*ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 16, No. 1. 2010*

# Electroreduction of Ni(II) and Co(II) from Pyrophosphate Solutions

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*Received 24 April 2009; accepted 08 March 2010*

Pyrophosphate solutions are of interest for electrodeposition of resistive to corrosion Mo-containing alloys with iron group metals. Some difficulties to describe the mechanism and kinetics of codeposition are related with rare data about the mechanism and kinetics of pure iron group metal complexes electroreduction. The aim of this work was to study the correlations between deposition rates of Ni and Co from pyrophosphate baths and ionic content of baths. Adding of $(NH_4)_2SO_4$ and further forming of ammonia in the solution accelerates sufficiently the rate of Ni electrodeposition. The effect well correlates with increasing the molar fraction of various ammonia complexes with Ni(II). The molar fraction of Ni(II) complexes with ammonia is 1000 times higher than ones of Co(II). Based on the different pH and $(NH_4)_2SO_4$ influence on the deposition rate it is possible to assume that $CoOH^+$ and $Ni(NH_3)^{2+}_{1\div6}$ can act as charge-transfer particles in the pyrophosphate-ammonia solutions.

*Keywords*: nickel, cobalt, electrodeposition, complexes, pyrophosphate.

## 1. INTRODUCTION

Baths containing Co(II) or Ni(II) citrate or pyrophosphate complexes are widely used for the electrodeposition of various alloys, especially containing molybdenum or tungsten, that are nanocrystalline, smooth and resistant to corrosion, see e. g. [1 – 12].

Pure molybdenum or tungsten cannot be electrodeposited from aqueous electrolytes, but can form alloys by codeposition with iron group metals – called “induced codeposition” by Brenner [13]. There are number of mechanisms proposed to explain the codeposition of W or Mo with iron group metals. Earlier models [14] are based on the following hypotheses:

- catalytic effect of the cathode surface;
- assuming the formation of joint complexes between tungsten and metal precipitates;
- considering the deposition improvement by tungsten through alloy formation;
- stages involving the formation of intermediate electrochemically active complex on the cathode;
- model involving the formation of intermediate phase film.

All mentioned models explaining codeposition might be confirmed in part. The model providing a mathematical network describing the induced codeposition was proposed by Podlaha and Landolt [16]. It is based on the reversible formation of intermediate compounds in form of film or complexes, namely: the codeposition of W or Mo with iron group metal is followed by the slow film formation of heteropolytungstates $[H_pNi_qW_rO_s]_w$ or adsorbed complex of $[M(II)LWO_2]_{ads}$ or $[M(II)LMoO_2]_{ads}$ and fast electrochemical reaction catalyzed by the adsorbed Co(II) or Ni(II) complexes [15].

Some difficulties to describe the mechanism and kinetics of codeposition are related with rare data about the mechanism and kinetics of pure iron group metal complexes electroreduction and identification of the electrochemically active complex of metal that participates in the electrochemical charge transfer reaction in complex solutions. Based on investigations of Ni and Ni-Fe electrodeposition from acidic sulfate baths (for ex.: [16 – 17]), it was found that nickel monohydroxide ($NiOH^+$) particles act as charge-transfer species. The sufficient amount of $NiOH^+$ can be formed near electrode surface in the absence of complexing agents due to pH increasing on the cathode surface caused by parallel hydrogen evolution reaction. So, in this case the slowest charge transfer reaction can be written in a following way:

$$NiOH^+ + e^- \rightarrow Ni(OH)_{ads} . \qquad (1)$$

It has been observed that the formation of Ni-W alloys is explained by chemical reactions where $NiOH^+$ participates as charge-transferring particle [16].

However, the situation near surface is changed by the presence of complexing agents. Citrate- or pyrophosphate ions increasing solubility of Ni(II) compounds with pH increasing due to complexation with them. Furthermore, such baths distinguish oneself by rather strong buffer capacity and any sufficient pH fluctuations with distance from electrode surface do not happen [14], i. e. the distribution of species both in the bulk and near surface is the same or close to that.

