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Electrodeposition of Silver-Cobalt Coatings. Electrolytes.

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Literature data on silver, cobalt and silver-cobalt electrolytes are presented and discussed. The electrodeposition of the silver-cobalt coating is carried out from appropriate cyanide-pyrophosphate electrolytes at 50 °C. The studies show possibilities for deposition of compact silver-cobalt coatings with high cobalt content (up to 50%). The deposited coatings could be successfully used for further investigation of their physico-mechanical and electrical properties.

Keywords: electrodeposition, electrolyte, morphology, pyrophosphate, silver-cobalt coatings

INTRODUCTION

The modern technology requires the development of new materials with designed properties. Often attempts were made to combine some properties of different metals and/or alloys in order to produce a new material with desired or sometimes unexpected properties. The interest in electrodeposition of silver-cobalt alloys is based on the possibility to synergize the unique electrical, thermal, catalytic and etc. properties of silver with the magnetic, mechanical, catalytic etc. properties of an element existing in two modifications and two valence states, like the cobalt. In principle, both metals are not miscible and dispersable in each other and acting trough very high developed interface they could offer very attractive properties, like the observed giant magnetoresistance phenomena, typical for this system [1].

A literature research is presented in this paper, including the information about silver and cobalt electrolytes. Data on known electrolytes for silver-cobalt deposition, published previously [2] are introduced again in order to complete the information.

The electrochemical processes during electrodeposition of silver-cobalt alloys from cyanide–pyrophosphate electrolytes carried out at room temperature was presented in a previous paper [2]. The electrolyte composition and the electrolysis conditions allow the deposition of smooth and compact coatings in a small range of current densities.

In order to extend the working range of the current densities, investigations at higher temperature (50 ºC) were performed. Preliminary results of these investigations were briefly reported elsewhere [3] .

More detailed investigations on the behavior of the electrolyte at higher temperature and on the composition and structure of the obtained coatings, are discussed in the following two papers, the one presented here is devoted to the morphological characteristic of the obtained silver, cobalt and silver-cobalt coatings, and the next, second one, reviews the electrode processes [4].

REVIEW

Electrodeposition of silver

The excellent thermal and electrical conductivities of silver retain when this metal is deposited as a galvanic coating onto different substrates. As result, the silver electrodeposition is a widely applied and well researched process. One of the first patents on silver deposition appeared in 1840 [5]. The cyanide electrolyte, described in this patent, is one of the most used electrolytes up to now. It is composed on the basis of potassium dicyanoargentate with an excess of free cyanide ions. A lot of other electrolytes are suggested – onto nitrate, iodide, urea, thiocyanate, sulfamate, thiosulphate, and other bases [6–15]. A comprehensive review of the electrolytes for silver deposition is presented in the theses of I. Krastev [16, 17]. The electrochemical processes of silver deposition are just marked in this paper, due to the well presented and systematic literature data on this topic.

Literature data about sulfamate, ethylene-diaminetetraacetate (EDTA), sulfosalicylate and etc. electrolytes for silver deposition are known [6, 11–17]. Some data on the most used non-cyanide silver electrolytes are presented in Table 1.

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Table 1. Non-cyanide (or without free cyanide) electrolytes for silver deposition.

Type of electrolyte, [References]	Electrolyte composition	Concentration, g dm-3	J, A dm-2	T, °C	Note
Ferrocyanide [6]	AgCl $K_4[Fe(CN)_6]$ K_2CO_3 $CO(NH_2)_2$	20–40 160–200 20	1–1.5	60–80	Soluble anodes can not be used because of the silver passivation in this solution
Ferrocyanide – thiocyanate [6]	AgCl $K_4\,[Fe(CN)_6]$ Na_2CO_3 KCNS	15–40 30–60 20–35 150	0.5 –1	20–60	One of the best substitutes for the hazardous cyanide electrolytes
Sulfite [6]	AgCl $K_4[Fe(CN)_6]$ Na_2CO_3 Na_2SO_3	40 60 25 100-150	0.2 –0.5	15–25	Unstable electrolyte, fast decomposition
Thiocyanate [6]	Ag NH_4CNS H_3BO_3	25 300 20	0.5 – 1	15-25	Low throwing power
Pyrophosphate [6]	Ag as $AgNO_3$ $K_4P_2O_7$ $(NH_4)_2CO_3$	15–90 100–350 20–145	0.5 – 3.5	room temper.	The throwing power is low, but the quality of the coating – very good
Iodide [6, 12, 14]	AgCl KJ Gelatine	30–60 400–450 1–2	0.1–0.25	20–40	Trend to electrolyte decomposition; the coatings absorb iodine
Bromide [12]	AgBr NH_4Br HBr Gelatine	40–50 600 8 2–4	1.3	18–20	Preliminary amalgam formation on the substrate is necessary
Succinimide [11, 14]	Ag Succinimide K_2SO_4	30 12–55 45	1	20–70	Low tarnish resistance
Thiosulfate [6, 14]	Ag $Na_2S_2O_3$ NaOH	30 300–500 Up to pH 8–10	0.4–1.0	15–30	Weak adhesion of the obtained coating, lower tarnish resistance, in comparison with coatings, from cyanide electrolytes

