-3} \text{ NiSO}_4 + 0.025 \text{ mol dm}^{-3} \text{ CoSO}_4 + 0.2 \text{ mol dm}^{-3} \text{ Co}_6\text{H}_5\text{Na}_3\text{O}_7$ , pH 4, solution, at stationary conditions, next to the voltammograms of  $0.2 \text{ mol dm}^{-3} \text{ Ni}(\text{II})$  and  $0.2 \text{ mol dm}^{-3} \text{ Co}(\text{II})$  solutions in the same complexing medium. At these conditions, the onset of the voltammetric reduction current appeared at intermediate potential value between those corresponding to nickel and cobalt. Complex oxidation response was recorded with no clear features. The stirring of solution during the deposition/oxidation process favoured the evolution of the hydrogen formed during the cathodic scan, minimizing its partial oxidation [17–19] and leading to more defined peaks for cobalt and alloy oxidation (Fig. 1B). A gradual decrease of the  $Q_{\text{ox}}/Q_{\text{red}}$  ratio in the order Co(II)/Co > Ni(II) + Co(II)/alloy > Ni(II)/Ni was observed.

Increasing sodium citrate concentration or solution pH, the deposition of the alloy was shifted to negative potentials and, simultaneously, the  $Q_{\rm ox}/Q_{\rm red}$  ratio was drastically decreased.

To analyse the initial stages of the Co–Ni deposition in citrate medium, potentiodynamic stripping of deposits was made under stirring. For deposits obtained at low deposition potentials and very low charges (around  $60-300 \text{ mC cm}^{-2}$ ) (Fig. 2A, points a and b) a small oxidation peak at negative potentials was detected (Fig. 2B, curves a and b) although no displacement in the oxidation peak was observed. Upon increasing the deposition time (Fig. 2A, points c and d), a second peak centred at more positive potentials was developed (Fig. 2B, curves c and d). This second oxidation peak gradually shifted to positive potentials as the deposition potential was made more negative (Fig. 3).

In order to elucidate the stripping response, a set of deposits prepared at low charges were chemically analysed using ICP-MS. The nickel percentage of the deposits, which oxidized only under the first peak, varied between 38 and 57% Ni, increasing Ni percentage as the deposition poten-



Fig. 1. Cyclic voltammograms at 50 mV s<sup>-1</sup> of (a) 0.2 mol dm<sup>-3</sup> NiSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, (b) 0.2 mol dm<sup>-3</sup> CoSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> and (c) 0.175 mol dm<sup>-3</sup> NiSO<sub>4</sub> + 0.025 mol dm<sup>-3</sup> CoSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, pH 4 solutions. (A) Quiescent conditions and (B)  $\omega = 100$  rpm.

tial decreased. However, the analysis of deposits obtained increasing deposition time showed a nickel percentage in the range 17–23%. These deposits oxidize mainly under the second peak. A second cobalt-rich deposit was formed on the first nickel-richer deposit, which oxidized at more positive potentials as the nickel percentage increased.

Deposits involving charges between  $600 \text{ mC cm}^{-2}$  and  $380 \text{ C cm}^{-2}$  were prepared. In order to assure the reproducibility of the results, three replicas were analysed at each condition and no differences higher than 1% were found. Table 1 shows the average percentages and confirms the presence of cobalt rich deposits whose specific composition was slightly dependent on the deposition potential. Results corroborate constant composition with increasing charge at the stirred conditions selected. Then, high [Ni(II)]/[Co(II)] ratios led to cobalt-rich deposits, showing that over an initial deposit with higher nickel percentage, anomalous codeposition takes place also in the citrate medium used, as occurs in other baths [1,20–24].



Fig. 2. Solution (c) of Fig. 1. (A) Potentiostatic curve from -500 to +980 mV.  $\omega = 100$  rpm. (B) Stripping curves of deposits obtained at different times from the *j*-*t* transient of (A). (a) 30 s, (b) 50 s, (c) 100 s and (d) 150 s;  $10 \text{ mV s}^{-1}$ .



