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*Scientific paper*
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# Electrodeposition of Sb-In, Sb-Co and In-Co alloys

*In the present work an attempt was made, to investigate the Sb-In, Sb-Co and In-Co alloy deposition from one basic citrate electrolyte depending on the current density. The conclusions were made, that the used di-ammonium hydrogen citrate electrolyte is appropriate for the deposition of Sb-In, Sb-Co and In-Co alloys with good quality. During electrodeposition of Sb-Co and In-Co alloy coatings a wide range of alloying metal percentages could be reached, depending on the applied current density. The electrodeposited Sb-In alloy coatings are antimony-rich with constant percentage independent of the applied current density. Most probably, the metal content in the solution should be varied and the indium concentration increased. The electrodeposited coatings could be used for the further investigation of their physicochemical and mechanical properties. The observed spatio-temporal structures onto the surface of Sb-Co (initial stage) and In-Co alloys and the big variety of the pattern are a very appropriate object for the studies of self-organization phenomena during electrodeposition of alloys.*

## INTRODUCTION

Some investigations on the electrode processes, on the physicochemical characteristics of the deposited silver-antimony (Ag-Sb) [1, 2] and silver-indium alloy (Ag-In) [3,4] coatings and on the pattern formation on their surface during electrodeposition were reported some years ago. Recently some results concerning the electrolytic deposition of silver-cobalt (Ag-Co) alloys were published [5]. In all these studies the electrodeposition of silver-based alloys was described.

In the present work an attempt was made to extend the investigations on non-silver containing binary alloys of the above mentioned alloying elements - antimony, indium and cobalt. The literature data about the electrodeposition of antimony-indium (Sb-In), antimony-cobalt (Sb-Co) and indium-cobalt (In-Co) alloy coatings are very scarce. Only a few works on the deposition of Sb-In alloys from aqueous electrolytes could be detected [6,7]. A short communication of Titov *et al.* [6] presents the electrodeposition process of Sb-In alloy from tartrate electrolytes. They propose an appropriate electrolyte for deposition of coatings of good quality.

In the work of Sadana [7], the conclusions are made that bright, antimony-rich indium alloys could be deposited from acid citrate solutions and the current density range for bright deposits depends on the temperature and the pH-value of the electrolyte [7].

The electrodeposition of Sb-Co alloys is presented in an other paper of Sadana *et al.* [8]. It is shown, that the electrodeposits ranging in composition from 1 wt. % Sb to pure antimony could be deposited by varying the composition of the solution and the current density. The effects of agitation, temperature and citric acid content in the electrolyte on the composition and appearance of the alloy deposits, as well as the current efficiency of deposition are reported.

The electrodeposited In-Co alloys are also not extensively investigated and we found only one paper on this topic [9]. Sadana *et al*. [9] have established, that the In-Co alloys, ranging in composition from 2.0 to 90.6 wt. % cobalt could be electrodeposited from aqueous solutions. The effect of current density on current efficiency and composition of the deposit has been studied. An increase in current density increases the cobalt content of the deposits. Addition of ammonium citrate improves current efficiency [9].

The papers of Sadana *et al*. [7-9] are excellent basic information sources for the further investigation of these three alloys. Despite of the extensive survey devoted to these alloys made by Sadana and coworkers the data about electrode processes and morphology of the deposits are very limited.

In the present work an attempt was made, to investigate the Sb-In, Sb-Co and In-Co alloy deposition from one basic citrate electrolyte depending on the current density.

## EXPERIMENTAL

The composition of the electrolytes for deposition of the alloy coatings is shown in Table1.

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*Table 1*

| Electrolyte composition | g $dm^{-3}$ |
|---|---|
| In as $InCl_3$ | 0 - 5 |
| Sb as $K(SbO)C_4H_4O_6.1/2H_2O$ | 0 - 5 |
| Co as $CoSO_4.\ 7H_2O$ | 0 -30 |
| $C_6H_{14}N_2O_7$ | 20 |

The electrolytes were prepared using chemicals of *pro analisi* purity and distilled water.

