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ELECTRODEPOSITION OF SILVER-INDIUM ALLOYS FROM NON-CYANIDE ELECTROLYTES

ELEKTOOSADZANIE STOPÓW SREBROWO-INDOWYCH Z ELEKTROLITÓW NIE ZAWIERAJĄCYCH CYJANKÓW

Non-cyanide electrolytes for silver-indium alloys deposition investigated in order to adjust electrolysis conditions thus to observe the formation of spatio-temporal structures onto the electrode surface. It was established that the electrolytes for silver-indium deposition prepared with the excess of thiocyanate and iodide complexing agents are stable in time. The alloy electrodeposition is of a regular type where the silver is the more positive metal. The observed oscillations of the potential during galvanostatic deposition of indium in the thiocyanate solution are suggested to appear due to the formation/destruction of some passive layers on the electrode surface. Spatio-temporal structures could be observed during electrodeposition of the alloy from thiocyanate electrolytes.

Keywords: electrodeposition; oscillations; silver-indium alloys; self-organization phenomena

Badano bezcyjankowe elektrolity do osadzania stopów srebrwo-indowych. Celem badań była optymalizacja procesu osadzania oraz obserwacja tworzenia się spiralnych struktur na powierzchni elektrody. Wykazano, że elektrolity do osadzania stopów Ag-In zawierające nadmiar rodanków i jodków jako czynników kompleksujących były stabilne. Obserwowane oscylacje potencjału w czasie galwanostaticznego osadzania indu z elektrolitów rodankowych wskazują na tworzenie i roztwarzanie się warstwek pasywnych na powierzchni elektrody. Obserwowano spiralne struktury w czasie osadzania stopu z elektrolitów rodankowych.

1. Introduction

The pattern formation observed on solid electrodes during electrodeposition of some alloys Ag-In [1], Ag-Sb [2], Ir-Ru [3], Ag-Bi [4], Ag-Sn [5] Ag-Cd [6] and In-Co [7] under well controlled electrochemical conditions is a very attractive and rare phenomenon, where the pattern are constituted of metals, while in other systems they are soft materials. Most probably, the formation of the structures belongs to a very complicated reaction mechanism, which includes the typical characteristics of the well known non-linear dynamic processes [8]. The experimental conditions of those systems can be reversibly and quickly changed by altering external parameters. That's why these systems could be used as models in the investigations of the self-organisation phenomena – the science of pattern formation deals with the visible, statistically ordered outcomes of self-organisation [9].

Electrodeposition of Ag-In alloys recently attracted our interest due to the observed spatio-temporal structures onto coated surface [10-13] mainly due to the advantage of the structures of the Ag-In system: they are visible with a naked eye during the deposition and it is possible to measure *in situ*, under small magnification (10X), their period and rotation speed.

The electrolytes for the deposition of silver-indium alloys are colourless. During electrodeposition of this alloy a wide variety of periodical spatio-temporal structures can be observed – waves, target patterns, left- and right-handed two- and three-arm spirals, annihilating and reappearing waves. Spirals with more than 25 turns could be found onto the coatings surface – Fig. 1.

