

Electrodeposition and structure of binary alloys of silver, tin and antimony

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Is it possible to obtain periodic spatio-temporal structures during electrodeposition of Ag-Sb and Ag-Sn alloys from non-cyanide electrolytes? To find out suitable electrolytes for the deposition of the antimony-tin alloy in order to obtain coatings in a wide range of compositions as well as the conditions for obtaining of heterogeneous coatings – these are the questions to be answered in the present study. It was established, that spiral structures formed by different alloy phases are observed during electrodeposition of silver-tin alloys from thiocyanate-pyrophosphate electrolytes. The phase analysis shows that the structures are formed by the phases Ag₃Sn and Sn.

Depending on the electrolysis conditions during deposition of Ag-Sb alloys it is possible to obtain structures with different level of spatio-temporal organization from thiocyanate electrolyte. The pyrophosphate-tartrate electrolytes for the deposition of Sb-Sn alloys is developed for deposition of alloy coatings appropriate for investigation of their phase heterogeneity and properties.

Keywords: alloys, antimony, electrodeposition, silver, tin, self-organization

INTRODUCTION

Finding out the proper electrolytes for obtaining of silver-antimony, silver-tin and antimony-tin alloys is an actual problem, regardless of fact, that these are not exotic alloys [1]. The main problems are connected with the necessity to avoid well-worked but toxic, containing free-cyanide ions electrolytes for deposition of the mentioned alloys. Our intensive investigations in the last years led to the challenge to obtain spatio-temporal structures onto the cathode surface during electrodeposition of alloys of silver with antimony and tin[2-4]. Some unsolved tasks during electrodeposition of binary alloys of silver, tin and antimony from aqueous solutions could be formulated:

Silver-tin alloy is a very important material for solders, especially after the strict regulations of EU on the use of lead. Despite the intensive efforts of the scientific community stable electrolytes for deposition of this alloy are still not formulated [5-7]. The main reason is the reduction of tetravalent tin ions to a two valent ones, wherein the silver ion is reduced immediately in the solution. One of the few electrolyte options for the deposition of silver-tin alloys is the cyanide-pyrophosphate electrolyte [4]. From this electrolyte deposited structures, especially waves, composed from different phases of the alloy could be observed onto the cathode

surface.

It is well-known that antimony, as an alloying metal to silver (up to 5 wt. %) provides lustre of the precious metal [1]. By increasing the composition of the antimony in the coatings a wide variety of structures could be observed and this electrodeposited system is one deeply investigated system, but the procedure of electrolyte preparation is awkward due to the difficulties of the preparation of the silver complex [8-12].

Is it possible to obtain periodic spatio-temporal structures during electrodeposition of Ag-Sb and Ag-Sn alloys from non-cyanide electrolytes?

Tin-antimony alloy, electrodeposited from aqueous electrolytes practically is not investigated. However, it has been found, that bright coatings of alloys based on tin provide good solderability with non-acid flux [13, 14]. The electrodeposited alloy containing 5-10 wt. % antimony prevents the transformation of the lead from white to grey modification and in this way provides the ability for soldering for long storage time of the parts. Furthermore, this alloy has shown anti-friction properties and higher corrosion resistance as compared to pure tin [15].

The phase diagram indicates the presence of intermetallic compounds, which suggests the possibility of deposition of heterogeneous coatings [16].

The next goal of the present study is to find out suitable electrolytes for the deposition of the antimony-tin alloy in order to obtain coatings in a

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wide range of compositions as well as the conditions for obtaining of heterogeneous coatings.

EXPERIMENTAL

The composition of the used electrolytes presented in Table 1.

Table. 1. Composition of the electrolytes

Components	Quantity, g dm ⁻³
Sn as Sn ₂ P ₂ O ₇ /Umicore/	0-30
Ag as KAg(CN) ₂ /Umicore/	0-16
Sb as K(SbO)C ₄ H ₄ O ₆ /Merck/	0-30
C ₄ H ₄ O ₆ KNa*4H ₂ O	0-60
K ₄ P ₂ O ₇ /Umicore/	0-280
KSCN _{Merck/}	0-60

Chemical substances of *pro analisi* purity and distilled water were used.

