Electrodeposition of silver-cobalt coatings

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The effect of the main components of the cyanide-pyrophosphate electrolyte on the deposition of silver-cobalt alloys was investigated by cyclic voltammetry. The experiments were carried out by means of a computerized PAR 263A potentiostat/galvanostat using the software Soft Corr II with a sweep rate of 25 mV·s⁻¹. The element composition of the coating surface was measured by EDAX and the surface morphology was studied by scanning electron microscopy. The obtained coatings contain up to 70% of cobalt. Compact coatings with a cobalt content of about 15% could be obtained only at low current densities. The results could be compared with those from other experiments trying to extend the range of current densities for deposition of high quality silver-cobalt coatings.

Key words: cyanide-pyrophosphate electrolyte, cyclic voltammetry, electrodeposition, silver-cobalt coatings and alloys.

INTRODUCTION

Silver is a noble metal, which keeps its excellent properties as a galvanic coating. The electrodeposition of silver and many silver alloys are important, widely applied, and well researched processes [1]. The electrodeposition of cobalt and its binary and ternary alloys (mainly due to their magnetic properties) is also a subject of extremely extensive research [2–4].

The literature data on the electrodeposition of silver-cobalt alloys are scarce. Table 1 demonstrates an attempt to summarize the current literature data about the used electrolytes [5–13]. The review of these data gives the impression that there is not any purposeful investigation of the coatings parameters. Mainly the electrolytes for the alloy coatings deposition have been investigated, without any further studies on the important physical-mechanical properties of the coatings such as internal stress, hardness, roughness, wear resistance, etc. Some investigations of microhardness, electrical contact resistance, and wear resistance of silver-cobalt alloys are known [6, 7], but the reported data about the content of cobalt in the measured coatings are contradictory.

One of the promising physical properties of the alloy system Ag–Co is the Giant Magnetoresistance [8, 10–13]. It is well known that this newly discovered characteristic of some materials has a significant importance for the production of mass-storage devices [14].

One of the best electrolytes for Ag–Co alloy electrodeposition is proposed by Burkat et. al. [6, 7].

EXPERIMENTAL

The composition of the used electrolyte was: Ag as KAg(CN)₂ (Degussa) – 1 g·dm⁻³; Co as CoSO₄·7H₂O (Riedel de Haen) – 5 g·dm⁻³; K₄P₂O₇ (Riedel de Haen) – 100 g·dm⁻³.

The electrolytes were prepared using chemicals of pro analysis purity and distilled water by the following procedure:

Depending on desired volume, each component was dissolved separately in distilled water as follows: KAg(CN)₂ and CoSO₄·7H₂O were dissolved each in water of about 1/5th of the end volume of the electrolyte and K₄P₂O₇ was dissolved in a water amount of 1/3 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 colour. After that, the silver salt was added therein. No changes in the appearance of the electrolyte were observed which remains stable in time.
Table 1. Current literature data about the used electrolytes.