Fig. 3. Solution (c) of Fig. 1. Stripping curves of deposits obtained potentiostatically at  $\omega = 100$  rpm, at (a) -980 mV, 150 s; (b) -1010 mV, 70 s and (c) -1050 mV, 30 s.

Table 1

Influence of deposition potential on the composition of the Co–Ni deposits obtained from a  $0.175 \text{ mol dm}^{-3} \text{ NiSO}_4 + 0.025 \text{ mol dm}^{-3} \text{ CoSO}_4 + 0.2 \text{ mol dm}^{-3} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7$ , pH 4 solution

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-E (mV)	t (min)	$Q (\mathrm{C} \mathrm{cm}^{-2})$	Ni (%)	Co (%)	
980	2.5	0.6	17	83	
	320	330	17	83	
1010	4.2	1.9	17	83	
	83	76	18	82	
	267	390	18	82	
1050	4.2	3.8	20	80	
	12	14	19	81	
	19	440	21	79	
1070	5.5	6.5	23	77	
	8.3	16	23	77	



Fig. 4. X-ray diffractograms of (A) nickel electrodeposited from a  $0.2 \text{ mol dm}^{-3} \text{ NiSO}_4 + 0.2 \text{ mol dm}^{-3} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7$ , pH 4 solution at -1000 mV,  $Q = 318 \text{ C cm}^{-2}$ ,  $\omega = 100 \text{ rpm}$  and (B) cobalt electrodeposited from a  $0.2 \text{ mol dm}^{-3} \text{ CoSO}_4 + 0.2 \text{ mol dm}^{-3} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7$ , pH 4 solution at -1025 mV,  $Q = 318 \text{ C cm}^{-2}$ ,  $\omega = 100 \text{ rpm}$ .

The structure of high-charge deposits prepared at different potentials was analysed from XRD. Pure cobalt and nickel electrodeposits obtained at different deposition potentials from the same medium were also analysed.

Diffractograms of nickel deposits (Fig. 4A) show the peaks of the fcc structure, with a cell parameter around a = 3.524 Å. Electrodeposited cobalt was hcp structure, with cell parameters a = 2.504 Å, c = 4.098 Å and 100 + 110 preferred orientation (Fig. 4B). All Co-Ni deposits showed several peaks that revealed their crystalline nature, but the diffraction peaks obtained varied as a function of the deposition potentials (Fig. 5). Deposits of 17% Ni obtained at low potentials (Fig. 5, curve a) showed the peaks of an hcp structure, with a small peak centred at  $51^{\circ} 2\theta$  assigned to a secondary fcc structure. Diffraction peaks were shifted to greater  $2\theta$  values with respect to those of hcp deposited cobalt as a consequence of nickel incorporation in the deposit. Cell volume of Co-Ni hcp deposits was lower than that of hcp cobalt. Deposits obtained at more negative potentials, evolved to fcc structure. Thus, for deposits of 23% Ni (Fig. 5, curve b), a clear fcc structure with 110 preferred orientation was detected. These structural modifications were accompanied by



Fig. 5. X-ray diffractograms of Co–Ni deposits of  $Q=318 \,\mathrm{C\,cm^{-2}}$  of charge obtained from a 0.175 mol dm<sup>-3</sup> NiSO<sub>4</sub> + 0.025 mol dm<sup>-3</sup> CoSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, pH 4 solution,  $\omega = 100 \,\mathrm{rpm}$ . (a)  $-980 \,\mathrm{mV}$ , 17% Ni and (b)  $-1050 \,\mathrm{mV}$ , 21% Ni.

morphological changes: clear acicular morphology was observed, similar to that of pure hcp cobalt, when main Co–Ni hcp structure was detected (Fig. 6A). On the other hand, deposits of fcc structure corresponded to nodular morphology (Fig. 6B). The structural–morphological changes observed



Fig. 6. SEM micrographs of the Co–Ni deposits of Fig. 5. (A)  $-980\,mV,$  17% Ni and (B)  $-1050\,mV,$  21% Ni.