The experiments were performed in a 100 cm³ tri-electrode glass cell at room temperature. The vertical working electrode (area 2 cm²), and the two counter electrodes were made from platinum. Prior to each experiment, the platinum working electrode was electrochemically etched in a solution of 0.1 M H₂SO₄ using platinum as a counter electrode till obtaining a clear surface. An Ag/AgCl reference electrode ($E_{Ag/AgCl} = 0.197$ V vs NHE) was used. The experiments were carried out at room temperature by means of a computerized potentiostat/galvanostat PAR 273 using the software Suite Corr. The polarization curves were recorded at the sweep rate of 20 mV s⁻¹.

The coatings were deposited under galvanostatic conditions at room temperature onto copper and brass substrates (4 cm²).

The surface morphology of the coatings was studied by scanning electron microscopes (SEM) – JEOL 6390 and Hitachi S-4000.

The content of antimony (respectively silver and tin) in the coatings depending on the electrolysis conditions was determined by X-ray fluorescence analysis (Fischerscope X-RAY XDAL) in 9 points (three points in the bottom, middle and top of the sample, respectively).

The phase composition was characterized by X-ray diffraction (XRD) using a PANalytical Empyrean device equipped with a multichannel detector (Pixel 3D) using (Cu-K α 45 kV-40mA) radiation in the 2 θ range 20–115°, with a scan step of 0.01° for 20 s.

RESULTS AND DISCUSSION

Silver-tin alloy

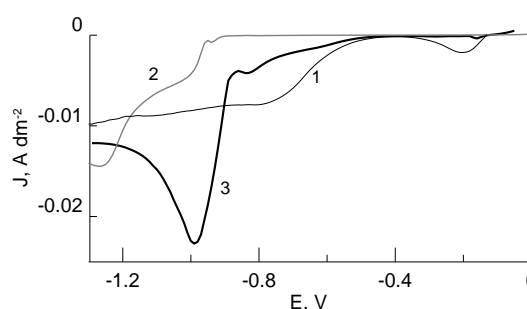


Fig.1. Polarization curves of an electrolyte, containing Ag and Sn separately or together, registered at $v=20$ mV s⁻¹, in g dm⁻³: Curve 1: Ag-5; K₄P₂O₇-280, KSCN-60; Curve 2: Sn-50; K₄P₂O₇-280, KSCN-60; Curve 3: Ag-5; Sn-50; K₄P₂O₇-280, KSCN-60.

Figure 1 shows cathodic part of the polarisation curves of electrolytes, containing silver and tin separately and together. Electrodeposition of silver (curve 1) is characterized by the cathodic maxima at a potential -0.2 V and this peak 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 [17]. 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. The electrode processes in the pyrophosphate electrolyte for the silver deposition are presented in details by S. Nineva et al. [18, 19]. It is worthy to note, that the instability constant of the pyrophosphate complex of silver has a value of about $K_{inst}=10^{-4}$. This is a weak complex of silver, compared with the silver-cyanide complex, which constant is about $K_{inst}=10^{-22}$ [20].

Curve 2 presents the behaviour of tin ions in the alloy electrolytes, without silver. Two well-visible waves with some indication of peak are situated at potentials at -1.0 V and -1.25 V. The first small cathodic maximum (at -0.8 V) in the alloy electrolyte (curve 3) corresponds to the deposition of silver. Some small shift of the peak in comparison with those in electrolyte without tin could be explained with a different amount of ligands around the silver ion. The second cathodic maximum, appearing at the potential of tin deposition from a pure tin electrolyte, corresponds to the tin and most probably some silver-tin phase formation

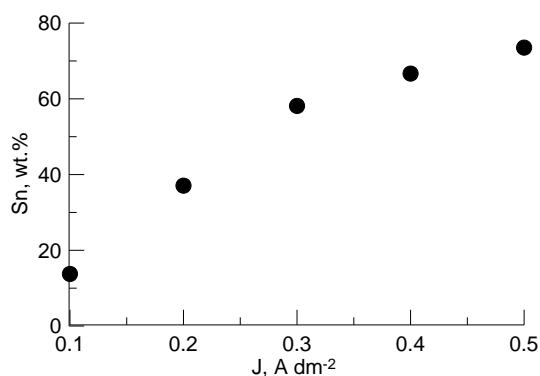


Fig. 2. Content of tin in the Ag-Sn coatings depending on the current density (The composition of the electrolyte is described in the caption of Figure 1).