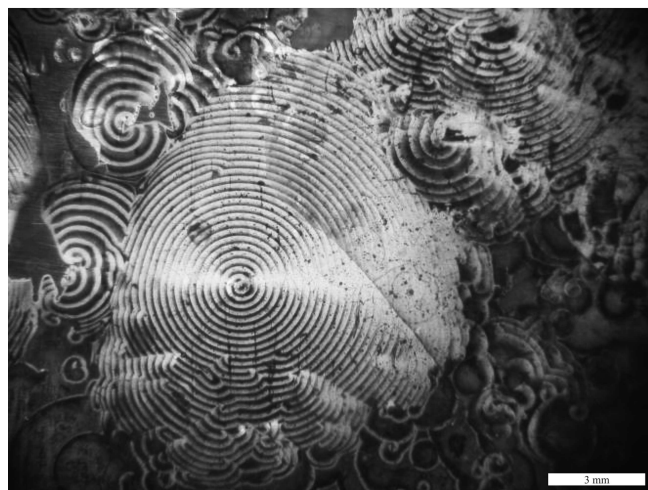


Fig. 1. Optical image of a silver-indium alloy coating

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The electrodeposition of silver-indium alloys in up to now was performed from cyanide electrolytes. In this study some attempts were made to obtain silver-indium alloys from non-cyanide electrolytes in order to broaden the usage of this alloy as a model system for the investigation of the self-organization phenomena, avoiding the toxic cyanide electrolytes. There is scarce information about deposition of Ag-In alloy from non-cyanide electrolytes: E. A Zakirova *et al.* [14] in a short communication suggested the polyethylenpolyamine electrolytes for the silver-indium electrodeposition; P. Warkala *et al.* [15] suggested an electrolyte on the basis of ammonium thiocyanate, Na-EDTA, and potassium carbonate and metal salts; Krastev presents the ammonium-thiocyanate electrolytes with the nitrate salts of the metals for the deposition of silver-indium alloys [16]. All the authors above reported about instability of the studied electrolytes.

The aim of this paper is to find out the appropriate electrolytes for the silver-indium alloys deposition and to adjust electrolysis conditions thus to observe the formation of spatio-temporal structures onto the electrode surface.

2. Experimental

The compositions of the investigated electrolytes are given in Table 1.

TABLE 1

Composition of the electrolyte	Concentration	
	g dm ⁻³	mol dm ⁻³
In as InCl ₃	0-10	0-0.088
Ag as CH ₃ SO ₃ Ag	0-1	0-0.009
KJ	0-166	0-1
KSCN	0-98	0-1

The pH value of the used electrolytes was about 2-3. The electrolytes were prepared using chemicals of *pro analisi* purity and distilled water. The cyclic voltammetry experiments were performed in a 100 cm³ tri-electrode glass cell at room temperature. Platinum working electrode (area 1 cm²) was used. The two counter electrodes were made from platinum. An Ag/AgCl reference electrode ($E_{Ag/AgCl} = 0.197$ V vs. SHE) was used.

The experiments were performed at room temperature by means of a computerized potentiostat/galvanostat Princeton Applied Research Model 263 using the software Soft Corr II. The alloy coatings with thickness between 1 and 3 μm were deposited onto copper cathodes with dimensions of 2×1 cm in the glass cell. The preliminary preparation of the cathodes includes a standard procedure of electrochemical degreasing followed by etching in a 20% solution of sulphuric acid. Two Pt/Ti counter mesh electrodes were used.

The In percentage in the coatings depending on the electrodeposition conditions was determined by X-ray fluorescence analysis (Fischerscope XDAL). The thickness and the percentage of the coatings were measured in 9 positions in the upper, middle and lower part of the electrode (3 measurements in each height).

The Ag (or In) distribution on the surface of the coatings was examined by energy dispersive X-ray analysis (EDX) and the morphology of the coatings surface was investigated by scanning electron microscopy (SEM).

3. Results and discussion

Different inorganic complexing agents, such as pyrophosphate, tartrate, succinimide and many others have been used for the preparation of the stable alloy electrolyte for the silver-indium deposition. It was not rare case, when the electrolytes for the silver or indium alone were clear but the alloy electrolyte precipitate. This is not surprising, due to easy reduction of the noble silver ion [17]. Only usage of thiocyanate and the iodide complex agents, in huge molar excess to the metal ions (see Table 1) allow obtaining stable electrolytes for the deposition of silver-indium alloys.

Figure 1 shows linear polarization curves obtained in the solutions of silver methanesulfonate in the water solution as well in the solutions, containing iodide and thiocyanate potassium salts. Curve 1 shows the polarisation behaviour of silver (as a simple salt, which is the silver methanesulfonate, used in the study) in water solution. In the investigated region of potentials the well-defined reduction peak can not be detected. The addition of the complexing agent as potassium iodide (curve 2) and potassium thiocyanate (curve 3) salts increases the rate of reduction. Difference in the deposition potentials of silver in both electrolyte is about 160 mV. According to literature data the instability constants of possible complexes are in the iodide electrolyte – AgJ_3^- with $K=1.4 \cdot 10^{-14}$; AgJ_4^{3-} with $K=1.8 \cdot 10^{-14}$ and in the thiocyanate electrolyte – $Ag(SCN)_2^-$ with $K=2.7 \cdot 10^{-8}$; $Ag(SCN)_3^2-$ with $K=8.3 \cdot 10^{-10}$; $Ag(SCN)_4^{3-}$ with $K=8.3 \cdot 10^{-11}$ [18].

