Electrodeposition of silver-cobalt coatings. The cyanide-pyrophosphate electrolyte

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The effect of the components in the cyanide-pyrophosphate electrolyte on the deposition of silver-cobalt alloy was investigated by means of cyclic voltammetry and other physico-chemical methods of analysis. Based on the results it could be assumed that the electrodeposition in the alloy electrolyte occurs from mixed cyanide-pyrophosphate complexes of silver and pyrophosphate-hydroxide complexes of cobalt.

Keywords: cyclic voltammetry, electrodeposition, pyrophosphate, silver-cobalt alloys, nuclear magnetic resonance (NMR)

INTRODUCTION

An extensive literature study about electrolytes for electrodeposition of silver, cobalt and silver-cobalt alloys was reported in a previous paper [1]. On the base of the literature data an electrolyte for deposition of the alloy was selected. It was shown, that compact coatings with up to 50 wt. % cobalt could be deposited from the selected cyanide-pyrophosphate electrolyte. However, the mechanism of obtaining of these coatings was not clarified, and the influence of the components in the electrolyte was not extensively studied, as well.

The aim of this work is to investigate the effect of the components in the cyanide-pyrophosphate electrolyte on the deposition of silver-cobalt alloys by means of cyclic voltammetry and other physico-chemical methods of analysis.

EXPERIMENTAL

The composition of the used electrolyte is:

Ag as $KAg(CN)_2$ – 1 g dm^{-3} (0.009 mol dm^{-3}); Co as $CoSO_4.7H_2O$ varies – 3 and 5 g dm^{-3} (0.051 and 0.085 mol dm^{-3}); $K_4P_2O_7$ – 100 g dm^{-3} (0.3 mol dm^{-3}). The electrolytes were prepared using chemicals of *pro analysis* purity and distilled water by the procedure, described in the previous part of this study [1].

The electrode processes for the deposition and dissolution of cobalt, silver and the alloy were investigated by means of cyclic voltammetry. The experiments were performed in a 100 cm^3 glass cell at 50°C without stirring of the electrolyte. The

working electrode with an area of 1 cm^2 and two counter electrodes were made by platinum. Prior to each experiment, the platinum working electrode was etched in a 50% HNO_3. A reference electrode Ag|AgCl ($E_{Ag|AgCl}$ = 0.197 V vs. SHE) was used. At the time of the experiments, the reference electrode was placed in a separate cell, filled with 3 M KCl solution (Merck) and connected to the electrolyte cell by a Haber-Luggin capillary through an electrolyte bridge, containing also a 3 M KCl solution. The dissolution of silver coatings (30 sec, 0.5 A dm^{-2}, 10 g dm^{-3} Ag, 65 g dm^{-3} KCN, galvanostatic conditions) in different electrolytes was investigated trough linear polarization. The experiments were carried out by means of a computerized PAR 263A potentiostat/galvanostat, using the Soft Corr II software with a sweep rate of 25 mV s^{-1}.

Infrared spectra of precipitates were registered in the range of 1200-400 cm^{-1} on a Nicolet-320 FTIR spectrometer using the KBr pellet technique.

Nuclear Magnetic Resonance (NMR) measurements were carried out on Bruker Advance II+ 600 NMR spectrophotometer at 293 K (Ultrashield™ magnet D 262/54, 14.09 T; Software - Topspin 2.1, NMR Guide).

The thermodynamic ion-associative model (software – PHREEQCI v.2.14) was used to determine the existence form of the elements in the cyanide-pyrophosphate electrolyte. The method is based on the extended Debay-Hückel equation for the calculation of activity coefficients of complex and simple ions in the solution. The used thermodynamical constants are shown in Table 1.