Figure 2 shows the dependence on the composition of the silver-tin coatings from the current density. It could be clearly seen that with increasing current density the content of tin in the coatings increases, which is consistent with the results from polarization curves, presented in Figure 1. At low current densities the coatings are bright, silver-like. With the increasing of the current density the coatings become visibly heterogeneous. In the upper part of the electrode the coatings are richer in tin, and in the bottom - of silver. Upon reaching up to about 42-50 wt. % tin on the surface of the electrode spirals with more than 10 runs could be seen even with naked eyes – Figure 3. It should be noted that similar structures were not observed when the electrodeposition is performed incyanide-pyrophosphate electrolytes[4]. In these electrolytes the spatio-temporal structures are only in the form of waves. In the present studies well-defined spiral structures together with waves could be seen.

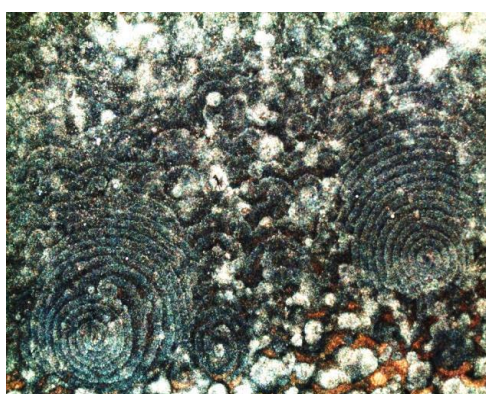


Fig. 3. Optical image of the spiral structures (Composition of the electrolyte is described in the caption of Figure 1), width of the image is 2 mm.

The Sn content of the structures is 41-43 wt. %. Scanning-electron images are pale, due to the approximately identical composition in the dark and light areas as well as the similar surface morphology in them (Figure 4). The image

presented was obtained at low energy of the accelerating voltage – 5 keV. Standard voltages for handling such images - about 20 keV good resolution of the structures cannot be observed. The difference in the composition in various areas of the well visible optical structures is minimal – the difference of the tin content is less than 1 wt. % in both zones. Some porosity is observed in the region, richer in tin.

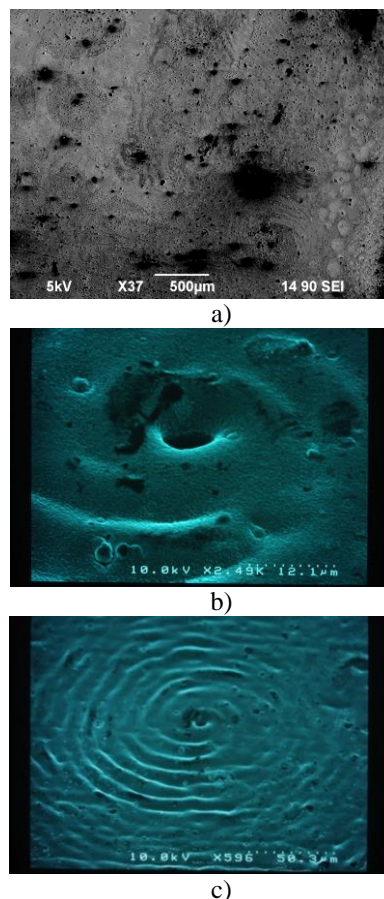


Fig.4. Scanning-electron images of the part of coatings, shown in Figure 3. Obtained in the SEM JEOL at 20 keV; b,c) at different magnifications, obtained in the SEM Hitachi at 10 keV.

Considering that the same structures are optically well visible and with good contrast, a conclusion could be drawn that the wave fronts move at a sufficiently high speed so that the thickness of the formed dark and light layers during deposition is substantially smaller than the penetration depth of the electron-beam during EDAX analysis. As a result the beam penetrates through several light and dark layers, and the estimated average content of tin in both zones is almost the same.

That is the reason for the observation of the both dark and light zones with high quality only at low accelerating voltages (5keV) of the electron beam.

Figure 4 b, c shows the morphology of the center of the spiral in the Belousov–Zhabotinsky reaction the rotating spiral waves with many turns could be created by breaking of a circular wave. In the case of silver-tin electrodeposited coatings some “initial” defect is observed in the core of the rotating spiral waves. It could be possibly formed by adsorption of some impurities or hydrogen evolution on this position of the surface.

Figure 5 presents the phase composition of the coatings with different tin content. When the tin content in the coating about 44-56 wt.% Sn (coatings with spatio-temporal structures) the reflexes of 2 different phases appear - these of Ag_3Sn and Sn. Further increasing the tin content (up to 56 wt.%) in the coating leads only to the changes of the intensity of reflexes.