According to the molar ratio, which is very high for the silver and complex agents in both solutions (see Table 1) the possible complexes in the electrolyte are: for thiocyanate solution $Ag(SCN)_4^{3-}$ and for iodide AgJ_4^{3-} . The maximum rate of the silver reduction is registered at potentials about – 0.25 V (for the thiocyanate) and – 0.4 V (for the iodide electrolytes). This seems reasonable electrolyte, because as stronger is the complex, as much the process is polarised. The pH of the electrolytes was about 2.8 (for iodide solutions) and 3.0 (for the thiocyanate one).

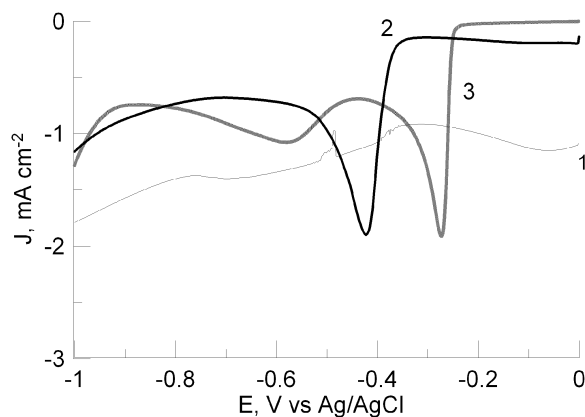


Fig. 2. Linear polarisation curves, obtained in the water solutions, containing: 1 g dm⁻³ Ag (curve 1), 1 g dm⁻³ Ag and 166 g dm⁻³ KJ (curve 2); 1 g dm⁻³ Ag and 98 g dm⁻³ f KSCN (curve 3)

The scanning electron microscopy images of the coatings obtained from silver iodide and silver thiocyanate electrolytes are shown in Fig. 3 a,b.

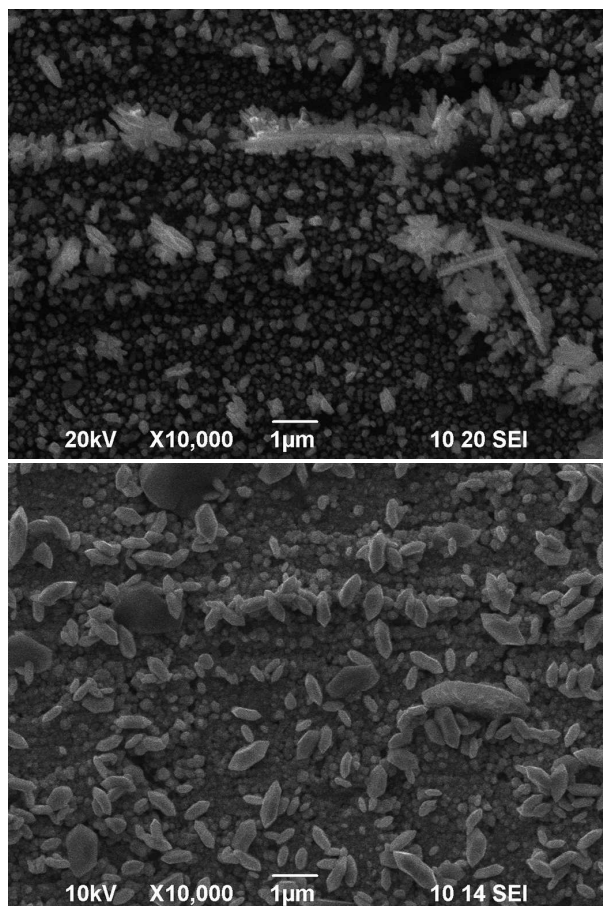


Fig. 3. Scanning electron images of the silver coatings, obtained at 0.7 A dm^{-2} for 10 minutes, from the electrolytes, containing: a) 1 g dm^{-3} Ag and 166 g dm^{-3} KJ, b) 1 g dm^{-3} Ag and 98 g dm^{-3} KSCN

Because of low silver concentration of the electrolyte the coatings are not very compact, they are grey-white and coarse.