Due to the absence of thermodynamic data about the formation of $Co(P_2O_7)_n^{4n-2}$ complexes in the

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Table 1. Termodynamic constants.

	lg K	Ref.
$H^+ + CN^- = HCN$	9.21	[2]
$Ag^+ + 2CN^- = Ag(CN)_2^-$	20.48	[2]
$Ag^+ + 3CN^- = Ag(CN)_3^{2-}$	21.7	[2]
$Ag^+ + 4CN^- = Ag(CN)_4^{3-}$	20.6	[2]
$Ag^+ + H_2O + CN^- = Ag(CN)OH^- + H^+$	−0.777	[2]
$Co^{2+} + 3CN^- = Co(CN)_3^-$	14.312	[2]
$Co^{2+} + 5CN^- = Co(CN)_5^{3-}$	23	[2]
$P_2O_7^{4-} + H^+ = HP_2O_7^{3-}$	0.82	[3]
$P_2O_7^{4-} + 2\,H^+ = H_2P_2O_7^{2-}$	1.81	[3]
$P_2O_7^{4-} + 3\,H^+ = H_3P_2O_7^-$	6.13	[3]
$P_2O_7^{4-} + 4\,H^+ = H_4P_2O_7$	8.93	[3]
$Ag^+ + 2P_2O_7^{4-} = Ag(P_2O_7)_2^{7-}$	3.74	[4]
$Cu^{2+} + 2P_2O_7^{4-} = Cu(P_2O_7)_2^{6-}$	12.57	[5]
$Cu^{2+} + P_2O_7^{4-} = CuP_2O_7^{2-}$	8.80	[5]
$Cu^{2+} + 2HP_2O_7^{3-} = Cu(HP_2O_7)_2^{4-}$	16.40	[6]
$Cu^{2+} + HP_2O_7^{3-} = Cu(HP_2O_7)^-$	6.40	[6]

literature, the existing information about copper-pyrophosphate complexes was used because of some similarities in the behavior of cobalt and copper pyrophosphate solutions [7, 8].

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammetric curve obtained in a water solution of potassium dicyanoargentate and potassium pyrophosphate.

The only cathodic peak at the potentials of around -600 mV results from the silver reduction from the silver cyanide complex, which confirms the previous results of silver deposition from water solutions of potassium dicyanoargentate onto different substrates [9]. This means that despite of the quantity, the pyrophosphate does not influence the polarization of the cathodic peak of the silver from potassium dicyanoargentate complex in the silver electrolyte. Two oxidation peaks are also registered: the first one at about –440 mV, and the second one, split in peaks at +160 mV and +405 mV. The dissolution of the coating occurs at the potentials of the split anodic maximum, while the first one is connected with the formation of passive film of silver insoluble compounds [10].

In order to elucidate the nature of the split peak in the anodic area, the experiment was carried out with changes of the scan direction at different cathodic potentials. Figure 2 shows the results. The splitting of the peak could be connected with the bonding of the dissolved silver by the different anions existing in the solution – the cyanide and the pyrophosphate ions. In the solution of potassium pyrophosphate the silver coating is dissolved at about +397 mV (Figure 3, curve 1). In the presence

of free cyanide ions in the pyrophosphate solution (curve 2) the silver dissolution peak is shifted with more than 250 mV in negative direction, which is a result of the strong complex-forming effect of the cyanide ions regarding to the silver. Curve 3 is obtained during dissolution of similar silver coatings in the solution of potassium dicyanoargentate and potassium pyrophosphate, in the absence of free cyanide.
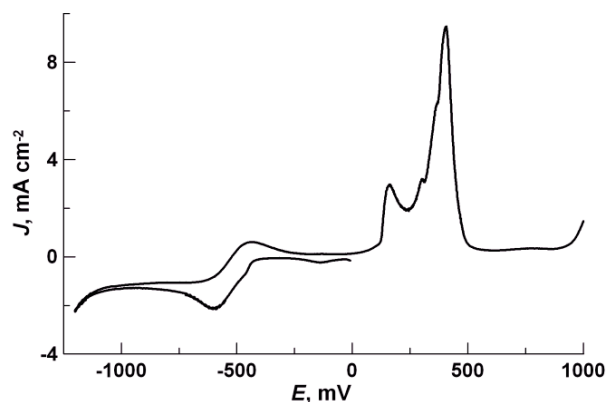