Some peculiarities of Ni and Co electrodeposition from the pyrophosphate solutions are summarized in [18], where the promotional effect of ammonium chloride is noted for nickel electrodeposition. Therefore, the aim of this work is to study the correlations between deposition rates of Ni and Co from pyrophosphate baths and ionic content of baths.

## 2. EXPERIMENTS AND CALCULATIONS

The total current density was controlled using AUTOLAB302 system. For the deposition a plating cell with two separated anodic compartments was used. The anodes were two plain graphite rods of area ca. 10 $cm^2$. The substrate was made of pure copper foil of working area 4 $cm^2$. Immediately before electrodeposition the

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surface was mechanically polished, degreased and then activated in dilute sulfuric acid. All experiments were carried out at room temperature (20 °C). The deposition rate of Co and Ni was expressed in electrical terms as a partial current density at certain conditions. Values of partial current density ($j_{Me}$) for the Co or Ni and electrodeposition conditions were calculated based on the Faraday law of electrolysis using a following equation:

$$j_{Me} = \frac{2mF}{MtA}, \qquad (2)$$

where $m$ is a weight of deposit; $F$ is a Faraday constant; $M$ is a molecular weight of the depositing metal (Co or Ni); $t$ is a deposition time; $A$ is a working area of cathode.

**Table 1.** Equilibrium constants used for calculations [19] ($\beta$ is cumulative complex stability constant, $K$ is ionization constant)

| Particle | log$\beta$ or log$K$ | Particle | log$\beta$ or log$K$ |
|---|---|---|---|
| $NiP_2O_7^{2-}$ | 5.94 | $CoP_2O_7^{2-}$ | 6.10 |
| $NiHP_2O_7^{-}$ | 3.71 | $CoHP_2O_7^{-}$ | 3.40 |
| $Ni(P_2O_7)_2^{6-}$ | 2.00 | | |
| $NiOH^+$ | 3.58 | $CoOH^+$ | 4.20 |
| $Ni(OH)_2$ | 8.10 | $Co(OH)_2$ | 8.50 |
| $Ni(OH)_3^-$ | 11.20 | $Co(OH)_3^-$ | 9.66 |
| $Ni(OH)_4^{2-}$ | 11.90 | $Co(OH)_4^{2-}$ | 9.54 |
| $NiNH_3^{2+}$ | 2.81 | $CoNH_3^{2+}$ | 2.10 |
| $Ni(NH_3)_2^{2+}$ | 5.08 | $Co(NH_3)_2^{2+}$ | 3.67 |
| $Ni(NH_3)_3^{2+}$ | 6.85 | $Co(NH_3)_3^{2+}$ | 4.78 |
| $Ni(NH_3)_4^{2+}$ | 8.12 | $Co(NH_3)_4^{2+}$ | 5.53 |
| $Ni(NH_3)_5^{2+}$ | 8.93 | $Co(NH_3)_5^{2+}$ | 5.75 |
| $Ni(NH_3)_6^{2+}$ | 9.08 | $Co(NH_3)_6^{2+}$ | 5.14 |
| $NH_4^+$ | 9.40 | | |
| $H_4P_2O_7$ | 0.80 | $H_3P_2O_7^-$ | 1.40 |
| $H_2P_2O_7^{2-}$ | 5.40 | $HP_2O_7^{3-}$ | 7.43 |

The ionic composition of solution was studied by means of mathematical simulation using “Maple 6” software. For this purpose an appropriate mathematical model has been developed. This model includes a system of equations containing three types of relations, namely: (a) equilibrium constants for all compounds added, including the ionization constants for acids and ammonia, cumulative complex stability constants; (b) mass balance for all forms in the equilibrium mixture:

$$[J]_{tot} = \sum_i \left[J_i^{n\pm}\right] \qquad (3)$$

and (c) charge balance

$$\sum_i n_i\left[Cat_i^{n_i+}\right] = \sum_j n_j\left[An_j^{n_j-}\right], \qquad (4)$$

where symbols “*Cat*” and “*An*” mean cations and anions, respectively.