Electrodeposition of cobalt

The beginning of the industrial electroplating of the cobalt dates back to the early 20th century [18]. In the beginning, the interest arouse from the decorative and corrosion–resistive properties of this metal [18, 19]. During the next 60 years of the 20th century the interest in the electrodeposition of cobalt and its alloys was renewed due to its magnetic properties [19, 20].

The electrodeposition of cobalt is described in details, including the applied aspects, in the review of F. R. Moral [19] which is related to the period before 1963, as well in some chapters in reference books, and in the scientific journals [20–24]. Later, Armyanov [25] carried out some investigations on electrodeposited cobalt and cobalt alloy coatings, connected with the magnetic properties of these materials.

Cobalt is deposited from acid up to low alkaline electrolytes – sulphate, chloride, sulfamate, fluoride and fluoroborate, triethanolamine, gluconate, citrate, pyrophosphate, hydroxide, and etc. electrolytes.

The most cited and used electrolytes are summarized in Table 2. Some other specified electrolytes, like non-aqueous electrolytes and chloride electrolyte, used for the investigation of the oxygen evolution reaction [23, 26–28], are mentioned in the literature.

An appropriate complex electrolyte for cobalt electrodeposition is the pyrophosphate electrolyte. The nature of the pyrophosphate compound of the cobalt has been investigated in the first half of the 20th century [39, 40], and some years later, the information, concerning the usage of pyrophosphate electrolytes for deposition of cobalt alloys with tungsten and some ternary alloys [20, 37, 38], started to appear in the literature.

Table 2. Electrolytes for cobalt deposition.

Type of electrolyte, [References]	Electrolyte composition	Concentration, g dm^{-3}	J, A dm^{-2}	T, °C	Note
Sulfate, Ammonium sulfate [19-21, 23, 29]	$CoSO_4.7H_2O$ $Co(NH_4)_2(SO_4)_2x$ $6H_2O$ NaCl H_3BO_3	0 – 504 0 – 175 0 – 17 0 – 45	4 – 17	20 – 45	The specified composition is the most frequently used and cited in the literature. In some cases Na_2SO_4 is used; pH 5–6.5 [4]
With Sulfuric acid [24]	$CoSO_4$ H_2SO_4	0.5 mol dm^{-3}	Up to 20	30	pH down to 2 (with H_2SO_4)
Chloride [19, 21, 23, 24, 30*, 31*]	$CoCl_2.6H_2O$ $CoCl_2$ H_3BO_3 $NH_4F.HF$ NH_4Cl HCl	0 – 400 0 – 10 mM 0 – 25 0 – 86 0 – 1 M	1 – 12	25 – 71	pH down to 5 (with HCl) * Electrodeposition at potentiostatic conditions 1.18-1.28 V (SCE)
Sulfamate [19, 21]	$Co(SO_3NH_2)_2$ Antipitting additive Formaldehyde H_3BO_3	250 – 450 0 – 375 0 – 30 0 – 30	0.5 – 6	25 – 40	pH 5.2–5.5
Fluoride and fluoroborate [19, 21, 23]	$Co(BF_4)_2$ CoF_2 H_3BO_3 HF	0 – 160 0 – 0.1216 ml dm^{-3} 0 – 15 0 – 0.623	4.1 – 6.5	25 – 50	pH 3.5
Triethanolamine [20, 21]	$CoSO_4.7H_2O$ $N(C_2H_4OH)_3$	75 70 ml dm^{-3}	2	no data	pH 2.6–6.6 The coatings are bright; after prolonged electrolysis $Co(OH)_2$ precipitates.
Citrate [32-35]	$CoSO_4.7H_2O$ $CoCl_2$ $Na_3C_6H_5O_7.2H_2O$ $C_6H_8O_7$ H_3BO_3	0 – 0.36 0 – 0.50 0.08 – 0.19 0.05 – 0.10 mol dm^{-3}	0.33-2	25 – 75	pH 2–7
Gluconate [36]	$CoSO_4.7H_2O$ Na–gluconate H_3BO_3	20 – 100 10 – 100* 0 – 50	2 - 3	25 – 50	*optimal amount of 50 g dm^{-3} pH 2–5
Pyrophosphate [21, 37*, 38*]	$CoCl_2.6H_2O$ $Na_2WO_4.2H_2O$ $K_4P_2O_7$ $NH_4C_6H_7O_7$	6 – 60 3.3 – 165 15.2 – 152 10 – 12	Up to 20	30 – 60	* Mainly used for codeposition of Co with W;
Hydroxide [21]	$Co(OH)_2$ NaOH EDTA Bone glue	10 140 64 0 –10	1.25 – 2.50	70 – 90	Electrolyte for flexible and well leveled coatings
Formaldehyde used as brightener [20, 21]	$CoSO_4.7H_2O$ NH_4COOCH_3 CH_3COOH HCHO $CdSO_4.8H_2O$	200 30 1 3 0.2	no data	no data	The addition of Cd increases the brightness of the coating and improves the leveling effect