<table>
<thead>
<tr>
<th>Composition of electrolyte</th>
<th>Electrolysis conditions</th>
<th>Quality of coating</th>
<th>Content of Co in the coatings</th>
<th>Investigated properties of the alloy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag as AgSO₄ – 2.2 g·dm⁻³, Co as Co(CN)₂ – 0.6 g·dm⁻³, NaCN – 12 g·dm⁻³</td>
<td>0.3–0.7 A·dm⁻², 18°C; Cathode current efficiency – 50%</td>
<td>No data available</td>
<td>20%</td>
<td>No data available</td>
<td>[5]</td>
</tr>
<tr>
<td>Ag as AgNO₃ – 11 g·dm⁻³, Co as Co(NO₃)₂·6H₂O – 6 g·dm⁻³, NaSCN – 98 g·dm⁻³</td>
<td>0.8 A·dm⁻², 50°C</td>
<td>Hard, brittle, and not readily polished</td>
<td>No data available</td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td>Ag as AgNO₃ – 10 g·dm⁻³, Co as Co(NO₃)₂·6H₂O – 6 g·dm⁻³, Thiourea – 215 g·dm⁻³</td>
<td>0.4 A·dm⁻², 47°C</td>
<td>No data available</td>
<td>2.4%</td>
<td>No data available</td>
<td>[5]</td>
</tr>
<tr>
<td>Ag as AgNO₃ – 11 g·dm⁻³, Co as Co(NO₃)₂·6H₂O – 6 g·dm⁻³, Thiourea – 215 g·dm⁻³</td>
<td></td>
<td>No data available</td>
<td>20%</td>
<td>No data available</td>
<td>[5]</td>
</tr>
<tr>
<td>Ag as KAg(CN)₂ – 1 g·dm⁻³, Co as CoSO₄·7H₂O – 5 g·dm⁻³, Ag+Co: 6 g·dm⁻³</td>
<td>0.1–1 A·dm⁻², Electrodes – Steel, K₃P₂O₇ – 100 g·dm⁻³</td>
<td>No data available</td>
<td></td>
<td>Controversial data: Micro hardness up to 130 kg·mm⁻²; ECR– up to 0.12 Ω·mm²·m⁻¹; Electrical resistance – up to 0.0047 Ω; wear resistance in comparison with silver max at 7.3%Co</td>
<td>[6, 7]</td>
</tr>
<tr>
<td>Ag as AgNO₃ – 11 g·dm⁻³, Co as Co(NO₃)₂·6H₂O – 6 g·dm⁻³, Thiourea – 215 g·dm⁻³</td>
<td></td>
<td>No data available</td>
<td>10–60 at. %</td>
<td>Magnetoresistance (MR) ratio of the Co-Ag film increases from 1 to 5%; On annealing the film at 250°C for 1 h, MR ratio decreases from 5 to 2.5%</td>
<td>[8]</td>
</tr>
<tr>
<td>CoSO₄·7H₂O – 5–16 g·dm⁻³, AgSO₄ – 0.1–5.5 g·dm⁻³, Na₃C₆H₅O₇·2H₂O – 76 g·dm⁻³, Na₅SO₄·10H₂O – 4 g·dm⁻³</td>
<td>1–10 mA·dm⁻², 85°C, pH – 9.5</td>
<td>No data available</td>
<td>20–65%</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>CoSO₄·7H₂O – 43 g·dm⁻³, Ag as 2 ml·dm⁻³ silver cyanide solution (KCN – 120 g·dm⁻³, AgCN – 40 g·dm⁻³; K₃CO₃ – 20 g·dm⁻³; K₃P₂O₇ – 120 g·dm⁻³)</td>
<td>1–40 mA·dm⁻², Cathode – copper foil, Anode – platinized Ti, inert. pH – 7–9.5, 40–45°C</td>
<td>No data available</td>
<td>Up to 97%</td>
<td></td>
<td>[9, 12]</td>
</tr>
<tr>
<td>CoSO₄·7H₂O – 10 g·dm⁻³, 60% HClO₄ – 50 ml·dm⁻³, Thiourea – 0.4 g·dm⁻³, AgNO₃ – 0.8 g·dm⁻³</td>
<td>3.75 mA·dm⁻², RT, Cathode – porous anodic Al oxide membranes, coated with Au; pH ≤ 1</td>
<td>No data available</td>
<td>No data available</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>NaCl – 2.42 mol·dm⁻³, AgNO₃ – 0.001 mol·dm⁻³, CoCl₂ – 0.01 mol·dm⁻³</td>
<td>No data available</td>
<td>5 at. %</td>
<td>The maximum measured percentage change in the magnetoresistance (MR) of as-grown AgCo nanowires is approximately 0.2%</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>AgI – 0.01 mol·dm⁻³, CoSO₄·7H₂O – 0.1 mol·dm⁻³, KI – 1 mol·dm⁻³; Cresol sulfonic acid – 0.01 mol·dm⁻³</td>
<td>100–700 A·m⁻², pH – 2.3, Cathode – Fe-Ni-Si-B alloy foils</td>
<td>No data available</td>
<td>Up to 96.7 at. %</td>
<td></td>
<td>[13]</td>
</tr>
</tbody>
</table>

Note: Current density in Table 1 – as it is given in the references.

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 cm³ glass cell at room temperature without stirring of the electrolyte. Prior to each experiment, the platinum working electrode with area of 2 cm² was etched in 50% HNO₃.

Two platinum counter electrodes (about 4 cm² each) and a reference electrode Ag/AgCl (E<sub>Ag/AgCl</sub> = 0.197 V vs. SHE) were used. The reference electrode was placed in a separate cell filled with 3 M KCl solution (Merck), connected to the electrolyte cell by a Haber-Luggin capillary through an electrolyte bridge containing also 3 M KCl solution. The experiments were carried out by means of a computerized PAR 263A potentiostat/galvanostat using the software Soft Corr II with a sweep rate of 25 mV·s⁻¹.

The alloy coatings were deposited in the cell for the cyclic voltammetric experiments under galvano-static conditions. Copper and stainless steel cathodes (2×1 cm) 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 element composition on the coating surface was measured by EDAX and the surface morphology was studied by scanning electron microscopy.
RESULTS AND DISCUSSION

The electrochemical processes in the cyanide electrolyte for the silver deposition with high metal concentration are well investigated [1]. However, using silver concentrations in the electrolyte as small as 1 g·dm$^{-3}$ it is not possible to obtain any silver coatings of good quality, and this is the reason for the lack of information in the literature about low concentrated electrolytes.