Figure 4 shows the polarization curves, obtained in the presence of indium salt in water solutions with the addition of with different complex forming agents – iodide and thiocyanate ions.

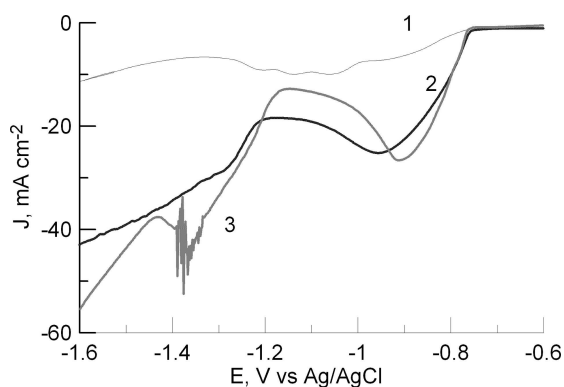


Fig. 4. Linear polarisation curves, obtained in the water solutions, containing: 10 g dm^{-3} In (curve 1), 10 g dm^{-3} In and 166 g dm^{-3} KJ (curve 2); 10 g dm^{-3} In and 98 g dm^{-3} of KSCN (curve 3)

Curve 1 is obtained in the water solution of indium chloride. This type of curves (with a different indium concentration in the solution) is described in a previous paper [10]. Curves 2 and 3 are obtained after addition of iodide and thiocyanate salts. The pH of the electrolytes is about 3.1 (for iodide electrolyte) and 3.2 (for thiocyanate electrolyte). The curves are almost identical with the some maximum of the potential of indium reduction of about -0.9 V . The possible complexes and their instability constants in both electrolytes are: in the iodide electrolyte – InJ^{2+} with $K=2.3 \cdot 10^{-2}$; InJ_2^+ with $K = 2.8 \cdot 10^{-3}$; InJ_3 with $K=3.3 \cdot 10^{-3}$ and in the thiocyanate electrolyte – InSCN^{2+} with $K=2.6 \cdot 10^{-3}$; $\text{In}(\text{SCN})_2^+$ = $1.0 \cdot 10^{-3}$; $\text{In}(\text{SCN})_3 = 2.3 \cdot 10^{-5}$ [18]. The probable complexes in the solutions are $\text{In}(\text{SCN})_3$ and InJ_3 due to high molar ratio of the complex forming agents and the metal (see Table 1).

The difference in the run of curves 2 and 3 is the presence of the potential oscillations in the thiocyanate electrolytes at the potential of about -1.4 V . Pospisil and de Levie [19] and M.T.M. Koper and Sluyters [20] observed current oscillations in this systems and the chemical nature of them was commented in their papers. On the anode in the iodide electrolyte a dark-red gas evolves, which could be referred to the oxidation of the iodide ions [21].

Figure 5 shows the morphology of the obtained indium coatings from iodide (Fig. 5a) and thiocyanate (Fig. 5b) electrolytes. The coatings are light grey and compact. The current efficiency increases with the current density (at 0.1 A dm^{-2} it is about 25% and at 0.8 A dm^{-2} it reaches 60%).