The critically selected equilibrium constants used in this study are listed in Table 1. Such procedure has been used and successfully applied to describe solubility phenomena in citrate-ammonia baths [1, 4].

## 3. RESULTS AND DISCUSSIONS

The study was carried out in solutions, containing 0.36M $Na_4P_2O_7$ and 0.14M $NiSO_4$ or 0.025M $CoSO_4$. The lower concentration of $CoSO_4$ than $NiSO_4$ was selected, because powdered Co electrodeposits, if Co(II) concentration is higher, and then it is difficult to balance correctly the weight of electrodeposits. The values of total current density were chosen close to that applied for electrodeposition of Mo or W alloys with iron group metals [3, 11]. The values of solution pH ranged from 6 to 9, and were corrected by adding NaOH or $H_2SO_4$ solutions. Ammonium sulfate was used as a source of ammonia as a ligand which is forming in the solution:

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+ . \qquad (5)$$

Initial concentrations ($[(NH_4)_2SO_4]_0$ were ranged 0M to 0.45M. Take a notice that the sum of total molar concentrations of ammonium-ion and ammonia in the solution is related with dissolved ammonium sulfate concentration as follows:

$$[NH_3]_{tot} + [NH_4^+]_{tot} = 2[(NH_4)_2SO_4]_0 . \qquad (6)$$

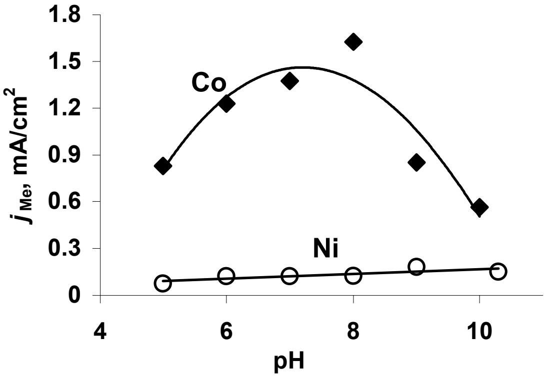

**Fig. 1.** Partial current densities for Ni and Co electrodeposition as a function of pH obtained from the pyrophosphate solutions without $(NH_4)_2SO_4$. The total current density 12.5 mA cm$^{-2}$

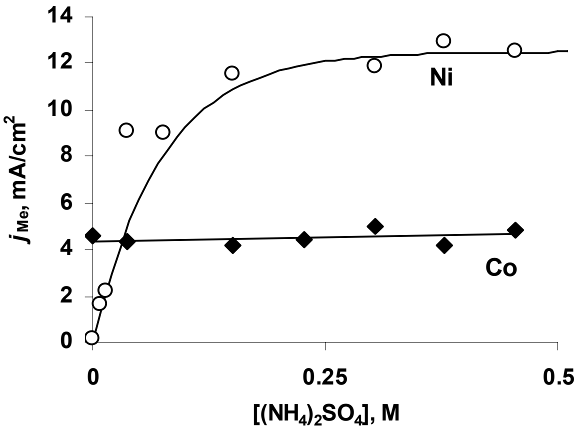

**Fig. 2.** The effect of initial $(NH_4)_2SO_4$ concentrations on partial current densities for Co and Ni at pH 8.0. Total current densities were: $j$ = 45 mA/cm$^2$ for Co, and $j$ = 30 mA/cm$^2$ for Ni

The different influence of pH on the deposition rate of Ni and Co from the solutions without $(NH_4)_2SO_4$ was found (Fig. 1). The rate of Co deposition increases in pH rage from 5 to 8, and then decreases at $pH > 8$. The decreasing in rate of Co deposition at $pH > 8$ probably is caused by the peculiarities of hydrogen evolution on the electrode from the alkaline solutions – see below on the next pages. Whereas, the values of pH do not have influence on Ni deposition rate which values are extremely low. Noticeably, Co deposition rate is few times higher than Ni regardless the sufficiently lower concentration of Co (II) in the solution.