Fig. 1. CV curves of an electrolyte containing 1 g dm^{-3} Ag as KAg(CN)$_2$ and 100 g dm^{-3} K$_4$P$_2$O$_7$.
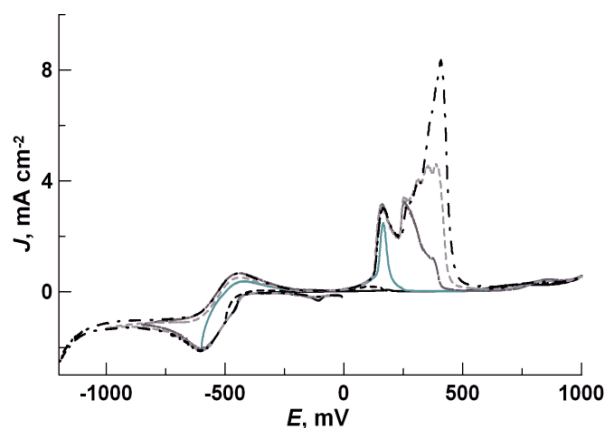
Fig. 2. CV curves of the electrolyte from Figure 1 with changes of scan direction at different cathodic potentials.

The curves, presented in Figures 2 and 3, allow for the conclusion that the dissolved silver, when in small amounts, combines together with the cyanide ions, released during its reduction in the cathodic period. This results in the appearance of the negative part of the split anodic peak. When higher amount of deposited silver in the case of more negative vertex potentials, is dissolved, the rest of the dissolved silver combines with the pyrophosphate anions, which results in the increase of the positive part of the split anodic peak (Figure 2).
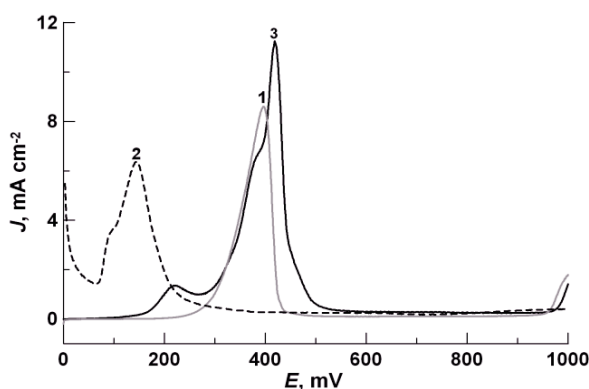
Fig. 3. Dissolution of silver coatings in different electrolytes. Curve 1 – pyrophosphate solution ($K_4P_2O_7$, 100 g.dm^{-3}); Curve 2 – in the presence of free cyanide anions in the pyrophosphate solution (KCN,1.207 g dm^{-3} and $K_4P_2O_7$, 100 g.dm^{-3}); Curve 3 – in the alloy electrolyte in absence of cobalt (Ag as $KAg(CN)_2$ – 1 g dm^{-3} and $K_4P_2O_7$ – 100 g dm^{-3}).

The increased amount of deposited silver is connected with the longer deposition time when shifting the vertex potential in a more negative direction. Moreover, released cyanide ions during silver deposition contribute to the formation of silver complexes with more cyanide ligands [11]. The instability constant of the pyrophosphate complex of silver has a value of about $K_{inst}=10^{-4}$ [4].

This is a weak complex of silver, compared with the silver-cyanide complex, which constant is of about $K_{inst}=10^{-22}$. In order to increase the polarization of the silver deposition from pyrophosphate electrolytes, the addition of a second complex-forming agent is recommended [12].

In order to determine the effect of the pyrophosphate ions on the strength of the bond between silver and cyanide ligands, measurements of the equilibrium potential of silver in dicyanoargentate-pyrophosphate solutions were performed. The data, as well as the obtained cyclic voltammetry curves in the presence of potassium dicyanoargentate and pyrophosphate separately and together, do not show any indications of a new complex formation. In order to clarify the nature of the possible chemical interactions of the silver metal ion with cyanide and pyrophosphate ligands, nuclear – magnetic resonance studies were performed. The NMR spectra of water solutions of potassium dicyanoargentate and potassium pyrophosphate have been registered separately and together. The techniques of the nuclear magnetic resonance require very high concentrations. By keeping the ratio of the investigated components constant (as in the electrolyte for alloy deposition –

100 g dm^{-3} $K_4P_2O_7$ for each gram of silver), the concentrations have been increased up to their solubility limit.