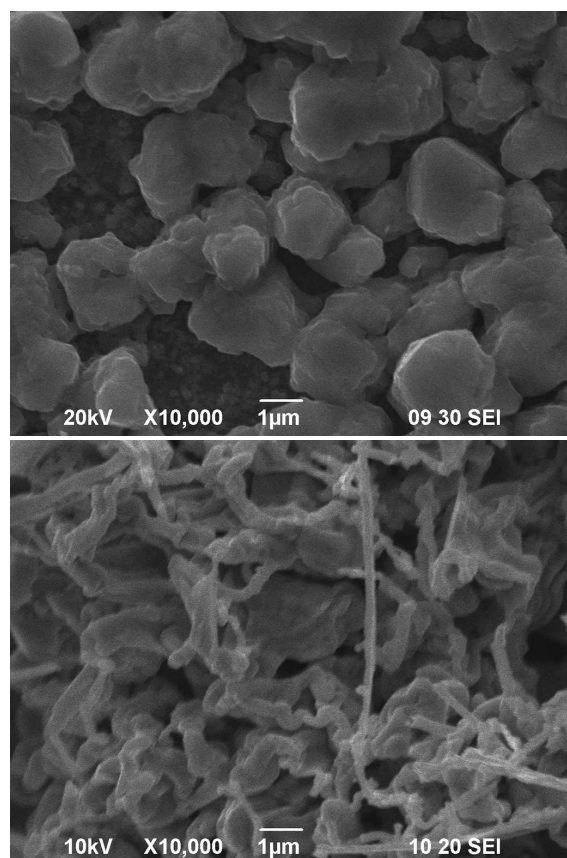


Fig. 5. Scanning electron images of the indium coatings, obtained at 0.7 A dm^{-2} for 10 minutes, from the electrolytes, containing: a) 10 g dm^{-3} In and 166 g dm^{-3} KJ, b) 10 g dm^{-3} In and 98 g dm^{-3} KSCN

Figure 6 shows the galvanostatic curves, obtained during the deposition of indium in the thiocyanate electrolytes onto platinum electrodes.

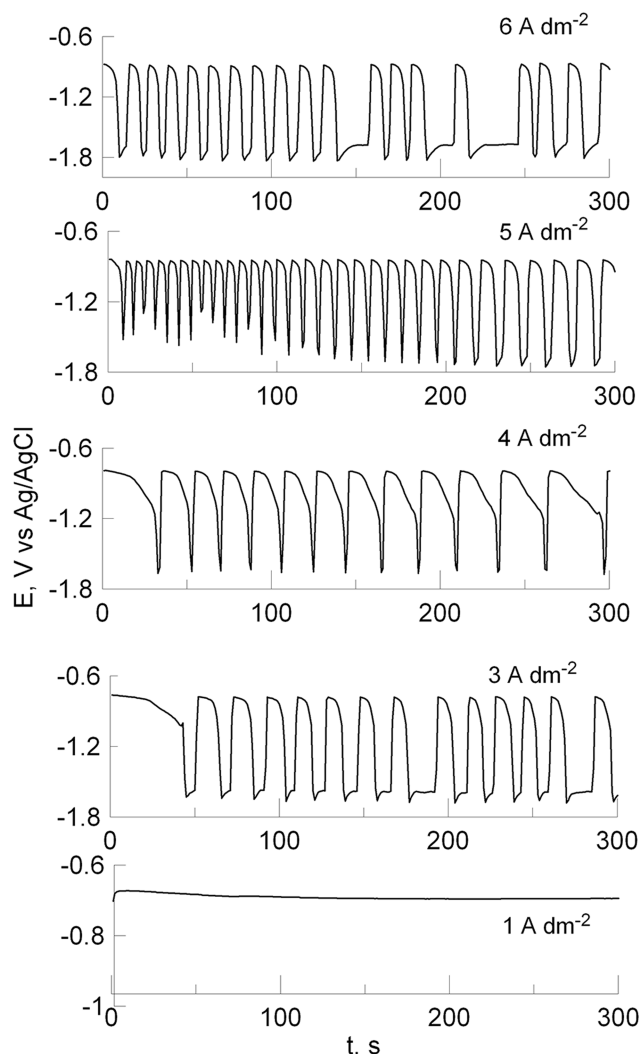


Fig. 6. Galvanostatic curves, obtained onto Pt electrode in the electrolyte, containing 10 g dm^{-3} In and 98 g dm^{-3} KSCN

It should be noted, that:

- in the presence of only silver ions the oscillations were not observed neither in iodide nor in thiocyanate electrolytes;
- in the indium iodide electrolytes oscillations of the potential were not observed;
- the oscillations were observed only in the indium thiocyanate containing electrolyte under sufficiently high current density – more than 2 A dm^{-2} .