Ammonium ions differently influence on the deposition rate of Ni and Co at given values of pH. Ni deposition rate sharply increases with increasing in concentration of ammonia up to 0.25 mol/l, and further increasing in ammonia concentration does not change the deposition rate sufficiently. Whereas, ammonia does not influence the Co electrodepositing rate sufficiently. The characteristic results are shown in Fig. 2. The lower partial current densities for Co(II) are caused by the lower concentration of Co(II) in solution.

The influence of pH on the Co(II) electroreduction rate (partial current density) at various concentrations of ammonium sulfate is shown in Fig. 3. The obtained effect can be represented by the single trend-line, which confirms a weak effect of ammonia concentration. As it can be seen, the variation of pH can cause the increase of deposition rate up to 4 times. Whereas, at the given concentration of ammonia the effect of pH is representing by the similar parabolic function with maximum at pH 8 like is shown in Fig. 1.

Whereas, the rate of Ni deposition is not so sensitive to the pH changes at the presence of ammonia, and values of partial current density vary in the range ±25 % with pH changes, and ones are defined rather by the concentration of ammonia in the solution (see Fig. 4). In all studied cases the partial currents for Ni and Co deposition is lower than the total current. Therefore, the obtained values of partial current for metal deposition we concern as maximally possible values at the given conditions.

These different peculiarities of Co and Ni electrodeposition impossible to explain by slightly different polarization of electrodes obtained during electrolysis or differences in current efficiency. Indeed, the values of current efficiency at the current densities applied are ranged 5 % to 40 %, i. e. the main electrodic process is hydrogen evolution. The values of electrode polarization also are close, and electrodeposition occurs at potentials from –0.9 V to –1.4 V dependently on current density applied.

In our opinion, these differences between Co and Ni electrodeposition rates and different influence of ammonia might be explained by the different ionic content of solution. As it is seen from the data presented in Table 1, the cumulative constants of Ni(II) with ammonia are higher than those for Co(II) complexes, and these differences in some cases could reach a factor up to $10^5$. Therefore, the ionic content of pyrophosphate-ammonia solutions is different in the presence of Ni(II) and Co(II) complexes (see Figs. 5 and 6 for metal-containing complexes distribution). As follows from the presented results, the fraction of ammonia complexes with Ni(II) are much higher (about 1000 times) than the fraction of ammonia complexes with Co(II). Moreover, more detailed analysis of complex distribution lead to the conclusion, that ammonia complexes are formed in cost of pyrophosphate complexes with Co(II) or Ni(II), whereas the concentration of other complexes and particles, e. g. various hydroxo- complexes, $Me^{2+}$, remains almost the same irrespectively on the amount of ammonia has been added into solution (see Figs. 7 and 8).

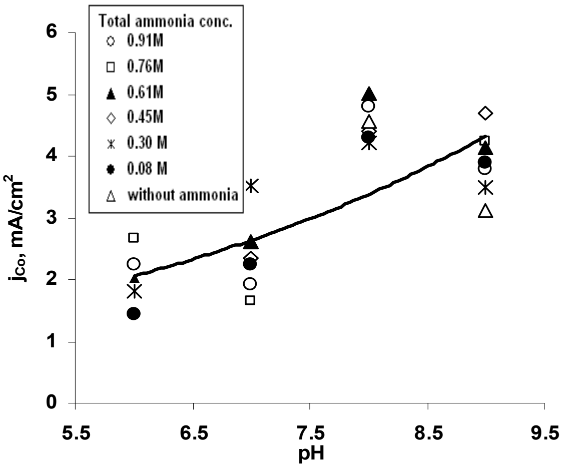

**Fig. 3.** The effect of pH on partial current densities obtained for Co(II) electroreduction at various concentrations of total ammonia (indicated in legend of pointers). Total current density $j = 30$ mA/cm$^2$