Figure 4a shows the spectrum of potassium dicyanoargentate in water. One peak at about 562 ppm is observed.

Figure 4b shows the spectrum of potassium pyrophosphate in water. Besides the peak of pyrophosphate ions (– 6.82 ppm) some other smaller peaks of unknown nature, most probably corresponding to another protonic compounds of a phosphorus, such as hydrogenphosphate, phosphate and etc., are observed.

In the solution, containing dicyanoargentate and potassium pyrophosphate, some shifting of the peak with about 20 ppm – up to 583 ppm is observed (Figure 4c).

In the literature, similar shifting of about 20 ppm is reported and attributed to the ligand changes in the complex. The confirmation needs additional experiments, and therefore, the carbon spectrum of the cyanide group in the water solution of potassium cyanide has been recorded. The comparison between both spectra confirms the idea that the addition of pyrophosphate to the dicyanoargentate ions do not result in the formation of some mixed cyanide-pyrophosphate complexes at a room temperature.

Figure 5 shows the cyclic voltammetric curve, obtained in the solution of cobalt sulphate and potassium pyrophosphate. Two maxima at about – 923 mV and –1107 mV are registered in the cathodic region. The dissolution of the formed coatings is represented by the peak at about –400 mV. The oxygen evolution reaction starts at very positive potentials. The existence of a pyrophosphate complex of cobalt has been mentioned in the literature [7], but data about its instability constant have not been found. In order to clarify the nature of the two peaks in the cathodic area, additional voltammetric investigations were performed.