The oscillations observed by Pospisil and de Levie and Koper and Sluyers are current oscillations. In order to avoid the formation of indium hydroxide (which forms at pH 3.3) the acidification of the solution were performed by the above mentioned authors. In this study there was not any addition of acid (or alkali). The oscillations with the same amplitude of the potential recently were observed during cadmium deposition [6]. Taking into account the works of Pospisil and de Levie, Koper and Sluyters as well as the observation of similar process during some previous experiments on the indium deposition behaviour in alkaline [10] and in acid [7] electrolytes it could be stated, that due to the alkalization of

the electrode/electrolyte interface some passive layer of indium hydroxide is formed. This film needs time to be formed in sufficient amount to be able to block the active surface. When the active surface is blocked, the potential increases rapidly to a level enough high to destroy the film and to start the hydrogen evolution. The hydrogen evolution reaction is well-visible during the galvanostatic process. The intensive hydrogen evolution leads to the 'stirring' around electrode/electrolyte interface and the processes are repeatable. With the increase in the applied current density the oscillations change their period (1 per 15 seconds at 3 A dm^{-2} and 1 per 6-7 seconds at 5 A dm^{-2}) without changing the magnitude (it is about 900 mV).

Figure 7 presents the polarisation curves, obtained in the electrolytes for the deposition of silver-indium alloy – with potassium iodide and with potassium thiocyanate. In both electrolytes the deposition of the alloy starts with a reduction of the silver ions (at the potential of about -0.4 V) and the indium deposition – at the potential of about -0.9V. As it was shown above, the values of the complexes of silver with both iodide and thiocyanate are stronger, than those of indium. The electrodeposition of silver-indium alloys from both electrolytes are of regular type, according to Brenner's classification [22], where the more noble metal deposits first in the alloy; the same behaviour is observed in the cyanide electrolytes [12,13].

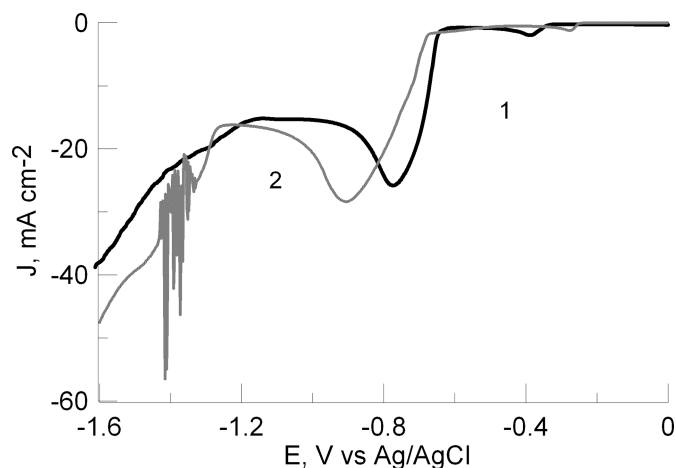


Fig. 7. Linear polarisation curves, obtained in the alloy electrolytes, containing 1 g dm^{-3} of Ag, 10 g dm^{-3} of In and 166 g dm^{-3} KJ (curve 1); 1 g dm^{-3} of Ag, 10 g dm^{-3} of In and 98 g dm^{-3} KSCN (curve 2)

It is expected, that with increasing of the current densities the indium content in the alloy coatings will increase. Some difference in both curves is the presence of oscillations (similar to the indium thiocyanate solutions (see Figure 4)) in the region of potentials negativer than -1.4 V in the thiocyanate solutions (see curve 2 in Figure 7).

The coatings from the iodide electrolyte from the beginning of electrolysis are brownish and contain significant amount of iodine (up to 30 wt. % Iodine is included in the deposit). Figure 8a shows the SEM image of the sample, obtained from the iodide electrolytes. There is not any idea about structure formation onto the surface. Figure 8b shows the morphology of the coating from Figure 8a at higher magnification. It is clearly seen the presence of some morphological instability – most probably due to the iodine inclusion. The content of coating is: 26 wt. % In, 38 wt. % Ag, 38 wt. % iodine [23,24].