Fig. 7. Parallel (a) and perpendicular (b) hysteresis loops for a Co–Ni deposit obtained from the solution of Fig. 5 at -1050 mV,  $Q = 318 \text{ C cm}^{-2}$ ,  $\omega = 100 \text{ rpm}$ .

seem more related to the different deposits growth rate than the involved compositional changes.

Magnetic properties of Co–Ni alloys were analysed by hysteresis loops. The magnetic response of Co–Ni deposits obtained at different potentials was similar because no great variation of composition was found as a function of the potential. Saturation magnetisation was in the range of  $120-140 \text{ emu g}^{-1}$  (150 for electrodeposited cobalt and 52 for electrodeposited nickel), and coercivity values ranged between 70–100 Oe (Fig. 7). When parallel and perpendicular magnetic fields were applied, slower response was obtained in the second case. The easy axis is the in-plane direction of the film parallel. Saturation field under the perpendicular field was clearly higher than the saturation field under the parallel one. These features indicated strong uniaxial anisotropy, in addition to the usual shape anisotropy [25]. Alloy films were spontaneously orientated in the direction parallel to the field.

#### 3.2. Influence of copper on Co-Ni electrodeposition

The influence of low copper(II) concentrations (in the range  $7 \times 10^{-4}$  to  $3 \times 10^{-3} \text{ mol dm}^{-3}$ ) on the Co–Ni electrodeposition from a 0.175 mol dm<sup>-3</sup> NiSO<sub>4</sub> + 0.025 mol dm<sup>-3</sup> CoSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub> O<sub>7</sub>, pH 4, solution was analysed.

Voltammograms recorded at different copper concentrations showed a main reduction peak that gradually advanced as copper(II) concentration increased (Fig. 8A). Zooming the initial reduction zone, low current, assigned to copper deposition, was detected. Low  $Q_{ox}/Q_{red}$  ratios were obtained in all cases. A main oxidation peak was detected that shifted to positive potentials as the copper(II) concentration increased, shifting to the position of the pure-copper oxidation in this medium (Fig. 8B).

For a fixed copper(II) concentration, the influence of cathodic limit was analysed. The oxidation peak was detected at more negative potentials decreasing the cathodic limit (Fig. 9) probably because of a decrease of copper percentage in the deposits. Similar behaviour was observed under stirring con-



Fig. 8. (A) Cyclic voltammograms at  $50 \, {\rm mV \, s^{-1}}$ of  $0.175\,mol\,dm^{-3}$  $NiSO_4 + 0.025 \text{ mol } dm^{-3}$  $CoSO_4 + 0.2 \text{ mol } dm^{-3}$  $Na_3C_6H_5O_7 + x \mod dm^{-3}$  CuSO<sub>4</sub>, pH 4 solutions. (a)  $x = 7.4 \times 10^{-4}$ . (b)  $x = 1.5 \times 10^{-3}$  and (c)  $3.0 \times 10^{-3}$ . Cathodic limit: -1300 mV. Quiescent conditions. (B) Cyclic voltammogram at 50 mV s<sup>-1</sup> of  $0.175 \, \text{mol} \, \text{dm}^{-3}$  $CoSO_4 + 0.2\ mol\ dm^{-3}$  $NiSO_4 + 0.025 \text{ mol } dm^{-3}$  $Na_3C_6H_5O_7 + 3.0 \times 10^{-3}$  mol dm<sup>-3</sup> CuSO<sub>4</sub>, pH 4 solution. Cathodic limit: -890 mV. Quiescent conditions.

ditions, although for a fixed cathodic limit the voltammetric oxidation peak appeared at more positive potential than under quiescent conditions. Stirring favours Cu(II) species arrival at the electrode making easy their incorporation in the film.



Fig. 9. Cyclic voltammograms at  $50 \text{ mV s}^{-1}$ . Same solution as in Fig. 8B.Quiescent conditions. Cathodic limit: (a) -1135 mV, (b) -1300 mV and (c) -1400 mV.