Electrodeposition of silver-cobalt alloys

The electrodeposition of silver-cobalt alloys is relatively rarely investigated. The existing literature data on the deposition of this alloy are insufficient and incomplete [41]. The reason for this is the big difference between the deposition potentials of both metals and the difficulties, connected with the preparation of stable electrolytes with high metal concentrations. Silver is a noble metal, more positive than cobalt, and this is the reason for the use of complex compounds to bring the deposition potentials of both metals close together. Table 3 shows the best known electrolytes for silver-cobalt alloy deposition [2].

Most of the investigations, described in the literature, are related to the silver-cobalt electrodeposition from cyanide-pyrophosphate electrolytes.

The electrodeposition of silver from cyanide complex electrolytes, as well as the influence of different anions onto the hydrogen evolution reaction from such electrolytes are well researched [5, 16, 48]. It is shown in the work of Haldar [40]

Table 3. Electrolytes for silver-cobalt deposition

Type of electrolyte, [References]	Electrolyte composition	Concentration, g dm^{-3}	J, A dm^{-2}	T, °C	Note
Cyanide [41]	Ag as Ag_2SO_4 Co as $Co(CN)_2$ NaCN	2.2 0.6 12	0.3 – 0.7	18	Cathodic current efficiency – 50%
Cyanide-pyrophosphate I [6, 42]	Ag as $KAg(CN)_2$ Co as $CoSO_4.7H_2O$ $K_4P_2O_7$	1 5 100	0.1 – 1	20 – 60	Ag + Co≤ 6 g dm^{-3} Cathodic current efficiency - 40 - 50%, pH 7 – 10
Cyanide-pyrophosphate II [43, 44]	$CoSO_4.7H_2O$ $K_4P_2O_7$ Ag as solution containing: KCN – 120 g dm^{-3}; AgCN – 40 g dm^{-3}; K_2CO_3 – 20 g dm^{-3}	43 120 0.15 (2 ml)	1 – 40 mA cm^{-2}	40-45	pH 7 – 9.5
Thiocyanate [41]	Ag as $AgNO_3$ Co as $Co(NO_3)_2.6H_20$ NaSCN	11 6 98	0.8	50	The coating is hard, brittle, and can not be easily polished
Nitrate [41]	Ag as $AgNO_3$ Co as $Co(NO_3)_2.6H_20$ Thiourea	10 18 215	0.4	47	-
Citrate [45]	$CoSO_4.7H_2O$ Ag_2SO_4 $Na_3C_6H_5O_7.2H_2O$ $Na_2SO_4.10H_2O$	5 – 16 0.1 – 5.5 76 4	1 – 10 mA cm^{-2}	85	pH 9.5
Perchlorate I [46]	$CoSO_4.7H_2O$ 60% $HClO_4$ Thiourea $AgNO_3$	10 50 0.4 0.8	3.75 mA cm^{-2}	no data	pH≤1
Perchlorate II [47]	$AgClO_4$ $Co(ClO_4)$ Thiourea Gluconate H_3BO_3 $NaClO_4$	0.01 0.1 0.1 0.1 0.3 0.1 /M/	-	25	pH 3.7; Electrodeposition at potentiostatic conditions between -770 and -850 mV; The deposits are black and rough.
Iodide [24]	AgI $CoSO_4.7H_2O$ KI Cresol sulfonic acid	0.01 0.1 1 0.01 /mol dm^{-3}/	100–700 A m^{-2}	no data	pH 2.3

that the pyrophosphate ions act as complexing agents for the cobalt ion. Literature data about silver-pyrophosphate complexes were found in the study of Orechova, cited in Gmelin [49]. More detailed investigations on the electrodeposition of silver from pyrophosphate electrolytes are presented by S. Pilauskene and V. Kajkaris [50].