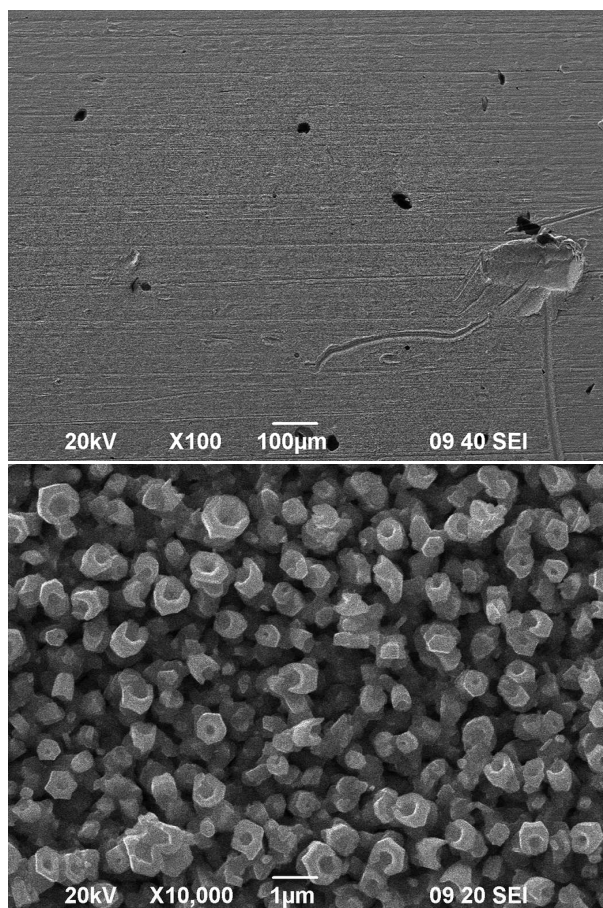


Fig. 8. a) Scanning electron images of the coatings, obtained from the electrolyte, containing 1 g dm^{-3} of Ag, 10 g dm^{-3} of In and 166 g dm^{-3} KJ, at 0.7 A dm^{-2} , for 10 minutes, b) part of the coating, from Figure 8a at higher magnification

In the thiocyanate electrolyte for the Ag-In deposition at low current densities ($0.1\text{-}0.2 \text{ A dm}^{-2}$) the coatings consist mainly from silver (1-3 wt. % In), at higher current density – 0.3 A dm^{-2} the coatings have an indium content of 10-12 wt. %. At 0.5 A dm^{-2} the indium content increases to 25 wt.% of In and some heterogeneity – some dark spots onto the milky-silver surface of the coatings are observed. At 0.7 A dm^{-2} the visible indication of the spatio-temporal structures onto the coatings surface could be detected.

Figure 9a shows the SEM image of the obtained coating – some targets could be observed. The Figure 9b shows the image of a part of Figure 9a under different magnification. The inhomogeneous spatial distribution of the different species is visible. The content of indium in the different areas is different – in point 1 - 20 wt. % of In, in point 2 - 32 wt. % of In and in point 3 - 72 wt. % of indium. The structure formation in the thiocyanate electrolyte appears at an average content of indium in the coatings about 20 - 25 wt %, which corresponds to those, observed in the cyanide electrolytes [11, 13].

At the current densities higher than 1 A dm^{-2} the coatings are indium-rich. The investigations on the galvanostatic deposition onto platinum electrode are presented in Figure 10. The oscillations of the potential starts latter than those, observed in the pure indium electrolyte. The potential oscillations start when the indium content of the deposit becomes sufficiently high (more than 70 wt. %). They are possibly connected with