Fig. 10. Same solution as in Fig. 8B. Stripping curves of deposits obtained potentiostatically at  $\omega = 100$  rpm, at (a) -950 mV, 30 s, (b) -975 mV, 20 s and (c) -1025 mV, 10 s.

Voltammetric stripping was recorded for low-charge deposits prepared potentiostatically at different deposition potentials (Fig. 10). In all scans, a single oxidation peak was detected that shifted to negative potentials as the deposition potentials was made more negative.

Deposits of  $9.5 \,\mathrm{C \, cm^{-2}}$  were prepared at different potentials and analysed by means of ICP-MS. The analysis showed the incorporation of copper in cobalt–nickel deposits. Specific deposit composition was dependent on deposition potential: at low deposition potentials copper deposition was favoured and copper-rich deposits were found. Copper percentage clearly decreased for more negative deposition potentials (Table 2). Ternary alloys maintain the anomalous codeposition for cobalt–nickel, deposits present greater proportion of cobalt than nickel, as in the binary alloy.

These results indicate that the position of both voltammetric and stripping oxidation peaks of the ternary alloy could be related to the alloy composition. Copper-rich deposits oxidized at positive potentials, whereas cobalt-rich deposits oxidized at more negative potentials.

Increasing deposition charge, deposits obtained at low deposition potentials showed high roughness whereas more uniform deposits were observed for more negative deposition potentials (Fig. 11). The favoured incorporation of ferromagnetic metals and the increase of nucleation involves the decrease of crystal size leading uniformity to the deposits. Ho-

Table 2

Composition of CoNiCu deposits of  $Q = 223 \text{ C cm}^{-2}$  obtained at different deposition potentials from a 0.175 mol dm<sup>-3</sup> NiSO<sub>4</sub> + 0.025 mol dm<sup>-3</sup> CoSO<sub>4</sub> + 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> CuSO<sub>4</sub> + 0.2 mol dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, pH 4 solution

-E (mV)	Co (%)	Ni (%)	Cu (%)
850	1	2	97
875	4	8	88
900	7	8	86
925	22	7	71
950	42	11	47
975	50	15	35
1000	58	16	26
1050	57	31	12



Fig. 11. SEM micrographs of the Co–Ni–Cu deposits obtained at  $\omega = 100$  rpm from the solution of Fig. 8B. Q = 223 C cm<sup>-2</sup>. (A) -950 mV, (B) -1000 mV and (C) -1025 mV.

mogeneous deposits, both in morphology and composition throughout deposit thickness, were obtained from potentials  $\leq -1025 \text{ mV}.$ 

Structure and magnetic properties of ternary Co–Ni–Cu deposits of low copper percentages, obtained from potentials more negative than -1000 mV, were analysed. These deposits presented a similar cobalt percentage and a gradual



Fig. 12. (A) X-ray diffractograms of a Co–Ni–Cu deposit obtained at -1050 mV using  $\omega = 100 \text{ rpm}$ ,  $Q = 318 \text{ C cm}^{-2}$ , from solution of Fig. 8B. (B) Detail of the fcc 1 1 1 peak in diffractograms corresponding to Co–Ni–Cu deposits of  $Q = 318 \text{ C cm}^{-2}$  obtained at  $\omega = 100 \text{ rpm}$  from the same solution, at (a) -1050 mV, 57% Co, 31% Ni, 12% Cu, (b) -1075 mV, 57% Co, 32% Ni, 11% Cu and (c) -1100 mV, 55% Co, 35% Ni, 10% Cu.

decrease of copper content that favoured the nickel incorporation when potential values decreased.