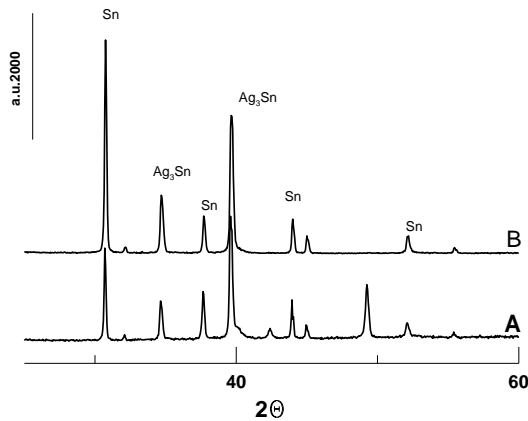


Fig. 5. XRD patterns of the samples, obtained from the electrolyte, described in Figure 1 (curve 3) ²A-sample with 44 wt. % Sn (0.2 A dm⁻²); B- sample with 56 wt. % Sn (0.3 A dm⁻²).

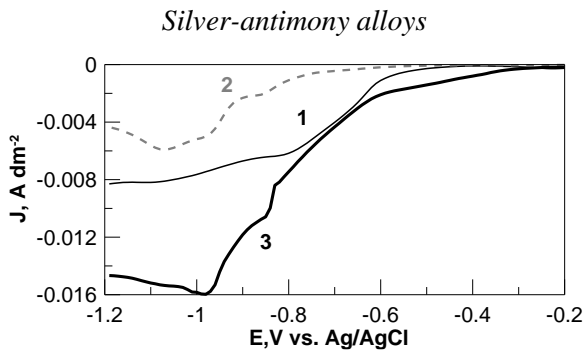


Fig. 6. Polarization curves of an electrolyte, containing Ag and Sb separately or together, registered at $v=20 \text{ mV s}^{-1}$, in $g \text{ dm}^{-3}$: Curve 1: Ag- 16; $C_4H_4O_6KNa \cdot 4H_2O - 60$; KSCN-150; Curve 2: Sb-7.5; $C_4H_4O_6KNa \cdot 4H_2O - 60$; KSCN-150; Curve 3: Ag- 16; Sb-7.5; $C_4H_4O_6KNa \cdot 4H_2O - 60$; KSCN-150.

Figure 6 shows the polarization curves obtained in the electrolytes for deposition of an alloy of silver-antimony in the presence of the metal ions separately or together. Silver in this system is the

more positive metal and its deposition starts at potentials around -0.5V (Curve 1). Antimony in this composition of the electrolyte is reduced at potentials of about -0.9V. The alloy curve shows regular type of according to the classification of Brenner [1].

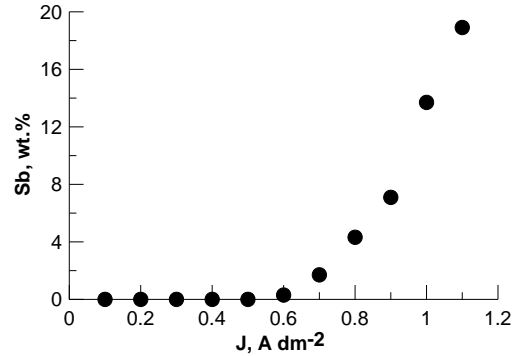


Fig. 7. Content of antimony in the Ag–Sb coatings depending on the current density (Composition of the electrolyte is described in the caption of Figure 6).

At low current densities up to 0.5 A dm^{-2} the coatings are silver-like in appearance and practically free of antimony (Figure 7). After 0.5 A dm^{-2} the content of antimony in the coatings increases and reaches 20 wt. % at 1.1 A dm^{-2} .

Coatings, containing between 7 wt. % and 13 wt. % of antimony show optical heterogeneity.

A similar phenomenon was observed by Krastev in a slightly different composition of the electrolyte, also in the simplified procedure of the preparation of electrolyte [3].

Figure 8a-c presents optical images depending on the current density. When the content of Sb is about 7 wt. % some spots could be seen (Figure 8a), and at higher current density these spots are formed into a more organized conglomerates (Figure 8b) where the content of Sb is 9 wt. % and afterward, at content of antimony about 11 wt. % a spiral formation could be clearly seen (Figure 8c).

The phase composition of the coatings with different content of antimony is shown in Figure 9. At the content of 2 wt. % Sb (curve A) only reflexes of the α -phase of silver are detected. According to the phase diagram of the alloy [16] the solubility of the antimony in the silver is about 6-7wt. %.

