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The study of Ni–Co alloy deposition on iron powder particles in a fluidized bed from sulphate bath

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Abstract This paper describes a process of electrolytic deposition of nickel-cobalt (Ni-Co) binary alloy on Fe powder. Electrochemical behavior of this binary alloy was studied by cyclic voltammetry with a paraffin impregnated graphite electrode as a working electrode. Deposition of individual metals (Ni, Co), as well as the simultaneous nickel-cobalt co-deposition, was performed in aqueous solutions (Watts-type electrolyte) both with and without Fe powder. Special attention was paid to the influence of suspension density on the electrode process. This density affects on the quality of iron powder electroplating. Preferential deposition of the less noble metal (Co) leading to its higher content in the deposit was observed in contrast to the more noble one (Ni) in spite of higher content of Ni in the plating solution. This anomalous phenomenon-known already for other metals (Zn, Cd, Sn)-has been confirmed and investigated for iron-group metals (Fe, Co, Ni) in this work. Electrolytic deposition of Ni-Co binary alloys, including anomalous behavior is a complicated process. Understanding the anomalous behavior would lead to better control of the deposition process and to explanation of the mechanism of Ni-Co co-deposition.

Keywords Nickel \cdot Cobalt \cdot Fe powder \cdot Paraffin impregnated graphite electrode (PIGE) \cdot Anomalous co-deposition \cdot Cyclic voltammetry \cdot Polarization curves

Abbreviations ϵ : Voidage factor $\cdot V_{powder}$: Volume of iron powder $\cdot V_{electrolyte}$: Volume of the electrolyte \cdot

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 α : Charge transfer coefficient · *CV*: Cyclic voltammetry · *PIGE*: Paraffin impregnated graphite electrode

Introduction

The electrodeposition technique has been used as an alternative method for preparing thin films of various alloys. Serious interest is still devoted to the investigation of electrodeposition of iron group metals because of their interesting mechanical and magnetic properties, which offer possibilities of industrial applications, e.g. in microsystem technology of sensors, actuators, in rocket technology, astronautics, for anticorrosive coatings, and for decorative purposes [1, 2, 3].

Electrodeposition of Ni–Co binary alloy has been performed in baths containing chloride [4, 5], sulphamate [6, 7], sulphate [8] and various additives, such as pyrophosphate, citrates, saccharine and sodium lauryl sulphate. Additives, pH, temperature, and current density affect the morphology and composition of the deposit and mechanism of co-deposition [4–9]. It is known that addition to the bath of boric acid increases current efficiency, improves deposit morphology, and hinders excessive hydrogen evolution [10, 11].

Temperature is the most important factor in Ni–Co co-deposition [12]. The rate of diffusion for sulphate and chloride baths increases with increasing temperature. Two opposite tendencies were observed. While the cobalt content increases with increasing temperature up to 60 °C, the deposition of nickel increases above 70 °C. Various baths with pH ranging from 2 to 5 have been used and various effects of pH observed [12]. Alkaline bath with pH ranging from 8.9 to 10.5 was used in electrochemical dissolution of ternary Ni–Co-metalloid alloys in carbonate–bicarbonate buffer [13]. These authors investigated the influence of pH and bath composition. Independently on the electrolyte composition, the pH near the electrode surface increases during the codeposition process [14]. This effect was induced by evolution of hydrogen followed by the precipitation of metal hydroxides on the electrode surface, and their occlusion into the growing deposit. The pH increases in the vicinity of the electrode surface more rapidly than in the bulk of electrolyte.