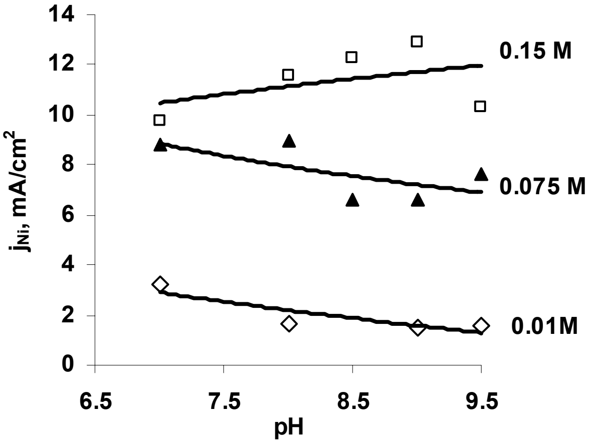

**Fig. 4.** The effect of pH on partial current densities obtained for Ni(II) electroreduction at various concentrations of initial $(NH_4)_2SO_4$ concentrations (indicated next to curves). Total current density $j = 40$ mA/cm$^2$

The different effect of ammonium sulfate on the deposition rate might be defined by the different origin of electrochemically active complex. There are tree types of Me(II) complexes formed in the solutions that might participate as a charge transferring complexes, namely with pyrophosphate, with $OH^-$, and with ammonia, as well as hydrated ions $Co^{2+}$ or $Ni^{2+}$. The rate of cobalt electrodeposition is sensitive to the pH irrespectively to the presence of complexes with ammonia and increases with increasing in pH up to pH 8. This fact confirms indirectly the role of hydroxo- complexes with Co(II), and especially Co monohydroxide $CoOH^+$ as a charge-transfer species. The concentration of these complexes linearly depends on pH that explains the obtained increasing rate of Co

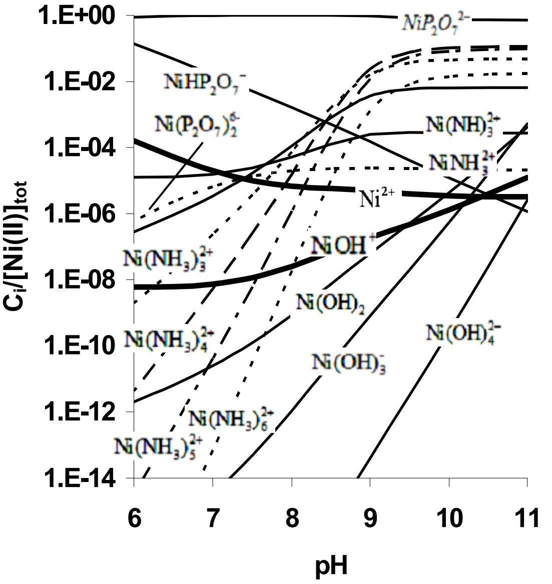

**Fig. 5.** Calculated molar fractions of Ni(II) complexes ($C_i$) in total Ni(II) ($[Ni(II)]_{tot}$) plotted versus pH. Solution composition: 0.36M $Na_4P_2O_7$ + 0.14M $NiSO_4$ + 0.3M ammonia

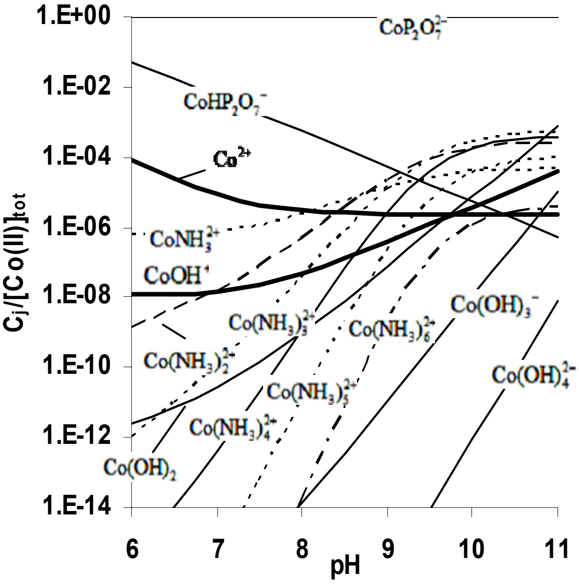

**Fig. 6.** Calculated molar fractions of Co(II) complexes ($C_i$) in total Co(II) ($[Co(II)]_{tot}$) plotted versus pH. Solution composition: 0.36M $Na_4P_2O_7$ + 0.025M $CoSO_4$ + 0.3M ammonia