By increasing the antimony content in the coatings (curve B, coating with 7 wt. % Sb and curve C, coating with 11 wt. % Sb, respectively) the reflexes of two phases appear – $Ag_{3.84}Sb_{0.16}$ and $Ag_{0.63}O_{6.1}Sb_{2.5}$. These results clearly confirm that the structure formation, i.e. formation of spatio-temporal structures appears at elemental and phase composition similar to those, presented in another investigations [21].

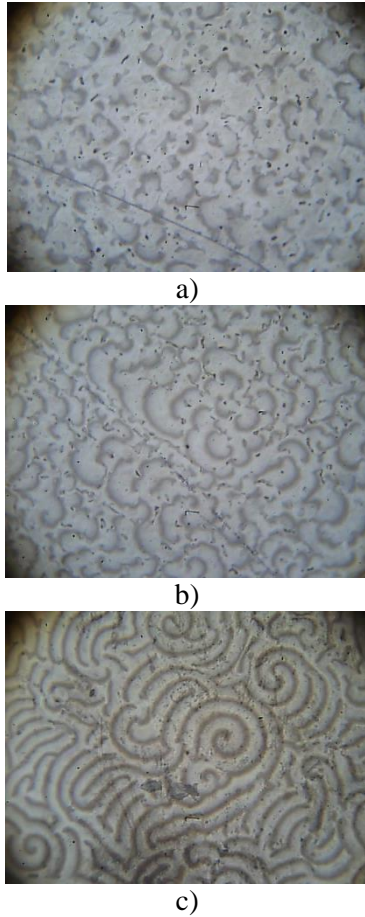


Fig.8. Optical images of the heterogeneous structures (The composition of the electrolyte is described in the caption of Figure 7), width of the image is 2 mm: a) 0.8 A dm⁻² (7 wt. % Sb); b) 1.0 A dm⁻² (9 wt. % Sb); c) 1.1 A dm⁻² (11 wt. % Sb);

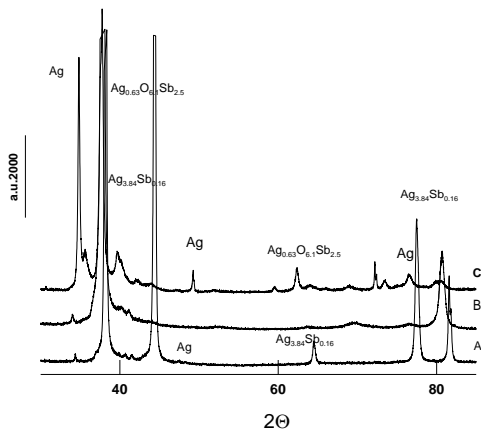


Fig. 9. XRD patterns of the samples, obtained from the electrolyte, described in Figure 6 (curve 3) A - 2 wt. % Sb-(0.6 A dm⁻²); B - 7 wt. % Sb (0.8 A dm⁻²); C- 11wt. % Sb (1.1 A dm⁻²).

Antimony-tin alloy

The electrodeposition of antimony-tin alloys was investigated in 3 electrolytes, where the concentrations of the metal ions have been varied. Figure 10 shows the polarization curves obtained in

electrolytes with the same metal ions concentrations - 5 g dm⁻³ Sn and 5 g dm⁻³ Sb.

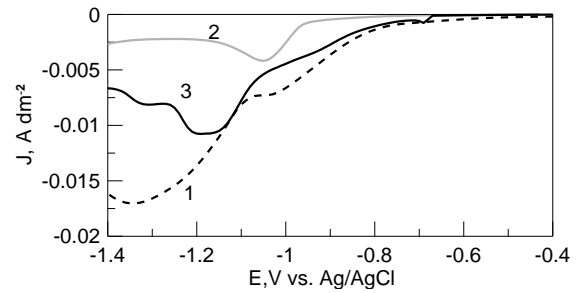


Fig. 10. Content of antimony in the Sn-Sb coatings depending on the current densities. Concentrations in g.dm⁻³. Curve 1: Sb- 5; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150; Curve 2: Sn-5; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150; Curve 3: Sb - 5; Sn-5; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150.

The reduction of antimony (curve 1) starts at about -0.75 V and two peaks are observed and the first one coincides with the reduction peak of the two-valenced tin ions in the investigated electrolyte (curve 2). The polarization curve of the alloy electrolyte repeats the runs between the curves of the separate metals.