An experiment, which was carried out with changes of the scan direction at different cathodic potentials, showed that the coatings deposited at potentials of both, the first and the second cathodic peaks, dissolve at the potentials of the mentioned above single anodic peak. The difference in the anodic behaviour is the deposit quantity which depends on the reached cathodic potential. According to Purin's studies [13] the cobalt electrodeposition from pyrophosphate electrolyte
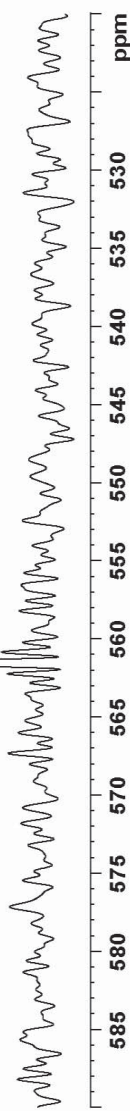
Fig. 4a. NMR spectrum of water solution of 0.1 mol dm^{-3} KAg(CN)$_2$.
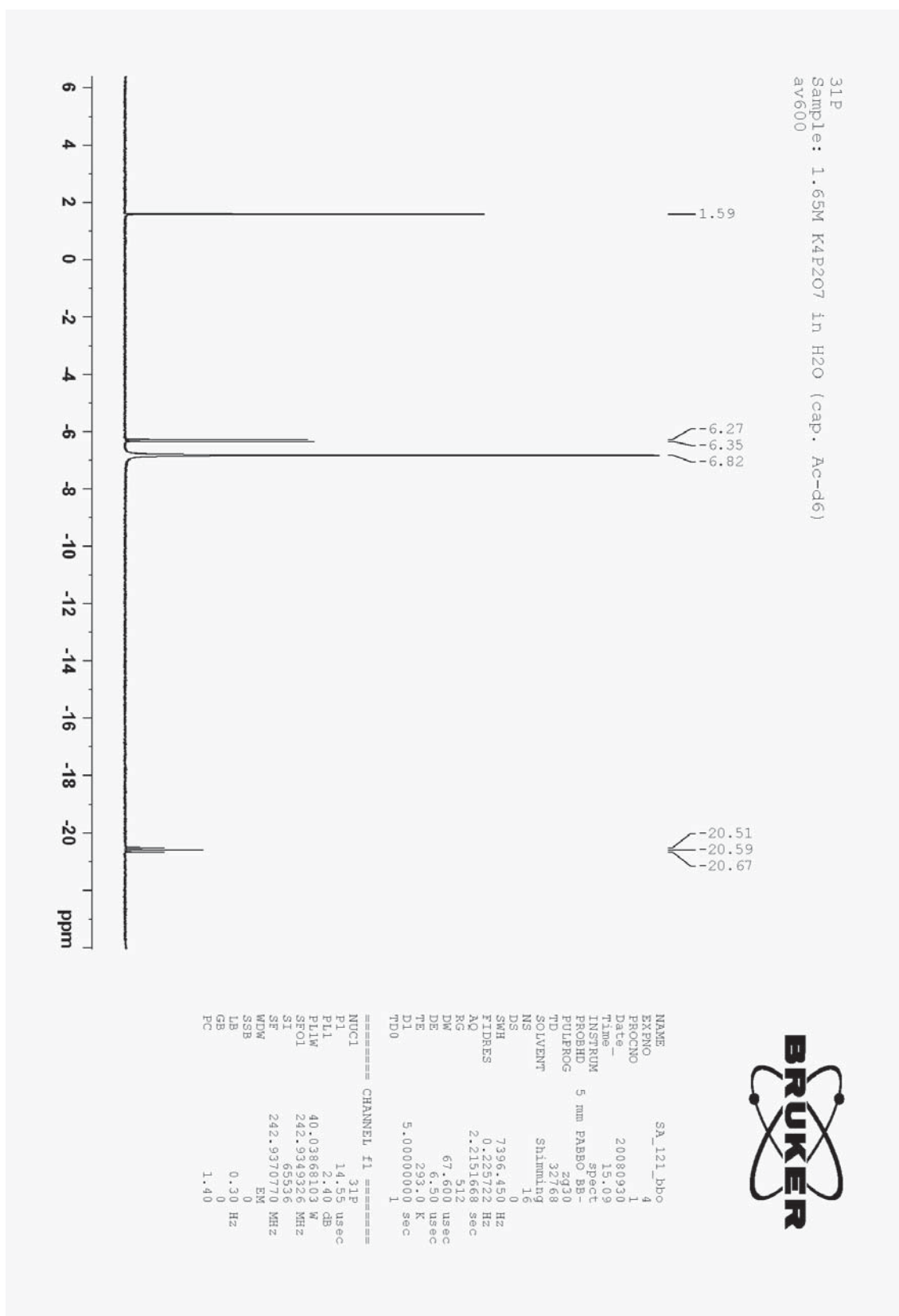
Fig. 4b. NMR spectrum of water solution of 1.65 mol dm^{-3} K$_4$P$_2$O$_7$.

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NAME   SA_122_bbo
EXPNO   107
PROCNO   1
Date_   20080930
Time   15.57
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG   2g
TD   65536
SOLVENT   Shimming
NS   420
DS   0
SWH   3084.197 Hz
FIDRES   0.470950 Hz
AQ   1.0617332 sec
RG   362
DW   16.200 usec
DE   31.49 usec
TE   293.0 K
D1   20.0000000 sec
TDO   1

======= CHANNEL f1 =======
NUC1   109Ag
P1   6.50 usec
PL1   0.00 dB
SFO1   27.9393964 MHz
SI   16384
SF   27.9272480 MHz
WDW   EM
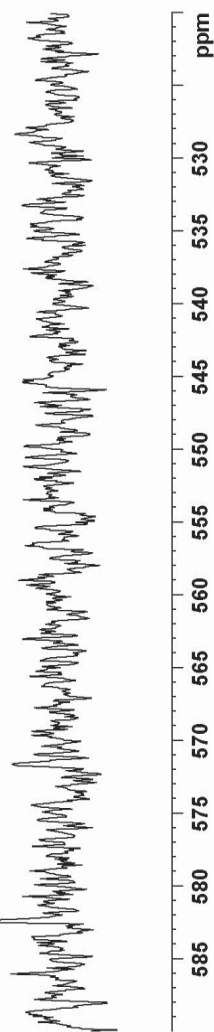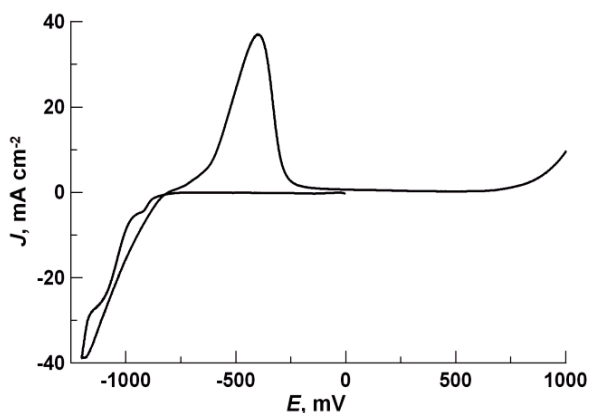SSB   0
LB   3.00 Hz
GB   0
PC   1.00