EXPERIMENTAL

The electrolyte has a very low metal concentration (sum of both metals – 6 g dm^{-3}), without free cyanide and with an excess of free pyrophosphate ions (the concentration of potassium pyrophosphate is 100 g dm^{-3}). The electrolyte is alkaline (pH 9–10), stable, with very well complexed ions of both metals, and it is appropriate for their co-deposition.

The composition of the electrolyte is:

Ag as $KAg(CN)_2$ – 1 and 10 g dm^{-3} (0.009 and 0.09 mol dm^{-3}); Co as $CoSO_4.7H_2O$ varies – 5 and 10 g dm^{-3} (0.085 and 0.17 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 following procedure:

Depending on the desired volume, each component was dissolved separately in distilled water as follows: $KAg(CN)_2$ and $CoSO_4.7H_2O$ were dissolved each in water of about 1/5th of the end volume of the electrolyte. $K_4P_2O_7$ was dissolved in a water amount of ½ of the end volume of the electrolyte. After that, the obtained solutions were mixed together as follows: the dissolved cobalt salt was added under stirring into the pyrophosphate solution which obtains a dark violet color. After that the silver salt was added therein. No changes in the appearance of the electrolyte were observed. It remains stable in time.

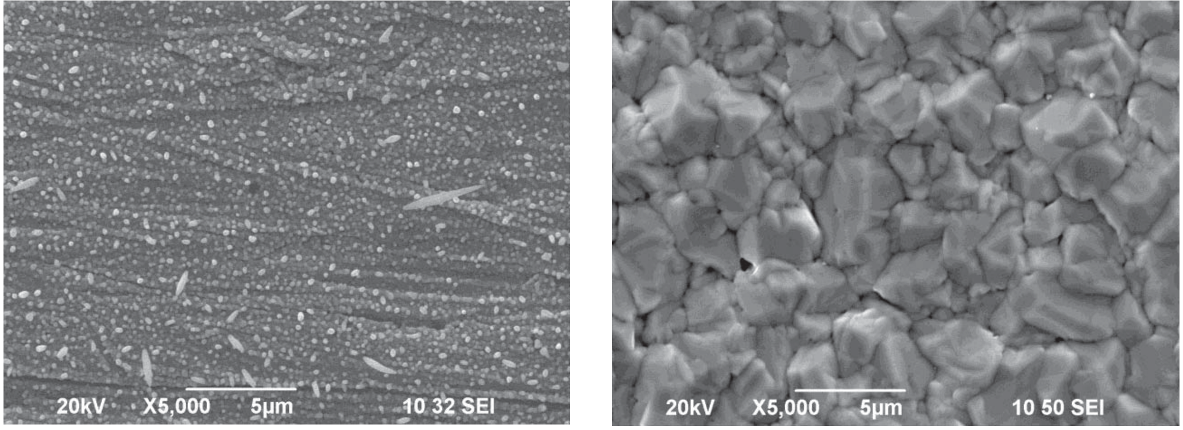
The experiments were performed in a 100 cm^3 glass cell at 50ºC without stirring of the electrolyte, under galvanostatic conditions. Copper cathodes (2 × 1 × 0.03 cm) and platinum anodes were used. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing followed by pickling in a 20% solution of sulphuric acid. In order to avoid the contact deposition of silver, the cathode was immersed into the electrolyte under current.