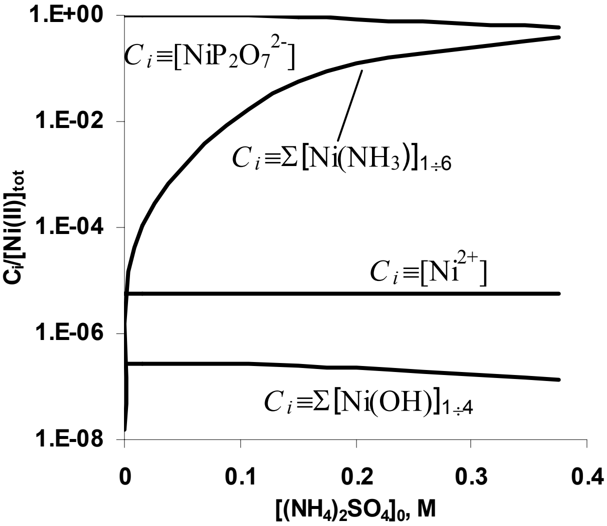

**Fig. 7.** Calculated molar fractions of some Ni(II) complexes ($C_i$) in total Ni(II) ($[Ni(II)]_{tot}$) as a function of total $(NH_4)_2SO_4$ concentration at pH 9. Solution composition: 0.36M $Na_4P_2O_7$ + 0.14M $NiSO_4$ + 0.3M ammonia

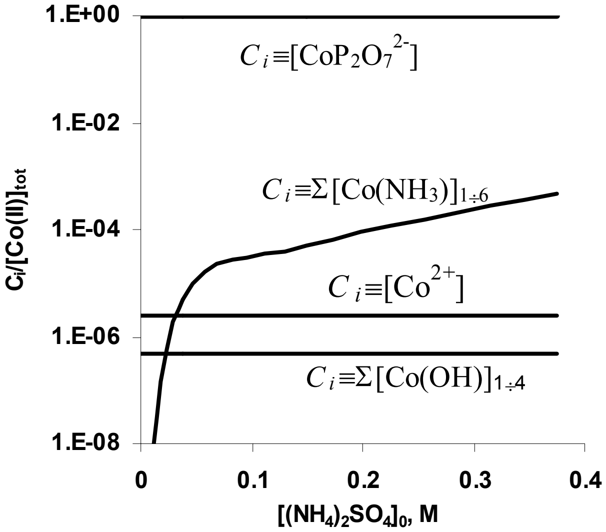

**Fig. 8.** Calculated molar fractions of Co(II) complexes ($C_i$) in total Co(II) ($[Co(II)]_{tot}$) plotted versus total $(NH_4)_2SO_4$ concentration at pH 9. Solution composition: 0.36M $Na_4P_2O_7$ + 0.025M $CoSO_4$ + 0.3M ammonia

electrodeposition with pH. The side reaction of importance of iron-group metals electrodeposition is hydrogen evolution reaction under Volmer-Heyrovsky mechanism in alkaline media [20 – 23]:

$$Co + H_2O + e^- \leftrightarrow Co\text{-}H_{(ads)} + OH^- ; \tag{7}$$

$$Co\text{-}H_{(ads)} + Co\text{-}H_{(ads)} \leftrightarrow 2Co + H_2 . \tag{8}$$

Actually, single iron group metal electrodeposition also can be described by sequence of stages involved intermediate ion adsorption and interactions in adsorbed stage. Based on the considerations provided in [23 – 24], the reaction pathway is assumed as follows:

$$CoOH^+_{(aq)} \leftrightarrow CoOH^+_{(ads)} ; \tag{9}$$

$$CoOH^+_{(ads)} + 2e^- \leftrightarrow Co + OH^- . \tag{10}$$

Increasing of pH in alkaline range facilitates hydrogen evolution reaction, also Co deposition rate increases due to increasing in concentration of $CoOH^+$ in the solution. However, because the competitive adsorption takes place, the Volmer's reaction occurs easier than reactions 9 or 10, therefore the Co deposition rates drops down at higher pH.