109Ag
Sample: 0.05M KAg(CN)2 + 1.65M K4P2O7   in H2O (cap. Ac-d6)
av600

582.47

ppm 530 535 540 545 550 555 560 565 570 575 580 585

Fig. 4c. NMR spectra of water solution of 0.05 mol dm^{-3} KAg(CN)$_2$ and 1.65 mol dm^{-3} K$_4$P$_2$O$_7$.

Fig. 5. CV curves of the electrolytes containing 5 g dm^{-3} Co as CoSO$_4$.7H$_2$O and 100 g dm^{-3} K$_4$P$_2$O$_7$.

Fig. 6. CV curves in the alloy electrolyte (1 g dm^{-3} Ag, 3–5 g dm^{-3} Co, 100 g dm^{-3} K$_4$P$_2$O$_7$). Curve 1 – 3 g dm^{-3} cobalt; Curve 2 – 5 g dm^{-3} cobalt.

shows strong pH dependence. He concludes that the main factors, determining the cathode processes are: destruction of cobalt-pyrophosphate complex, caused by alkalization in the vicinity of the electrode, and the following formation of passive layer which consists of hydroxide complexes and hydroxides of the cobalt.

In order to confirm Purin's conclusions, the experiments with changes in the pH value of the electrolyte were performed. The cobalt electrolyte was alkalized using 2 g dm^{-3} KOH which results in pH shifting up to 10.4 (initial pH value is 9.4). A change in the violet electrolyte colour was observed with intensification of the blue nuance. The CVA curve of the alkalized cobalt electrolyte shows the absence of the first cathodic peak, which refers to cobalt deposition from cobalt-pyrophosphate complex. This cathodic reaction is polarized probably due to the cobalt electrodeposition from mixed hydroxide-pyrophosphate complexes, formed easily in the preliminary alkalized cobalt electrolyte.

The obtained experimental results allow for the suggestion that the cobalt-pyrophosphate complex is destroyed by the alkalization and following accumulation of hydroxides in the vicinity of the electrode (as a result of simultaneous reduction reaction of both hydrogen and cobalt). This leads to formation of more complicated hydroxide-pyrophosphate complexes as well as to passivation effects on the cathode. As a result, the cobalt reduction from such complexes runs at higher polarization at the potential of the second cathodic maximum.

The temperature has a strong influence on the destruction process of the cobalt-pyrophosphate complex. During the previous experiments, carried out at a room temperature [14], the existence of well defined cathodic peaks was not established. This study shows how the increase in temperature results in intensifying of the electrode processes in the cobalt electrolyte.

The cyclic voltammetric curves, obtained in the alloy electrolytes with different concentrations of cobalt – 3 g dm^{-3} (curve 1) and 5 g dm^{-3} (curve 2), are presented in Figure 6. The first cathodic peak, connected with the deposition of silver, is situated at potentials of about –400 mV, i.e. at about 200 mV more positive potentials, compared to the electrolyte in the absence of cobalt (see Figure 1). Probably the depolarization effect is due to the changes in the silver complex type present in the electrolyte, i.e. from stronger cyanide to a weaker mixed cyanide-pyrophosphate. The depolarization effect is smaller at a room temperature [14].