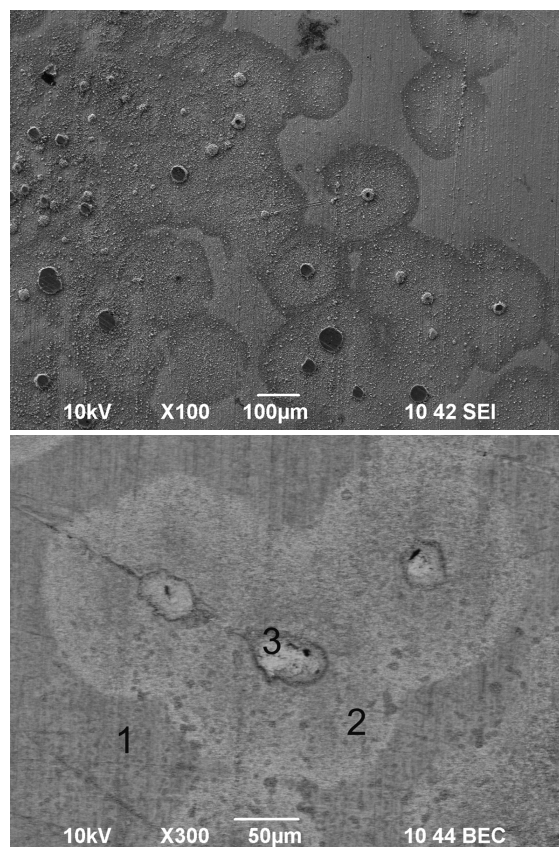


Fig. 9. a) Scanning electron image of a Ag-In coatings, from the thiocyanate electrolyte, containing 1 g dm^{-3} of Ag, 10 g dm^{-3} of In and 98 g dm^{-3} KSCN, at 0.7 A dm^{-2} , for 10 minutes; b) part of the coating from Figure 9a at higher magnification

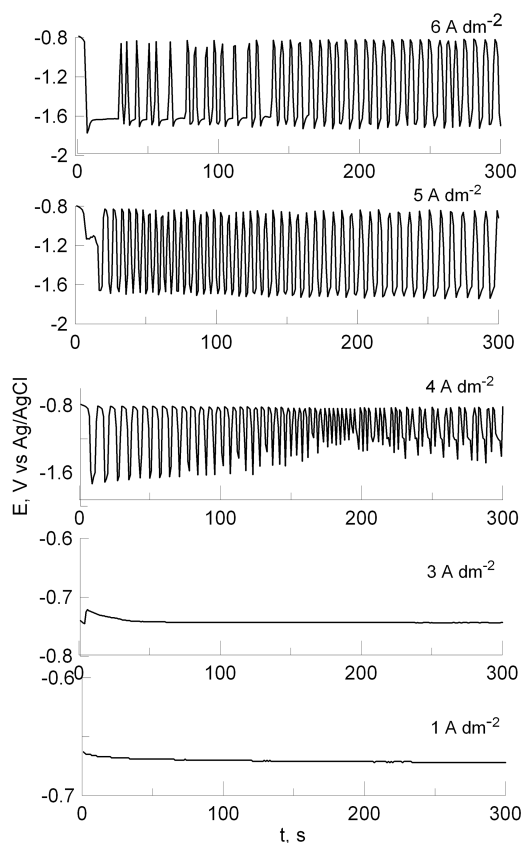


Fig. 10. Galvanostatic curves, obtained onto Pt electrode in the electrolyte, containing 1 g dm^{-3} of Ag, 10 g dm^{-3} In and 98 g dm^{-3} KSCN

the decreased hydrogen overvoltage on the indium-rich alloy substrate and the formation of passive films which most probably have the same nature as those observed during pure indium electrodeposition.

At the current densities up to 3 A dm^{-2} the coatings have quite high content of silver as the more positive metal in the system [7, 24]. With increased deposition time the oscillations become more regular and reproducible and their period increases. With increased indium content the oscillations become similar to those in the case of pure indium (compare Figure 10 with Figure 6).

4. Conclusions

1. The electrolytes for silver-indium deposition prepared with the excess of thiocyanate and iodide complexing agents are stable in time. The alloy electrodeposition is of a regular type where the silver is the more positive metal.
2. The observed oscillations of the potential in the thiocyanate solution of indium are formed due to the formation/destruction of some passive layers on the electrode surface.
3. The spatio-temporal structures could be observed during electrodeposition of the alloy from thiocyanate electrolytes.

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