Because of nickel does not electrodeposit without ammonia from pyrophosphate solutions at significant rates, no one of pyrophosphate or hydroxo – complexes with Ni(II) can be considered as a charge-transferring complex. Only after ammonium sulfate has been added, the Ni deposition rate increases sufficiently, and the deposition rate remains almost constant, if total concentration of ammonia > 0.2M – 0.3M. Moreover, this result well-correlates with changes in total concentration of ammonia complexes with Ni(II): the fraction of complexes with $NH_3$ does not increases sufficiently if concentration of, ammonia exceeds 0.1M – 0.3M – see Fig. 7.

## 4. CONCLUSIONS

1. Ni electrodeposition rate from pyrophosphate baths without ammonia is relatively small. Whereas, the rate of Co electrodeposition is much higher and function of pH has maximum at pH 8. This maximum is explained by the competitive adsorption of $CoOH^+$ and hydrogen on the surface regardless of the presence of ammonia or ammonium salt in the solution.
2. The molar fraction of Ni(II) complexes with ammonia is 1000 times higher than ones of Co(II). Adding of $(NH_4)_2SO_4$ and further forming of ammonia in the solution accelerates sufficiently the rate of Ni electrodeposition. The effect well correlates with increasing the molar fraction of various ammonia complexes with Ni(II).
3. Based on the different pH and $(NH_4)_2SO_4$ influence on the deposition rate it is possible to assume that $CoOH^+$ and $Ni(NH_3)_{1\div6}$ can act as charge-transfer particles in the pyrophosphate-ammonia solutions.

### *Acknowledgments*

The study was partially supported by Lithuanian Science and Study Foundation (contract B-34/2008-2010) and program FP7-PEOPLE-2009-IRSES (Project "TEMADEP", Ref. No. 247659).