The elemental composition on the coating surface was measured by Energy-dispersive X-ray spectroscopy (EDAX), and the surface morphology was studied by Scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

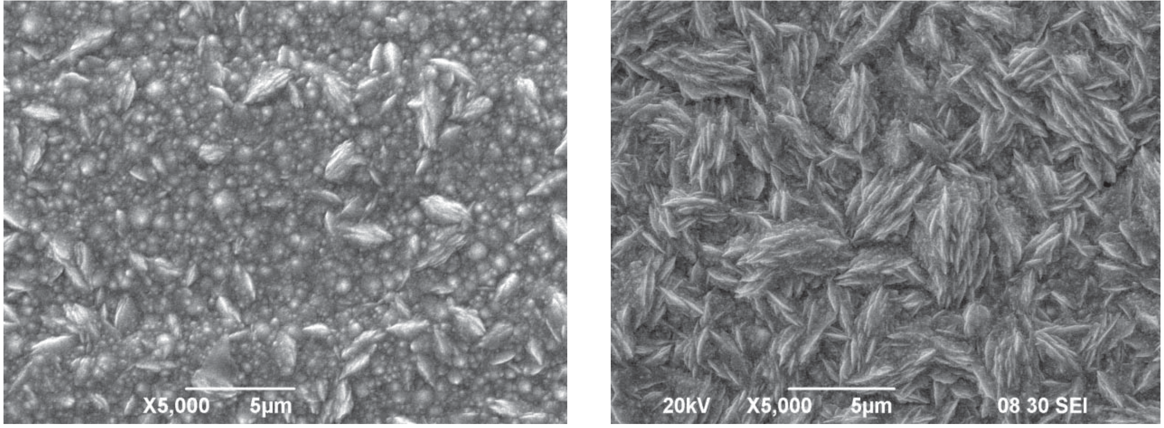
The surface morphology of a silver coating, obtained at 0.2 A dm^{-2} from the cyanide–pyrophosphate electrolyte, containing 1 g dm^{-3} Ag, is shown in Figure 1a. The coating is not compact due to the low metal concentration in the electrolyte. Generally (in the plating technologies), the silver is deposited from electrolytes with higher concentrations of the silver cyanide salt in order to increase the effectiveness of the deposition process. Such electrolytes are stable and do not precipitate. The surface morphology of a silver coating, obtained from cyanide–pyrophosphate electrolyte, containing 10 g dm^{-3} Ag, is shown in Figure 1b. The well-formed silver crystallites are visible on the electrode surface.

The surface needle-like morphology of the cobalt coatings, deposited under galvanostatic conditions from the pyrophosphate electrolyte, is presented in Figure 2. The appearance of the coating could be related to the morphology of the cobalt coatings onto Cu- substrate, containing mixture of hcp Co and fcc Co [51].



(a) **(b)**

Fig. 1. SEM images of the surface morphology of galvanostatic deposited silver coating at 0.2 A dm^{-2} from electrolytes containing 100 g dm^{-3} $K_4P_2O_7$; **(a)** - 1 g dm^{-3} Ag; **(b)** - 10 g dm^{-3} Ag.



(a) **(b)**

Fig. 2. SEM images of the surface morphology of galvanostatic deposited cobalt coating at 0.3 A dm^{-2} from an electrolyte containing 100 g dm^{-3} $K_4P_2O_7$ and: **(a)** - 5 g dm^{-3} Co; **(b)** - 10 g dm^{-3} Co.

The silver-cobalt coatings from the cyanide–pyrophosphate electrolyte, obtained at low current densities (0.1 A dm^{-2}), are white and contain practically only silver. With the increase of the current density to up to 0.5 A dm^{-2}, the coatings become grey and in the investigated range of current densities remain dark-grey, but compact.

Figure 3 shows the morphology of an alloy coating with a cobalt content of about 40 wt.%. The coating has well-formed spheroids and the cobalt is distributed uniformly. At cobalt contents more than 25 wt. %, the coatings are stressed and some cracks appear. With the increase in the current density to up to 0.4 A dm^{-2}, the deposition of coatings with up to 50 wt. % cobalt is possible. They are heterogeneous, consisting of light and dark regions, but compact. The cathodic current efficiency is about 70-80%.