Anomalous behavior observed during binary alloy deposition of iron-group metals is characterized by preferential deposition of the less noble metal (Co) [12]. Many authors described as anomalous deposition the fact that higher content of the less noble metal (Co in comparison with Ni) was found in the deposit, even though the concentration ratio of the metals in the bath was reversed [12, 14, 15]. This behavior is, however, independent on the anion composition of the bath [14], and was observed for very thin coating layers and small values of current density [16]. One explanation of this phenomenon is the above mentioned precipitation of the less noble metal hydroxide on the cathode surface, due to hydrogen evolution and subsequent increase of pH in the vicinity of electrode surface accompanying the binary alloy electrodeposition. Some studies showed that this phenomenon was observed at lower pH at the electrode surface than in previous cases. Hessami and Tobias [17] and Grande and Talbot [18] assumed the formation of monohydroxide ions NiOH⁺ and FeOH⁺, acting as charge-transfer species for Ni-Fe co-deposition. Formation of these species indicates that the anomalous Ni-Fe co-deposition occurs without an increased pH and precipitation of metallic hydroxides. Matlosz [19] concluded that anomalous Ni–Fe codeposition relates to the different kinetic constants for the electrodeposition of individual metals. These models characterize quite well the Ni-Fe co-deposition. The anomalous features of Ni-Co co-deposition have been described in details in several papers [20–22]. Hu and Bai [20] suggested formation of $M(OH^+)_{ads}$ or even $M(OH)_2$ intermediates during cathodic deposition. The main reason for their formation was the hydrogen evolution followed by alkalization of solutions in the vicinity of an electrode surface. On the basis of experimental results [21], the authors proposed mathematical model [22] describing anomalous co-deposition of iron group metals. The result described in this paper [21] indicated that the less noble elements have a stronger influence on the behavior of its partners resulting in their enhanced deposition. The mechanism of co-deposition of Ni-Fe, Ni-Co, Fe-Co, and individual metals was reported by Zech et al. [22].

$$\mathbf{M}_{1}(\mathbf{II}) + \mathbf{e}^{- \xrightarrow{\kappa_{1}}} \mathbf{M}_{1}(\mathbf{I})_{ads} \tag{1}$$

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$$\mathbf{M}_{1}(\mathbf{I})_{ads} + e^{-} \xrightarrow{k_{2}} \mathbf{M}_{1}(s) \tag{2}$$

In these equations, $M_1(II)$ is a dissolved metal ion, hydrolyzed or not, $M_1(I)_{ads}$ is a adsorbed intermediate

which may contain a hydroxyl group, $M(OH)^+$, and $M_1(s)$ is the deposit metal.

$$\theta = \frac{k_1 C_{M_1}(II)}{k_2 + k_1 C_{M_1}(II)}$$
(3)

On the basis of the fractional surface coverage of the $M(OH)^+$ (ads) intermediate θ , authors [22] predicted two limit conditions. They supposed that if $k_2 < < k_1$, where k_1 and k_2 are rate constant for first and second electron transfer respectively, the reaction was controlled by second electron transfer. Then the $\theta \approx 1$ and the deposition rate were only slightly dependent on the intermediate and/or metal ion concentration. If $k_1 < k_2$, the surface coverage was in the range $0 < \theta < 1$ and the rate determining step (rds) was the first electron transfer. The deposition rate was significantly depending on the concentration of metals, therefore the authors supposed that rds is the first electron transfer. For co-deposition of iron-group metal, it was assumed that an adsorbed intermediate $[M_2M_1(III)]_{ads}$ was formed in the first oneelectron step. In the case of Ni-Co co-deposition, the adsorbed intermediate corresponds to [CoNi(III)]_{ads} and in the following reaction steps cobalt metal and nickel ions are formed.

This paper describes the electrodeposition of binary Ni–Co alloy on Fe powder in fluidized bed. The charge transfer in fluidized bed was mathematically described and experimentally verified in works [23-25]. Fleischmann and Oldfield [23] assumed that the charge transfer in a fluidized bed electrode was realized at the contact of particle with the solid electrode or other charged particles. These authors introduced the collision time and the collision frequencies. The collision was classified as elastic one. Moreover, it was assumed that the charge was distributed uniformly on the surface of iron particles [24]. It was experimentally found that the particle size and the particle density in the bath (suspension density) most influenced on the charge distribution and on the amount of metal coating. Using impedance measurements [25], the following results were obtained: with increasing suspension density, the charge-transfer resistance decreased, and the ohmic resistance of the suspension, indicating the presence of uncharged particles, increased.

This work was mainly aimed at the study of the influence of suspension density on the electroplating process, and the anomalous behavior has been investigated as well.