The cyclic voltammetric curve of the clear and transparent water solution of KAg(CN)$_2$, measured on an etched electrode is presented in Figure 1, curve 1. One cathodic maximum at about –830 mV and two peaks of oxidation, respectively at –400 and +230 mV are observed. Only one cathodic peak is also observed during deposition of silver from similar electrolytes, but with higher concentration (4 and 8 g·dm$^3$ silver) onto different substrates (silver, gold and carbon glass) [16].

The silver coating formed during the cathodic cycle is dissolved mainly at the potentials of the second anodic maximum, because the first one is connected with the formation of passive layers from insoluble silver compounds [1, 16]. An oxygen evolution reaction was not observed in the studied range of the anodic potentials.

The water solution of CoSO$_4$.7H$_2$O has a clear, pink-reddish colour, due to the aqua-complex of Co$^{2+}$ – [Co(OH$_2$)$_6$]$^{2+}$ [17, 18]. The cobalt deposition from this solution (Fig. 1, curve 2) starts from potentials of about –750 mV. At the reverse scan in positive direction, a hysteresis in the cathodic region of the curve is observed, which is possibly connected with a rough and sponge coating formed on the cathode (leading to changes in the active surface of the electrode). A very big anodic peak with a maximum around +1000 mV is observed. The oxygen evolution reaction starts after +550 mV.

The cyclic voltammetric curve of the colourless water solution of K$_4$P$_2$O$_7$ (Fig. 1, curve 3) shows that the hydrogen evolution starts at potentials more negative than –750 mV in this solution. The oxygen evolution starts in the range of very positive potentials after +900 mV.

Figure 2 shows the cyclic voltammetric curves of the electrolytes, composed on the basis of the three components KAg(CN)$_2$, CoSO$_4$.7H$_2$O and K$_4$P$_2$O$_7$, containing both metals separately and together. The deposition of silver in the presence of potassium pyrophosphate (Fig. 2, curve 1) is characterized by a cathodic maximum at –660 mV, which is about 160 mV depolarized than in the pure KAg(CN)$_2$ solution (Fig. 1, curve 1).

![Fig. 1. CV curves, registered at v = 25 mV·s$^{-1}$ in the water solutions of: 1 — KAg(CN)$_2$; 2 — CoSO$_4$.7H$_2$O; 3 — K$_4$P$_2$O$_7$. Inset — curve 1 in different current scale.](image)

![Fig. 2. CV curves of the electrolytes containing both metals separately and together. 1 — KAg(CN)$_2$ + K$_4$P$_2$O$_7$; 2 — CoSO$_4$.7H$_2$O + K$_4$P$_2$O$_7$; 3 — KAg(CN)$_2$ + CoSO$_4$.7H$_2$O + K$_4$P$_2$O$_7$.](image)

It could be assumed that at silver concentration of about 1 g·dm$^{-3}$ and in the presence of 100 g·dm$^{-3}$ of potassium pyrophosphate, the very strong cyanide complex $K_{KAg(CN)2} = 8\times10^{-22}$ [19] is partially destroyed due to the presence of other high concentrated complex-forming agents. In positive direction one peak at –450 mV is observed, which probably has the same nature as the similar one in the absence of pyrophosphate ions in the electrolyte and is due to the formation of an insoluble passive film of AgCN onto the electrode surface. The small shift (from –400 to –460 mV) in the negative direction (depolarization) compared to the peak in the absence of the pyrophosphate ions is due to the higher quantity of the complex-forming compounds in the electrolyte (in this case, the presence of pyrophosphate ions). A second anodic peak can be found in the same range of potentials like in the absence of pyrophosphate ions in the electrolyte, but it splits in two peaks in the potential range from +100 mV to +500 mV. They could be explained with the dissolution of the deposited in the cathodic
period silver in a pyrophosphate and in a cyanide complex. Pyrophosphate electrolytes for the deposition of silver are described in literature [20], but silver in such electrolytes is applied as nitrate salt and they contain significant quantities of ammonium carbonate so that direct comparison is impossible.