The CV experiments were performed in a 100 $cm^3$ tri-electrode glass cell at room temperature. The working electrode (area 1 $cm^2$) and the two counter electrodes were made from platinum. An Ag|AgCl reference electrode ($E_{Ag|AgCl}$ = 0.197 V vs. HE) was used.

The experiments were performed at room temperature by means of a computerized potentiostat/galvanostat (GAMRY Reference 600) using PHE 200, version 5.5 software (Gamry Instruments).

The alloy coatings with thickness about 5-7 μm were deposited onto copper cathodes with an area of 2 x 1 cm in the glass cell. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing followed by pickling in a 20% solution of sulphuric acid. Two Pt (Ti) counter electrodes (about 4 $cm^2$ each) were used.

The elemental composition on the coating surface was measured by EDX.

The morphology of the coating surface was investigated by scanning electron microscopy.

## RESULTS AND DISCUSSION

### *Electrode processes*

The standard electrode potentials of the three investigated metals are as follows:

$E^0_{(Sb3+/Sb)}$ = +0.212 V [10], $E^0_{(Co2+/Co)}$ = -0.277 [11], $E^0_{(In3+/In)}$ = -0.34 V [12]. The antimony is the nobler metal and this fact determines the use of complex forming agents in order to shift the deposition potentials of antimony with indium and cobalt closer. As antimony salt $K(SbO)C_4H_4O_6.1/2H_2O$ was used. The electrolyte containing di-ammonium hydrogen citrate was selected empirically, after working with boric acid, potassium citrate, K-Na-tartrate and etc.

Figure 1 shows the CV curves of the electrolytes containing each metal separately.

The deposition of indium (black curve) starts at a potential of about -400 mV and is characterized by the absence of a well-defined peak in cathodic region and with very small anodic maxima. The passivation of the indium in this electrolyte (pH=3.1) is surprising and is similar to the behavior of indium in the strong alkaline solutions. Most probably, some alkalization during the cathodic process takes place and this leads to the formation of insoluble films of indium oxides and hydroxide [13].

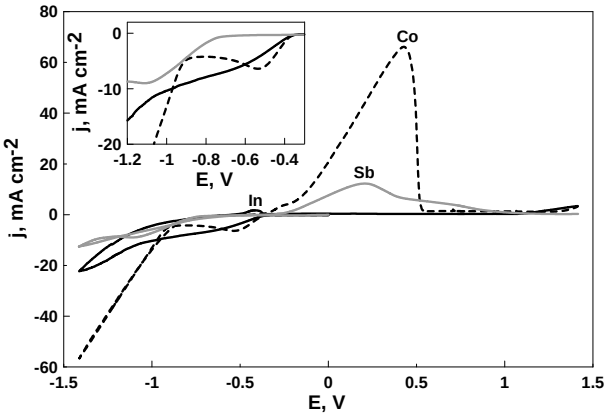


*Figure 1. CV curves, obtained in the single metal electrolytes; scan rate 25 mV $s^{-1}$: indium (black curve); antimony (grey curve) and cobalt (dashed curve).*

The cyclic voltammetry curve of cobalt electrodeposition (dashed line) is presented also in Figure 1. The electrodeposition of Co starts at -400 mV and after -500 mV appears a shoulder up to -1000 mV, where the process commences at the limiting current densities. One, well–defined peak of the coatings dissolution could be observed during anodic scan with maximum at 430 mV.

The electrodeposition of antimony starts at potentials, more negative than -800 mV (grey curve in Figure 1). There is no well defined peak but some hysteresis due to the fast growth of the deposits in the positive scan direction could be seen. A wide hump during antimony dissolution in the anodic part of the cyclic voltammetry curve could be detected.