Materials and methods

Composition of electrolytes

Watts-type electrolytes (Table 1) were used for the electrodeposition/dissolution of individual metals and the binary alloy. The measurements for individual

 Table 1 Composition of electrolytes used for voltammetric measurements (individual metals and binary alloy)

No.	Composition of electrolyte	Concentration (mol/dm ³)	pН
(1)	NiSO ₄ ·7 H ₂ O	1.20	2.0 ± 0.2
	NaCl	0.60	
	H ₃ BO ₃	0.60	
(2)	$CoSO_4 \cdot 7 H_2O$	1.20	3.0 ± 0.2
	NaCl	0.50	
	H ₃ BO ₃	0.50	
(3)	NiSO ₄ ·7 H ₂ O	0.70	2.0 ± 0.2
	$CoSO_4$. 7 H_2O	0.70	
	NaCl	0.26	
(4)	NiSO ₄ ·7 H ₂ O	0.70	2.0 ± 0.2
	$CoSO_4 \cdot 7 H_2O$	0.13	
	NaCl	0.26	

metals Ni and Co were performed in the baths marked as nos. 1 and 2 in Table 1. Bath nos. 3 and 4 was used for the deposition of the binary Ni–Co alloy in absence and in the presence of iron powder, respectively. To predict the mechanism of Ni-Co co-deposition, the pH was measured before and after each experiment.

Anomalous co-deposition of Ni–Co binary alloy was studied in the electrolytes containing: (1) 0.70 mol/dm³ NiSO₄ ·7H₂O + (0.04–0.10) mol/dm³ CoSO₄ ·7H₂O + 0.26 mol/dm³ NaCl; (2) 0.13 mol/dm³ CoSO₄ ·7H₂O + (0.24–0.60) mol/dm³ NiSO₄ ·7H₂O + 0.26 mol/dm³ NaCl. All measurements were performed using 50 ml of electrolyte at 25 °C. The pH was adjusted by addition of H₂SO₄ (1:1) or NaOH (approximately 20% solution) before each experiment.

Fe powder

The grain size of Fe powder was $63-100 \mu m$ in diameter. Before each experiment the surface of the powder was activated in 10% solution of hydrazine dihydrochloride for 5 min, after which the powder was rinsed with distilled water and acetone, and finally dried on filter paper.

Paraffin impregnated graphite electrode

The graphite cylinder was 152 mm long and 6 mm in diameter. Its electric resistance was 1,000 $\mu\Omega$ cm⁻¹, porosity 30%. The graphite contained (in ppm) B: 0.01; Ca: 0.1; Cu: 0.1; Fe: 0.2; Mg: 0.01; Si: 0.1; Al: 0.05; Ti: 0.01. It was impregnated with paraffin in vacuum at about 150–200°C for 3 h [26].

Apparatus

The polarization curves were recorded using a potentiostat EcaStat, Model 110 V (Istran, Bratislava, Slovak Republic). The electrochemical cell with three electrodes is shown in Fig. 1. Paraffin impregnated graphite



Fig. 1 Electrochemical cell for measurements of polarization curves: 1 working electrode, 2 auxiliary electrode, 3 reference electrode, 4 stirrer

electrode (PIGE) with an area of 2.83×10^{-5} m² was used as a working electrode. The auxiliary electrode was a Pt foil with an area of 87.9×10^{-5} m², and the potential was referred to the Ag/AgCl/KCl (3.0 mol/dm³) electrode. The surface of PIGE was mechanically polished with fine sand and filter paper before each measurement. Platinum electrode was cleaned in nitric acid (1:1) and rinsed with distilled water.

In order to eliminate the diffusion of ions (Ni^{2+}, Co^{2+}) in the thin solid/liquid layer during measurements the electrolyte was continuously stirred at 600 rpm and 200 rpm with and without Fe powder, respectively.

The polarization rate was 10 mV/s for all measurements. The working electrode was polarized in the potential range $0 V \div -1.5 V \div +2.0 V \div 0 V$ (vs. Ag/AgCl/ 3 M KCl).