The thermodynamic ion-associative modeling shows the possible existing ionic forms in the alloy electrolyte (Table 2).

The results of these theoretical calculations show the absence of a cobalt-cyanide complex and silver pyrophosphate complex in the solution and do not show any possibility of mixed complex formation.

However, the depolarization during electrodeposition of silver in the alloy electrolyte assumes the conclusion that a process of "recomplexation" of silver appears. The preparation

Table 2. The possible existing ionic forms in the alloy electrolyte, according to thermodynamical ion-associative modeling.

Ag species	%	Co species	%	K species	%	P species	%	S species	%	CN species	%
$Ag(CN)^{2-}$	99.9	$Co(P_2O_7)_2^{6-}$	73.87	K^+	98.42	$P_2O_7^{4-}$	51.27	SO_4^{2-}	77.26	$Ag(CN)_2^-$	99.95
$Ag(CN)OH^-$	0.05	$CoP_2O_7^{2-}$	26.13	KSO_4^-	1.58	$Co(P_2O_7)_2^{6-}$	41.41	KSO_4^-	22.74	$Ag(CN)OH^-$	0.05
$AgSO_4^-$	0.03	–	–	–	–	$CoP_2O_7^{2-}$	7.32	–	–	–	–
Ag^+	0.02	–	–	–	–	–	–	–	–	–	–

procedure of the alloy electrolyte includes a formation of cobalt pyrophosphate, and an already prepared cobalt electrolyte is added to the silver electrolyte. We can assume that the cobalt ions reduce the strength of the bonds between the silver and the cyanide ligands, and due to this fact, a new mixed cyanide-pyrophosphate complex of silver appears. The depolarization of the electrodeposition of silver in the alloy electrolyte at a room temperature is less than at a higher temperature. It could be assumed, that some destruction of the cyanide complex of silver and a following "re-complexation" could be the result of increase in the operation temperature. Moreover, the influence of the temperature onto the polarization of pyrophosphate electrolytes is mentioned by other authors [12].

The cobalt deposition peak is registered at about –1160 mV (3 g dm^{-3} cobalt), or –1150 mV (5 g dm^{-3} cobalt) (Figure 6), i.e., at potentials, similar to these in pure the pyrophosphate electrolytes (compare with Figure 5).

In the anodic part of the curve, the first dissolution peak is shifted to a positive direction in comparison with the peak, observed in the absence of silver (see Figure 5). This shift suggests for increased passivity of cobalt in the alloy electrolyte or its ennoblement due to the silver contribution to the cobalt phase. The increase of the cobalt concentration in the electrolyte leads to the increase of this dissolution peak, which is connected with a higher amount of deposited cobalt during the cathodic period.

The attempts to increase the metal concentrations lead to precipitation. The investigation of the precipitate with an IR-spectroscopy shows that it consists mainly of potassium sulphate. This allows for the conclusion that by removing of the precipitation, the metal concentration in the electrolyte could be successfully increased, leading to extended working conditions for electrodeposition.

CONCLUSIONS

Different experimental studies were performed in order to establish the mechanism of the electrodeposition of silver cobalt alloys from cyanide-pyrophosphtae electrolytes. The obtained results showed that: the increase in the working temperature has a very strong influence on the investigated processes; the electrodeposition in the alloy electrolyte most probably occurs from mixed cyanide-pyrophosphate complexes of silver and pyrophosphate-hydroxide complexes of cobalt.

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ЕЛЕКТРО-ОТЛАГАНЕ НА СРЕБЪРНО-КОБАЛТОВИ ПОКРИТИЯ ИЗ ЦИАНИДНО-ПИРОФОСФАТЕН ЕЛЕКТРОЛИТ

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(Резюме)

Чрез циклична волтамперометрия и други физикохимични методи на анализ е изследвано влиянието на компонентите на цианидно-пирофосфатния електролит върху отлагането на сребърно-кобалтовата сплав. Съгласно получените резултати, може да се приеме, че електрохимичното отлагане в изследвания електролит се осъществява от смесен цианидно-пирофосфатен комплекс на среброто и пирофосфатно-хидроксиден комплекс на кобалта.