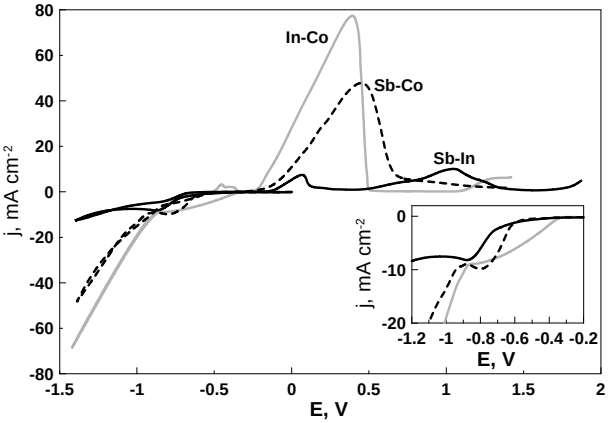


*Figure 2. CV curves, obtained in the electrolytes for deposition of the binary alloys; scan rate 25 mV $s^{-1}$; Sb-In (black curve); In-Co (grey curve); Sb-Co (dashed curve)*

Figure 2 shows the cyclic voltammetric curves, obtained in the electrolytes for deposition of the binary alloys.

The grey curve in Figure 2 presents the behavior of the In-Co electrolyte. Obviously, the process of deposition in the alloy electrolyte starts at the potential of pure indium (-400 mV) and the cathodic peak (-760 mV) (gray curve, inset in Figure 2), appearing in the potential interval of indium and cobalt deposition in the single metal electrolytes (see Figure 1) corresponds to the deposition of a cobalt-indium phase. During the anodic period a small peak between -500 and -300 mV is observed, corresponding to the dissolution of the formed in the cathodic period cobalt-indium phase and the second big anodic peak at more positive potentials with maximum at -400 mV corresponds to the dissolution of pure cobalt.

The deposition of the alloy from this electrolyte is of anomalous type (the more positive metal (indium) during electrodeposition dissolves at more negative potential) according to Brenner [14].

In the case of Sb-Co alloy the electrodeposition starts at potentials corresponding to deposition of antimony (-800 mV). The co-deposition of cobalt starts simultaneously with the hydrogen evolution reaction at potentials more negative than -1000 mV. The anodic part of the curve shows only one peak which could be attributed to the dissolution of the alloy.

The cyclic voltammetry curve corresponding to the deposition of Sb-In alloys is presented also in Figure 2 (black curve). The deposition process starts from the deposition potential of antimony, with well-defined peak around -850 mV. In the anodic part of the curve two peaks appear: the first one (around 0 mV) is responsible for dissolution of antimony and the second one (around 1000 mV), most probably belongs to the dissolution of some antimony-indium phase, formed in the cathodic period.

The deposited coatings of In-Co and Sb-Co alloys are fully dissolved during the anodic scan.

The Sb-In alloy can not be totally dissolved during the anodic scan. Figure 3 shows the curves, obtained in the electrolyte for the deposition of Sb-In alloys, where the first curve is obtained after standard procedure of cleaning of the platinum electrode, and the next curves – without cleaning the working electrode.

The Sb-In curve (black curve) of Figure 2 is presented in Figure 3 again. It is obtained on the fresh surface of the working electrode. The other curves (gray and dashed) show that the process of electrodeposition starts at the potential of pure indium (see Figure 1). Most probably, this effect is connected with the easier deposition of indium onto the surface with traces of undissolved phases of antimony and indium. This process does not change during the cycling (the presented curves are 2nd and 5th of the consequence cycles).

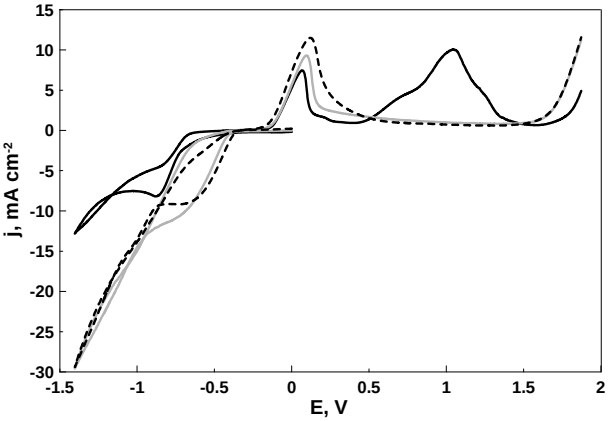


*Figure 3. CV curves obtained in the electrolyte for deposition of Sb-In alloys; scan rate 25 mV s$^{-1}$; black curve – 1st cycle, grey curve - 2nd cycle, dashed curve - 5th cycle*

*Galvanostatic deposition and morphology*

*Sb-In alloys*

The electrodeposition of the alloys was investigated in the current density range between 0.1 and 2.0 A dm$^{-2}$.