Results and discussion

Cyclic polarization curves for individual metals and binary alloy without Fe powder

The polarization curves for individual metals and binary alloy deposited on PIGE without Fe powder in solution are presented in Fig. 2. The cathodic part of the curves reflects a reduction process of metallic ions on the working PIGE. It is characterized by nearly linear increase of the current after having reached an appropriate deposition potential. Table 2 shows the experimental deposition potentials of metals on PIGE versus Ag/ AgCl/3M KCl and SHE reference electrodes. It was observed that the deposition potential for nickel was more negative than that for cobalt (Table 2). The experimentally found deposition potentials for



Fig. 2 Polarization curves for individual metals (Ni, Co) and binary alloy (Ni–Co) electrodeposition on PIGE without Fe powder performed in baths summarized in Table 1

individual metals (Ni, Co) are not in accordance with the corresponding theoretical standard potentials. The order of measured deposition potentials in mixtures of Ni and Co ions was opposite to what would be expected from the standard potentials of individual metals. The deposition potential of the binary alloy is situated very close to the deposition potential of cobalt.

The anodic part of the polarization curves corresponds to the dissolution of deposited metallic layer. One oxidation peak for every polarization curve (Ni, Co and Ni–Co) was observed. We assume that either dissolution of the binary alloy progresses simultaneously, or the dissolution processes of Ni and Co in the binary alloy proceed very close to each other.

All experiments were carried out in the presence of oxygen dissolved in the electrolyte because high concentration of protons in the bath preferred the hydrogen evolution. The generation of H₂ could be realized from reduction of protons and from water [20–22, 27, 28]. While the proton reduction was mass transport controlled, the water decomposition was kinetically controlled. It is well known that the diffusion controlled oxygen reduction depends on pH value and predominates in weak acid and neutral solutions (pH > 4.0) [27]. Therefore, we assumed that the oxygen reduction could be neglected and that if has not influenced the deposition

 Table 2 Values of theoretical standard and deposition potentials for individual metals (Ni, Co) and binary Ni–Co alloy

	Theoretical standard potential (vs. SHE) (V)	Experimental deposition potential (vs. Ag/AgCl/ 3M KCl) (V)	Experimental deposition potential (vs. SHE) (V)
Ni	-0.23	-1.12	$-0.89 \\ -0.78 \\ -0.78$
Co	-0.27	-1.00	
Ni–Co	-	-1.00	

Table 3 Values of suspension density $(1 - \epsilon)$ calculated using Eq. (4), difference of pH before and after voltammetric measurements and the charge transfer coefficient α for various amount of Fe powder added

m_{Fe} (g)	$(1-\epsilon) \times 10^3$	Δ pH (mean)	α
1.7	4.3	0.45	0.81
3.3	8.3	1.10	0.52
5.0	12.5	1.20	0.41
6.7	16.7	1.35	0.42
8.3	20.6	1.85	0.23

process realized on the graphite electrode for experimental conditions presented here.

The widely accepted model for electrodeposition of all iron-group metals and alloys is a multistep reaction pathway of Bockris [8]. The rds can be switched from first to second electron transfer as the cathodic potential becomes more negative. With respect to the Bockris mechanism and our experimental conditions (intensive stirring), it was assumed, that co-deposition of nickel and cobalt was a charge transfer controlled process. In this context, the charge transfer coefficients were determined to study of electrodeposition of Ni, Co and Ni-Co. Tafel plots were made at low potentials in narrow interval around the deposition potential of metals. The values of charge transfer coefficient were 0.40, 0.43 and 0.32 for Ni, Co and Ni–Co, respectively. These values indicated that the electrode processes on the PIGE were not reversible, and can be classified as quasi-reversible or irreversible ones.

The side reaction during the deposition of iron-group metals and alloys is hydrogen evolution on the electrode. In a higher pH solution, the diffusion controlled proton reduction can proceeds in almost whole cathodic part of metals (Ni, Co, Ni–Co) reduction. On the other hand, the decomposition of water can occur at more negative potentials.

The value of α for Ni–Co binary alloy reduction was lower, therefore, we assumed that the common reaction intermediate was formed and led to mutual inhibition of both metals. Presented experimental results correlate well with predicted co-deposition model [22] and it will be discussed in next chapter.