X-ray diffractograms of the films exhibited a low signal noise ratio; however show a clear collection of narrow peaks that reveal their crystalline nature (Fig. 12A). The adjustment of these peaks leads to an fcc structure. Each peak appeared at position near that of cobalt fcc and midway between those of copper and nickel (both of structure fcc). Only one peak appeared for each orientation revealing the formation of the ternary alloy and no peaks assigned to the pure metals were observed. An accurate zoom of each diffraction peak shows that the position depends on the specific composition of deposit. Diffraction peaks moved as a function of the global composition of the alloy (Fig. 12B) shifting to higher  $2\theta$  values when nickel percentage increases. Peaks adjustment allows estimate cell parameter for each composition. The cell parameter a varies in the range 3.548–3.544 Å as the percentage of Cu decreases. The position of the peaks was concordant with those deduced assuming the formation of a solid solution. All deposits show high roughness and nodular morphology.



Fig. 13. (A) Magnetisation versus magnetic field and magnified detail of Co–Ni–Cu deposits obtained from the solution cited in Fig. 8B. (a) –900, (b) –950, (c) –1000 and (d) –1050 mV,  $Q = 223 \text{ C m}^{-2}$ . (B) Parallel (a) and perpendicular (b) hysteresis loops for a Co–Ni–Cu deposit obtained at –1050 mV,  $Q = 318 \text{ C cm}^{-2}$ ,  $\omega = 100 \text{ rpm}$ .

Similar magnetic response was obtained for these deposits. The incorporation of copper in cobalt–nickel films provoked a decrease of the saturation magnetisation, but a clear decrease of the coercivity of the material (Fig. 13A). As was observed for binary alloy slower response was obtained when perpendicular magnetic fields were applied (Fig. 13B) being the easy axis the in-plane direction of the film parallel.

# 4. Conclusions

In the sulphate–citrate medium at pH 4 was confirmed the character anomalous of the codeposition of cobalt–nickel alloys. The electrochemical study combined with compositional analysis of the films formed in the first stages allows assure the anomalous behaviour of deposition process even at the initio of deposition. In all conditions Co/Co + Ni ratio in the deposit is great than the corresponding in solution. The anomalous character of the codeposition of ferromagnetic materials maintains during the codeposition of ternary cobalt–nickel–copper system.

The properties of the binary Co–Ni alloys obtained from sulphate–citrate solutions can be controlled by adjusting de-

position potential due to the total miscibility of the two metals. In the first stages of the alloy formation films around 1:1 Co:Ni ratio are formed, over which the growth of cobalt-rich alloys occurs. A main oxidation peak of the alloy is detected in voltammetric experiments, which slightly shifts to more positive potentials as the cathodic limit is decreased related to the slight variation of alloy composition. The incorporation of nickel into deposit leads to coatings that are less oxidizable than pure cobalt.

By adjusting the deposition rate, it is possible to control the morphology and structure of Co-Ni alloys. Acicular deposits of hcp structure can be obtained with a slow growth. On the other hand, nodular, fcc, deposits are favoured at higher deposition rates. This behaviour has been previously observed for pure-cobalt deposition in different bath compositions [26]. However, no notable differences have been observed in the magnetic properties of the Co-Ni films as a function of these different structures.

The sulphate-citrate medium at pH 4 has been useful for incorporating different copper percentages in cobalt-nickel alloys. The incorporation of low percentages of copper in Co-Ni alloy causes a great variation of alloy properties. Lower copper content is achieved as the potential gradually decreases. In all cases, even at very low copper percentages fcc structure is found, regardless of the deposition rate.

Electrochemical response, both in voltammetric and in stripping experiments, informs about alloy properties. More oxidizable films are formed for copper-containing deposits. Moreover, the position of the oxidation peak informs on the copper content in the deposits. The increase of the  $Q_{\rm ox}/Q_{\rm red}$ ratio and the shift of the oxidation peak to more positive potentials reveal the gradual increase of the copper percentage. The detection of a single oxidation peak of variable position as a function of the deposition potential also reveals the formation of a solid solution, corroborated by X-ray diffraction experiments.

Respect to the magnetic character of the ternary system, varying the electrodeposition conditions seems feasible to control the ferromagnetic behaviour of the metallic films as a function of the copper percentage in the deposits.

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