The cobalt deposition in the presence of the complex-forming pyrophosphate ions in the electrolyte starts at a potential around 180 mV more negative than in their absence (Fig. 2, curve 2) (compare with Fig. 1, curve 2). The potential of the cobalt dissolution is shifted about 500 mV in the negative direction compared to the electrolyte in the absence of pyrophosphate ions, which shows their strong complex-forming effect. The peak decreases in the pyrophosphate electrolyte due to the dissolution of a smaller quantity of the deposited metal in the cathodic period compared to the pure CoSO₄·7H₂O electrolyte, as a result of the processes of polarization and inhibition during the deposition of cobalt from a complex electrolyte.

The electrochemical deposition of the silver–cobalt system is of a regular type, according to Brenner [5], i.e. the nobler metal – silver, deposits predominantly.

The deposition of silver from the alloy electrolyte (curve 3) starts at more positive potentials compared to the cobalt-less electrolyte. The appearance of a hump on the positive side of the cathodic maxima means a new cathodic process. It is probably a process of the deposition of silver from the pyrophosphate complex K₇[Ag(P₂O₇)₂], with an instability constant K = 1.4×10⁻⁴ [21], formed as a result of the following reaction:

\[
K_4[Co(P_2O_7)_2] + K[Ag(CN)_2] \leftrightarrow K_3[Co(CN)_6] + K_7[Ag(P_2O_7)_2]
\]

The reaction runs during the preparation of the electrolyte and is based on the much stronger bonds of the cyanide ions to the cobalt ions than to the silver ones.

During potentiostatic deposition at potentials up to ~800 mV, the coating contains only silver. The co-deposition of cobalt starts after ~950 mV, i.e. after reaching the deposition potential of pure cobalt. In the anodic cycle, a more positive peak of the alloy dissolution appears instead of the dissolution peak of pure cobalt. The second, split anodic peak, surely could be connected with the dissolution of the pure silver coating (compare Fig. 2, curves 1 and 3). The results are reproducible when the measurements are performed on previously etched electrodes.

The surface of the galvanostatic deposited alloy coatings changes in dependence on the current density. At low current density (0.2 A·dm⁻²) the coatings contain 11–16% of cobalt, and their appearance is dark-grey, matt, and compact. The morphology of such a coating is presented in Fig. 3.

**Fig. 3.** SEM image of a coating, deposited from the alloy electrolyte at 0.2 A·dm⁻² onto copper substrate.

**Fig. 4.** The SEM images of coatings, deposited from the alloy electrolyte onto copper substrate; current density 0.4 A·dm⁻²; a. Compact area; b. “Burned” area.
The surface morphology of the coatings, deposited at 0.4 A·dm\(^{-2}\) is presented in Fig. 4a and b. Both images correspond to areas of the same sample with different cobalt contents. With the increase in the current density, the coating is dark one, in some areas incompact. According to the performed EDAX analysis, the content of cobalt in the compact areas is about 24% (Fig. 4a). In the areas, where the layer is “burned” and powder-like, the content of cobalt reaches 76% (Fig. 4b).

CONCLUSIONS

The performed investigations, allow to draw the following conclusions:

The investigated cyanide – pyrophosphate electrolyte is clear and stable in time. The cyclic voltammetric investigations show that the deposition of the alloy is of a regular type, and silver is deposited predominantly.

From the investigated electrolyte it is possible to obtain coatings, containing up to 70% of cobalt. Compact coating with a cobalt content of about 15% could be obtained only at low current densities.

The main problem of the investigated electrolyte is the low metal concentration and the resulting narrow range of current densities where compact coatings could be obtained. This complicates the investigations of the coatings properties depending on the electrolysis conditions.

The results could be compared with results from other experiments trying to extend the range of current densities for deposition of high quality silver-cobalt coatings [7].

The increasing of the metal concentration in the electrolyte was unsuccessful, due to the precipitation of silver pyrophosphate. However, with the increase in temperature the working range of the current densities could be successfully extended [22].

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REFERENCES

ЕЛЕКТРОЛИТНО ОТЛАГАНЕ НА СРЕБЪРНО-КОБАЛТОВИ ПОКРИТИЯ

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(Резюме)

Влиянието на компонентите на цианидно-пирофосфатен електролит при отлагането на сребро и кобалт, е изследвано с циклична волтамперометрия. Експериментите са проведени чрез потенциостат-галваностат модел 263А на PAR, използана е програма за корозионни изследвания SoftCorr II, при скорост на развивка 25 мВ·с⁻¹. Химичният състав на покритието е определен чрез рентгенов микроанализ (EDAX), а морфологията е изследвана със сканираща електронна микроскопия (SEM). Получените покрития съдържат до 70% кобалт. При ниски плътности на тока се получават компактни покрития със съдържание на кобалт 15%. Получените резултати са сравнени с резултатите от други експерименти, позволяващи разширяване на работния интервал от плътности на тока, при които се получават добри сплавни покрития.