Effect of suspension density

Suspension density influences the electrode process and the composition of the deposited layer both on PIGE and on Fe particles. The density of suspension (Fe powder in plating solution) was calculated according to equation:

$$(1 - \varepsilon) = \frac{V_{\text{powder}}}{V_{\text{electrolyte}} + V_{\text{powder}}}$$
(4)

The calculated values are summarized in Table 3. The essential condition for electroplating of iron powder

particles is fluidization of the powder material. This was achieved by stirring of the suspension in circular motion during voltammetric measurements. While in motion in the cell powder particles collide with the solid PIGE cathode, become electrically charged and act themselves as electrodes. The particles of Fe powder repeat contact with the working electrode and become coated with a thin layer of the binary alloy. A few particles may be trapped with the coating on the electrode surface. For electroplating of powder material only those particles, which have not been immobilized on PIGE, are important. The number of contacts increases with increasing suspension density. Due to intense interaction of iron powder with PIGE electrode surface, higher stirring rate of more than 200 rpm was applied. Increased stirring rate from 200 rpm to 600 rpm did not influence the deposition process.

Figure 3 shows the polarization curves for deposition of binary Ni-Co coating on iron powder particles in fluidized bed for various densities of suspension, as adjusted by using varying mass of Fe powder particles added to the plating bath. Of course the deposition occurs also on PIGE. The anodic part of polarization curve represents the dissolution of the deposited metallic layer from PIGE. Three anodic peaks were observed for the dissolution of binary Ni-Co alloy in the presence of iron powder (Fig. 3). The first oxidation peak (I) increases with increasing amount of iron powder particles in fluidized bed, i.e. with suspension density. It may be assumed that the first anodic peak corresponds most likely to oxidation of Fe trapped in the deposited layer on PIGE. The content of Fe in the Ni-Co deposit may has its origin in: (1) Fe particles trapped in the deposit, (2) the low content of Fe in the Ni–Co alloy, which had been reduced from electrolyte in the cathodic part of polarization curve. The added iron particles partially



Fig. 3 Polarization curves for electrodeposition of the binary Ni–Co coating on iron powder particles in fluidized bed for various densities of suspension (from plating bath no. 4 according to Table 1)

dissolve in acidic electrolyte to ferrous ions, which are reduced together with cobalt and nickel ions.

We assume that the second (II) and third (III) anodic peaks in Fig. 3 correspond to the dissolution process of the Ni–Co binary alloy at PIGE. The height of peaks II and III decreases with increasing suspension density. Increasing amount of added Fe powder particles increases significantly the surface area available for the electrodeposition of the metallic layer. The amount of coating deposited on powder particles increases while the amount of coating deposited on the solid cathode decreases with increasing suspension density.

An important factor, which must be taken into account simultaneously with the electrodeposition of metals, is the hydrogen evolution connected with the increase in pH. With increasing amount of the powder particles in fluidized bed, the difference between pH value before and after voltammetric experiment increases (Table 3). As the pH change is proportional to the amount of hydrogen evolved from electrolyte during cathodic process one can conclude that the electrode surface extends due to contacts with powder particles.

The charge transfer coefficient for the deposition of binary Ni–Co coating on powder particles was determined for different densities of suspension. Applied polarization rate was the highest limit value of usual range used for Tafel plots [29], but this choice was acceptable to characterize the tendency of charge transfer coefficient values with increase of suspension density and/or metal concentrations. It was found that with increasing amount of powder particles the value of α decreases (Table 3). The mentioned increase of electrode surface, as a consequence of higher number of particle contacts, reduces the current density and the rate of the electrodeposition process. This effect is in accordance with the decrease of peaks II and III on polarization curves in Fig. 3.