### REFERENCES

1. **Cesiulis, H., Baltutiene, A., Donten, M., Donten, M. L., Stojek, Z.** Increase in Rate of Electrodeposition and in Ni(II) Concentration in the Bath as a Way to Control Grain Size of Amorphous / Nanocrystalline Ni-W Alloys *Journal of Solid State Electrochemistry* 6 2002: pp. 237 – 244.
2. **Donten, M., Cesiulis, H., Stojek, Z.** Electrodeposition of Amorphous/Nanocrystalline and Crystalline Ni-Mo Alloys from Pyrophosphate Baths *Electrochimica Acta* 50 (6) 2005: pp. 1405 – 1412.
3. **Donten, M., Cesiulis, H., Stojek, Z.** Electrodeposition and Properties of Ni-W, Fe-W and Ni-Fe-W Amorphous Alloys. A Comparative Study *Electrochimica Acta* 45 (20) 2000: pp. 3389 – 3396.
4. **Cesiulis, H., Podlaha-Murphy, E.J.** Electrolyte Considerations of Electrodeposited Ni-W Alloys for Microdevice Fabrication *Materials Science* (*Medziagotyra*) 9 (4) 2003: pp. 329 – 333.
5. **Fan, C., Piron, D. L., Steb, A., Paradis, P.** Study of Electrodeposited Nickel-molybdenum, Nickel-tungsten, Cobalt-molybdenum, and Cobalt-tungsten as Hydrogen Electrodes in Alkaline Water Electrolysis *Journal of the Electrochemical Society* 141 (2) 1994: p. 382.
6. **Donten, M., Stojek, Z.** An Improved Bath Composition for Electroplating of the Amorphous Cobalt-tungsten Alloys *Polish Journal of Chemistry* 68 (6) 1994: pp. 1193 – 1197.
7. **Gromova, V. A., Yapontseva, Y. S., Bersirova, O. L., et al.** Influence of Structure of Electrolyte on Corrosion Properties of Electrolytic Alloys of Co-Mo *Metallofizika i noveishie tekhnologii* 28 2006, pp. 83 – 90.
8. **Tsyntsaru, N. I., Belevskii, S. S., Volodina, G. F., Bersirova, O. L., Yapontseva, Yu. S., KubIanovskii, V. S., Dikusar, A. I.** Composition, Structure, and Corrosion Properties of Coatings of Co-W Alloys Electrodeposited under Direct Current *Surface Engineering and Applied Electrochemistry* 43 (5) 2007: pp. 312 – 317.
9. **Gómez, E., Pellicer, E., Vallés, E.** Developing Plating Baths for the Production of Cobalt-molybdenum Films *Surface and Coatings Technology* 19 (2–3) 2005: pp. 238 – 246.
10. **Gómez, E., Pellicer, E. Vallés, E.** Electrodeposited Cobalt-molybdenum Magnetic Materials *Journal of Electroanalytical Chemistry* 517 (1–2) 2001: pp. 109 – 116.
11. **Bersirova, O., Cesiulis, H., Donten, M., Królikowski, A., Stojek, Z., Baltrunas, G.** Corrosion and Anodic Behavior of Electrodeposited Ni-Mo Alloys *Physicochemical Mechanics of Materials* (*ISSN 0430-6252*) 4 2004: pp. 620 – 625.
12. **Cesiulis, H., Donten, M., Donten, M. L., Stojek, Z.** Electrodeposition of Ni-W, Ni-Mo and Ni-Mo-W Alloys from Pyrophosphate Baths *Materials Science* (*Medziagotyra*) 7 (4) 2001, pp.237 – 241.
13. **Brenner, A.** Electrodeposition of Alloys. New York, Academic Press Inc., 1963.
14. **Vas'ko, A. T.** Tungsten. In "Encyclopedia of Electrochemistry of Elements. Vol. 5." Edited by A. J. Bard, N-Y, 1976: pp. 69 – 126.
15. **Podlaha, E. J., Landolt, D.** Induced Codeposition. III. Molybdenum Alloys with Nickel, Cobalt and Iron *Journal of the Electrochemical Society* 144 (5) 1997: pp.1672 – 1679.
16. **Gómez, E., Pellicer, E. Vallés, E.** Detection and Characterization of Molybdenum Oxides Formed during the Initial Stages of Cobalt–molybdenum Electrodeposition *Journal of Applied Electrochemistry* 33 (3 – 4) No. 1 – 2 2003: pp. 245 – 252.
17. **Grande, W. C., Talbot, J. B.** Electrodeposition of Thin Films of Nickel-iron. 1. Experimental *Journal of the Electrochemical Society* 140 (3) 1993: pp. 669 – 674.
18. **Grande, W. C., Talbot, J. B.** Electrodeposition of Thin Films of Nickel-iron. 2. Modelling *Journal of the Electrochemical Society* 140 (3) 1993: pp. 675 – 681.
19. **Kotrly, S., Šucha, L.** Handbook of Chemical Equilibria in Analytical Chemistry. Ellis Horwood Ltd., 1985.
20. **Purin, B. A.** Electrodeposition of Metals from Pyrophosphate Solutions. Riga, 1975.
21. **Okido, M., Depo, J. K, Capuano, G. A.**. The Mechanism of Hydrogen Evolution Reaction on a Modified Raney Nickel Composite Coated Electrode by AC Impedance *Journal of the Electrochemical Society* 140 (1) 1993: p. 128.
22. **Mahdavi, B., Miousse, D., Fournier, J., Menard, H., Lessard, J.** Hydrogen Evolution Reaction at Nickel Boride Electrodes in Aqueous and in Aqueous Methanolic and Ethanolic Solutions *Canadian Journal of Chemistry* 74 (2) 1996: pp. 380 – 388.
23. **Sasaki, K. Y., Talbot, J. B.** Electrodeposition of Iron-group Metals and Binary Alloys from Sulfate Baths. II. Modeling *Journal of the Electrochemical Society* 147 (1) 2000: pp. 189 – 197.