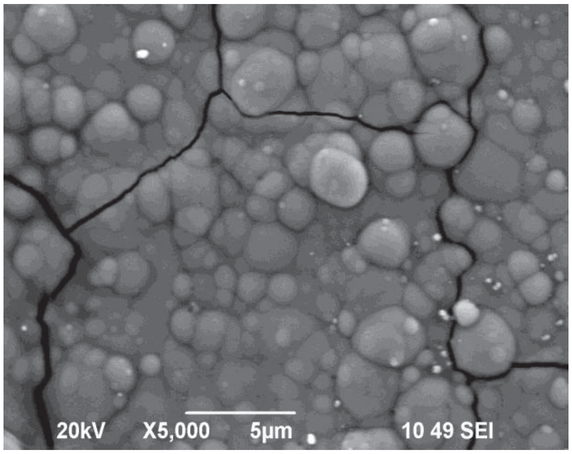
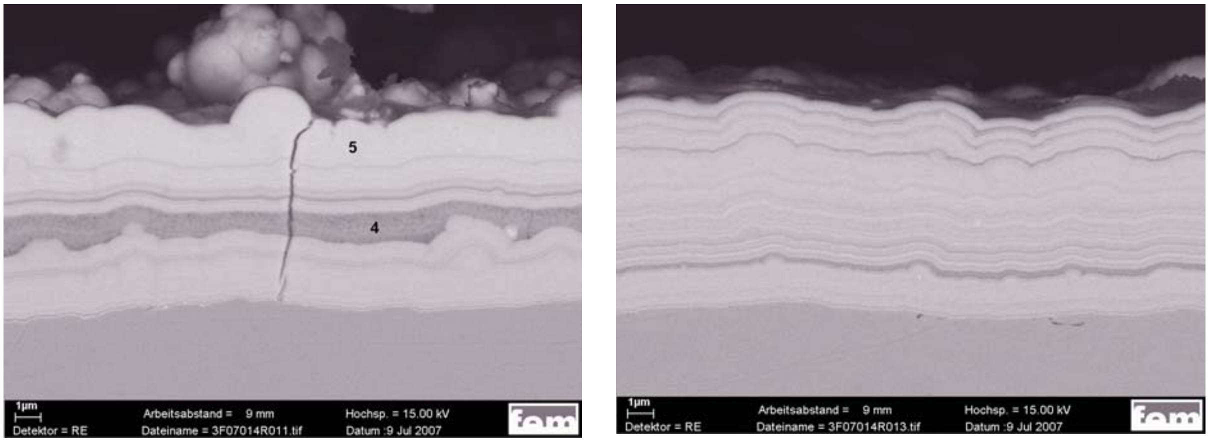


Fig. 3. SEM image of the alloy coating (1 g dm^{-3} Ag, 5 g dm^{-3} Co, 100 g dm^{-3} $K_4P_2O_7$) deposited at 0.3 A dm^{-2}.



(a) **(b)**

Fig. 4. SEM image of cross-sections of alloy coatings (1 g dm^{-3} Ag, 5 g dm^{-3} Co, 100 g dm^{-3} $K_4P_2O_7$) deposited at: **(a)** - 0.3 A dm^{-2}:Spectrum 4-14.37 wt.% Ag, 80.99 wt. % Co, 4.64 wt. % O;Spectrum 5–90,25 wt. % Ag, 9,75 wt.% Co; **(b)** - 0.4 A dm^{-2}.

Figures 4a and 4b present cross-sections of alloy coatings, obtained at different current densities – 0.3 A dm^{-2} and 0.4 A dm^{-2}, respectively. Some layered structure of the coatings is observed. After exhaustion of the more positive element in the vicinity of the electrode during deposition of a sublayer of about 2 – 3 µm thickness, the mechanism changes, and the formation of cobalt-richer sublayers starts (Figure 4a). With the increase of the current density, the influence of the natural convection also increases due to the faster exhaustion of the strong complexed metal ions, discharging on the cathodic surface which leads to a better defined multilayered structure (Figure 4b) with sublayers of about 100–150 nm thickness.

CONCLUSIONS

On the basis of an extensive literature study the possible electrolytes for deposition of silver, cobalt and silver-cobalt alloy are reviewed. The possibilities for deposition of compact coatings with high cobalt content (of up to 50%), in a range of current densities of up to 0.4 A dm^{-2} at 50 ºC, are shown using a cyanide-pyrophosphate electrolyte. Cross-sections of the alloy deposits show spontaneous formation of structured multilayer coatings. The electrolyte could be successfully used for deposition of silver-cobalt compact coatings and further investigation of their physico-mechanical and electrical properties.

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ЕЛЕКТРОЛИТНО ОТЛАГАНЕ НА СРЕБЪРНО-КОБАЛТОВИ ПОКРИТИЯ. ЕЛЕКТРОЛИТИ

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(Резюме)

Представени са и са дискутирани литературни данни за електролити за отлагане на сребърни, кобалтови и сребърно-кобалтови покрития. Проведено е електроотлагане на сребърно-кобалтови покрития от цианидно-пирофосфатни електролити при 50°C. Резултатите от изследванията показват възможности за отлагане на компактни сплавни слоеве с високо съдържание на кобалт (до 50%). Отложените покрития биха могли да бъдат успешно използвани за по-нататъшно изследване на физикомеханичните и електрични свойства на тази система.