The mechanism of the electrolytic deposition process in the fluidized bed is a very complex problem. The charge can be transported between electrode/particles and/or particle/particle interface. We assume that: (1) the powder particles have a spherical shape, (2) the charge transfer occurs during collision with the electrode and/or particle, and (3) the charge is uniformly distributed on the whole surface of powder. The value of charge transfer coefficient, characterizing the distribution of potential on the interface, was determined for the heterogeneous system described above. On one hand, the authors [25] found that the charge-transfer resistance decreased with increasing number of particles, but on the other hand the ohmic resistance of the suspension and the number of uncharged particles increased with the increasing suspension density. Taking into consideration these facts, our results indicated that the number of active iron particles increased with increasing suspension density, and the deposition of Ni-Co metallic layer took place especially on the surface of these particles. Therefore, we assumed that the value of transfer coefficient reflected the distribution of potential



Fig. 4 a Polarization curves for the binary Ni–Co alloy electrodeposition on PIGE for different concentrations of Co^{2+} ions $(0.04-0.10 \text{ mol/dm}^3)$ and constant concentration of Ni²⁺ ions (0.70 mol/dm^3) in the bath **b** Zoom in cathodic part of

on the iron particle/liquid interface at higher suspension density.

Anomalous co-deposition

Measurements with changing individual metal concentrations in the bath were carried out without powder particles with the aim to reveal the anomalous codeposition of the binary Ni-Co alloy. Figure 4a shows the polarization curves for various concentrations of cobalt ions and constant concentration of nickel ions (0.70 mol/dm^3) in the bath. It can be seen that both the current at the switching potential (-1.5 V), and current of the anodic peak increase with concentration of cobalt ions. In the cathodic part of cyclic voltammogram one peak was observed in all experiments with the only exception of 0.1 mol/dm³ concentration of Co²⁺ (Fig. 4b), which was outside studied potential range. The cathodic peak potential shifted to more negative values at reverse sweep with increased concentration of Co^{2+} in the bath.

Similar experiments were performed for various concentrations of Ni²⁺ ions and constant concentration of Co²⁺ ions (0.13 mol/l) in the bath (Fig. 5). The increase of current at the cathodic reversal potential and at the anodic peak potential was smaller in comparison with the previously mentioned experiments for different concentrations of cobalt ions (Fig. 4a), in spite of more significant changes in nickel concentration. With the aim to achieve the usual concentrations of cobalt (0.13 mol/l) and nickel (0.70 mol/l) ions in binary plating bath the increase of nickel concentration was greater then that of cobalt concentration.

For both series of experiments presented in Fig. 4a and Fig. 5, the charge transfer coefficients for binary coating deposition on PIGE were determined. The distinct course of concentration dependencies of α for



polarization curves for the binary Ni–Co alloy electrodeposition on PIGE for different concentrations of Co^{2+} ions (0.04–0.10 mol/dm³) and constant concentration of Ni^{2+} ions (0.70 mol/dm³) in the bath

nickel and cobalt can be seen from Fig. 6a, b. The α value increases with cobalt concentration in the bath (Fig. 6a) but slightly decreases with increase of nickel concentration (Fig. 6b). Consequently, it can be concluded that the rate of the Ni–Co binary alloy electro-deposition increases with cobalt concentration, while increasing nickel concentration moderately inhibits the deposition process.

Our results indicate that the mechanism of co-deposition of Ni–Co binary alloy is consistent with the predicted model [22] (see Introduction). In this model the adsorbed intermediate containing both metal ions is responsible for both the inhibition of the more noble species and the enhancement of the less noble species.



Fig. 5 Polarization curves for the binary Ni–Co alloy electrodeposition on PIGE for different concentrations of Ni²⁺ ions (0.24– 0.60 mol/dm³) and constant concentration of Co²⁺ ions (0.13 mol/ dm³) in the bath



Fig. 6 a Dependence of charge transfer coefficient– α for electrodeposition of the binary Ni–Co coating on PIGE on concentration of Co²⁺ ions in the bath. *open square* c(Co²⁺)=0.04–0.10 mol/ dm³, c(Ni²⁺)=0.70 mol/dm³, c(NaCl)=0.26 mol/dm³ **b** Depen-

Conclusions

The aim of this work was to study the electrodeposition process of Ni–Co binary alloy on iron powder particles in fluidized bed using voltammetric measurements.