At low current densities (up to 0.8 A dm$^2$) the Sb-In coatings are bright, grey with good adhesion. At higher current densities (up to 1.5 A dm$^{-2}$), the surface of the coatings becomes black at the edges, again with good adhesion. The content of the elements in the coatings almost does not change and remains about 82-85 wt. % of antimony.

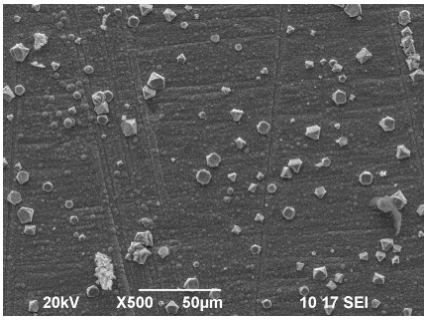


*Fig. 4a*

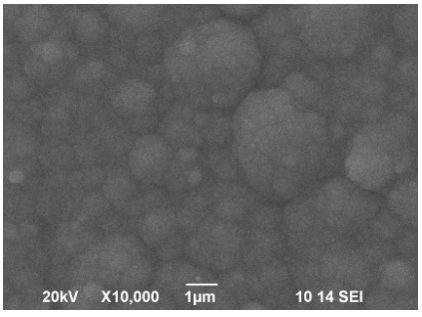


*Fig. 4b*

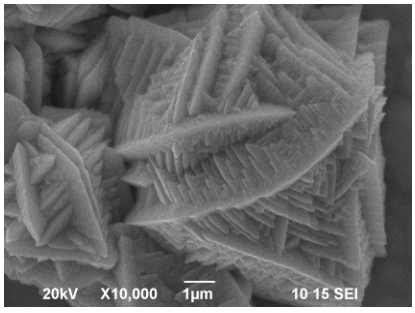


*Fig 4c*

*Figure 4. SEM images of the Sb-In alloys, obtained at 1 A dm$^{-2}$. The average Sb content of the coating is 82 wt. %*

Figure 4 a-c show the scanning electron microscopy images of a coating, obtained at 1 A dm$^{-2}$. The image in Figure 4a shows the typical morphology of the surface of the geometrical center of the sample. Figure 4b and c show different positions of Figure 4a under higher magnification. The EDX analysis shows that the content of antimony is approximately the same in the smooth part of the surface (81 wt. % in Figure 4b), and in the crystal (85 wt. % Sb) presented in Figure 4c.

Figures 4b and 4c represent different parts of the image of Figure 4a.

*Sb-Co alloys*

At current densities (up to 0.8 A dm$^{-2}$) the Sb-Co alloy coatings are black and have good adhesion.

At higher current densities the coatings became bright, and very heterogeneous. At current densities, higher than 1.5 A dm$^{-2}$ (the antimony content of coatings is about 52 wt. %) the deposition is accompanied with intensive hydrogen evolution on the cathode, which leads to the formation of pits on the coatings surface.