Electrodeposition of individual metals (Ni, Co) and binary alloy (Ni–Co) without powder material was compared. The deposition potentials were found to be -1.000 V, -1.000 V, and -1.120 V for Co, Ni–Co, and Ni, respectively. One anodic peak was observed for the dissolution of each metallic layer (Ni, Co, Ni–Co). Three oxidation peaks were recorded for the dissolution of the binary Ni–Co film with powder particles presented in the cell.

Tafel plot was used for the calculation of the chargetransfer coefficient in close proximity to the deposition potential of metals. It was found that with the increase of the number of powder particles in the bed the chargetransfer coefficient α decreases, i.e. electrodeposition of the binary Ni-Co layer slows down. Preferential deposition of the less noble metal (Co) from Ni+Co mixture baths was observed. The values of charge transfer coefficient α for the Ni–Co co-deposition were lower than that for individual metals. It was found that the rate of binary alloy deposition increases with increasing cobalt ions concentration but it decreases with increasing nickel ions concentration. We concluded that the codeposition of Ni-Co was enhanced by less noble metal (Co) and inhibited by more noble metal (Ni). The model proposed by Zech, Podlaha and Landolt [22] for Ni-Co co-deposition was confirmed by the results of our experiments.

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References

- 1. Tutovan V, Velican N (1971) Thin Solid Films 7:219
- 2. Kefalas JH (1966) J Appl Physics 3:37
- 3. Clauss RJ, Klein RW, Tremmel RA, Adamowicz NC (1971) American Electroplates Society, New York, p 679
- 4. Burzynska L, Rudnik E (2000) Hydrometallurgy 54:133
- 5. Correia AN, Machado SAS, Avaca LA (2000) J Electroanal Chem 488:110
- Goldbach S, Kermadec R, Lapicque F (2000) J Appl Electrochem 30:277
- Golodnitsky D, Gudin NV, Volyanuk GA (2000) J Electrochem Soc 147:4156
- 8. Sasaki KY, Talbot JB (2000) J Electrochem Soc 147:189
- 9. Bai A, Chi-Chang Hu (2002) Electrochim Acta 47:3447
- 10. Lupi C, Pilone D (2001) Miner Eng 14:1403
- 11. Lupi C, Pilone D (2002) Waste Manage 22:871
- Brenner A (1963) Electrodeposition of alloys, principles and practice, vol II. Academic, New York, p 239
- Barbosa MR, Gassa LM, Ruiz ER (2001) J Solid State Electrochem 6:1
- Golodnitsky D, Rosenberg Yu, Ulus A (2002) Electrochim Acta 47:2707
- 15. Fan Ch, Piront DL (1996) Electrochim Acta 41:1713
- 16. Correia AN, Machado SAS (2000) Electrochim Acta 45:1733
- 17. Hessami S, Tobias CW (1989) J Electrochem Soc 137:3611
- 18. Grande WC, Talbot JB (1993) J Electrochem Soc 140:669
- 19. Matlosz M (1993) J Electrochem Soc 140:2272
- 20. Hu CC, Bai A (2002) J Electrochem Soc 149:C615
- 21. Zech N, Podlaha EJ, Landolt D (1999) J Electrochem Soc
- 146:2886 22. Zech N, Podlaha EJ, Landolt D (1999) J Electrochem Soc
- 22. Zech N, Podlana EJ, Landolt D (1999) J Electrochem Soc 146:2892
- 23. Fleischmann M, Oldfield JW (1971) J Electroanal Chem 29:231
- 24. Gálová M, Oriňáková R, Lux L (1998) J Solid State Electrochem 2:2
- Gál MF, Gálová M, Turoňová A (2000) Collect Czech Chem Commun 65:1515
- 26. Scholz F, Meyer B (1994) Chem Soc rev 23:341-347
- 27. Lorbeer P, Lorenz WJ (1980) Electrochimica Acta 25:375
- 28. Zhuang Y, Podlaha EJ (2000) J Electrochem Soc 147:2231
- 29. Greef R, Peat R, Peter LM, Pletcher D, Robinson J (1985) Instrumental methods in electrochemistry. Ellis Horwood Limited, Great Britain, p 44