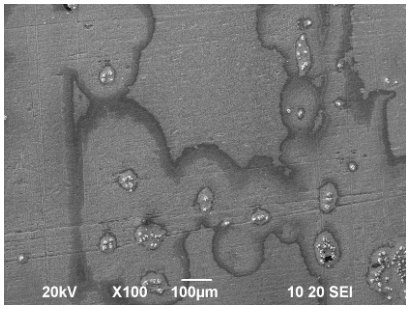


*Fig. 5a*

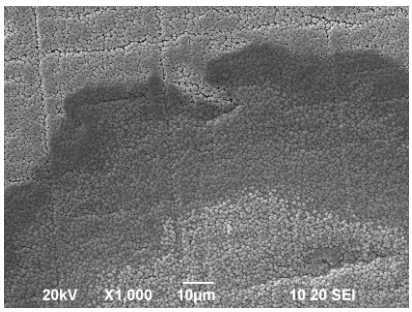


*Fig. 5b*

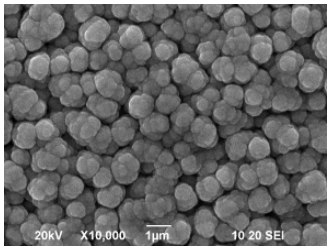


*Fig. 5c*

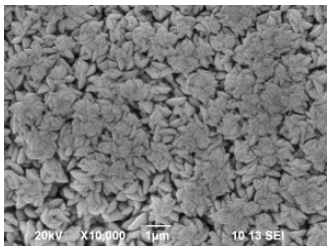


*Fig. 5d*

*Figure 5. SEM images of Sb-Co alloys, obtained at 1 A dm$^{-2}$; b), c) and d) – different positions of the surface of Figure 5a at higher magnifications.*

Pattern formation could be registered on the surface of the coatings, obtained at 1-1.2 A dm$^{-2}$ (70-87 wt. % Sb) (Figure 5a). These patterns are not very well organized, but the typical fronts of different colored phases are visible (Figure 5b). The morphology in the different areas of these fronts is different.

*In-Co alloys*

Almost pure indium coatings are obtained at low current density (about 0.2-0.5 A dm$^{-2}$) from the electrolyte for In-Co alloy deposition. At increased current density (0.6-1.2 A dm$^{-2}$) the surface of the electrode is covered by patterned structures – targets, waves and spirals.

Scanning electron microscopy images, of the same coating in different magnifications are shown in Figures 6a-c. The morphology of the different areas is different due to the phase heterogeneity. The EDX analysis shows that the cobalt content of the different zones is about 68-72 wt. %.

The observed self-organization phenomena allow the conclusion, that pattern formation can be investigated not only during electrodeposition of silver-based alloys, but also in binary alloys formed by the alloying metals antimony, cobalt and indium.

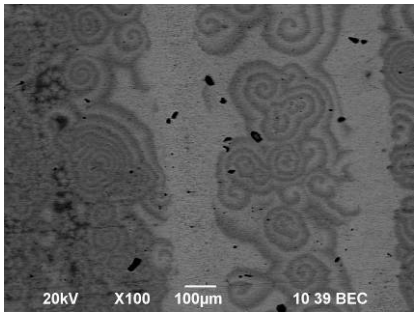


*Fig 6a*

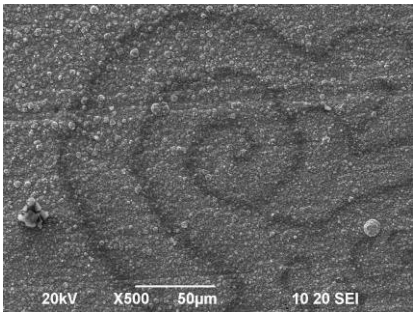


*Fig 6b*

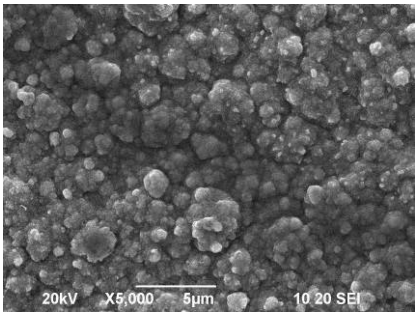


*Fig 6c*

*Figure 6. SEM images of In-Co alloys, obtained at 1 A dm$^{-2}$; Figures 6b) and 6c) – different magnification of the image of Figure 6a).*

## CONCLUSIONS

1. The used di-ammonium hydrogen citrate electrolyte is appropriate for the deposition of Sb-In, Sb-Co and In-Co alloys with good quality. During electrodeposition of Sb-Co and In-Co alloy coatings a wide range of alloying metal percentages could be reached, depending on the applied current density. The electrodeposited Sb-In alloy coatings are antimony-rich with constant percentage independent of the applied current density. Most probably, the metal content in the solution should be varied and the indium concentration increased.

2. The electrodeposited coatings could be used for the further investigation of their physicochemical and mechanical properties.

3. The observed spatio-temporal structures onto the surface of Sb-Co (initial stage) and In-Co alloys and the big variety of the patterns are a very appropriate object for the studies of self-organization phenomena during electrodeposition of alloys.

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