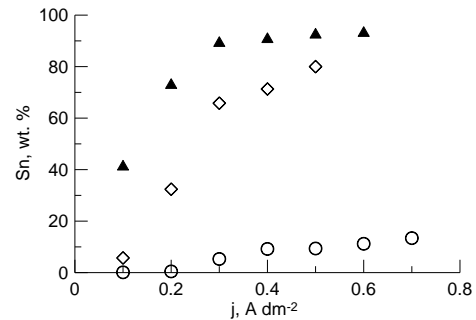


Fig.11. Content of tin in the Sn-Sb coatings depending on the current density. Composition of the electrolytes: ▲ Sn - 30; Sb - 5; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150; ◊ Sn - 5; Sb - 5; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150; ○ Sn - 5; Sb - 30; C₄H₄O₆KNa*4H₂O - 60; K₄P₂O₇-150

The dependence of the content of the coatings on the current densities is presented in Figure 11. The obtained results confirm the fact, that the antimony is the more positive element in this alloying system and with the increasing of the current density its content in the coatings decreases. The electrolytes are stable and at concentrations of 5 g dm⁻³ Sn and 5 g dm⁻³ Sb ensure wide range of the percentage of Sn (from 0 to 80 wt. % of Sn). The optical heterogeneity onto the coatings with 50-70 wt. % of Sn could be detected, but without any indications of the structures similar to those, observed in the Ag-Sn and Ag-Sb alloys.

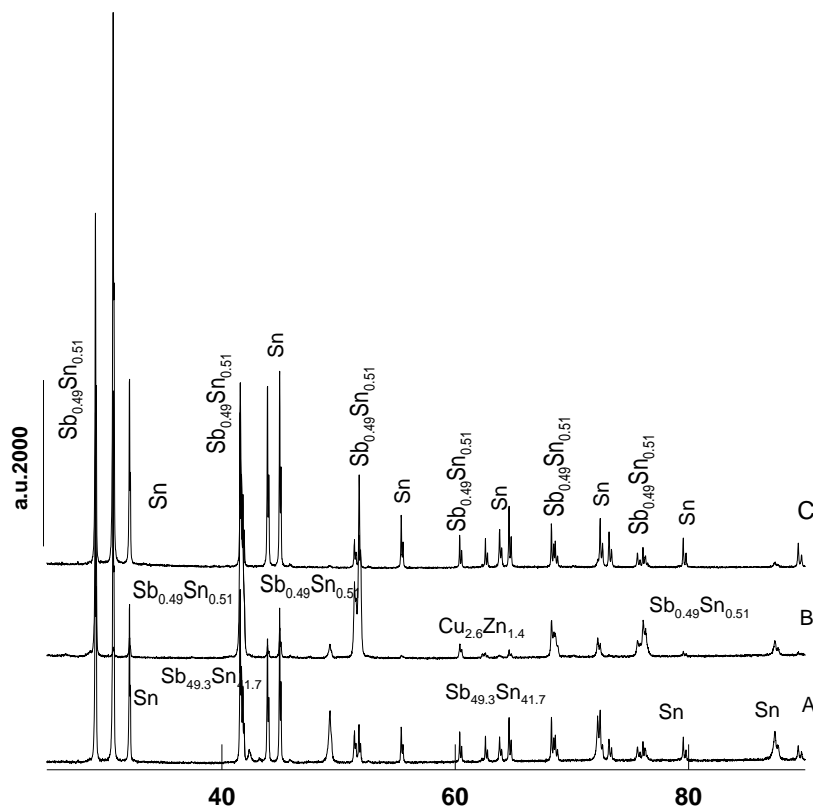


Fig. 12. XRD patterns of the samples, obtained from the electrolyte, described in Figure 10 (curve 3); A - 41 wt. % Sn; (0.2 A dm⁻²); B - 66 wt. % Sn (0.3 A dm⁻²); C- 77 wt. % Sn (0.4 A dm⁻²).

Figure 12 shows the phase composition of the coatings with a content of Sn between 41 and 77 wt. %.

The diffractogram A corresponds to the coating with 41 wt. % Sn and the reflexes of the phases Sb_{49.3}Sn_{41.7} and Sn could be detected. At higher content of Sn in the coatings (curves B and C) reflexes of the phases Sb_{0.49}Sn_{0.51} and Sn are observed.

The obtained results could be a basis for future investigations on the formation of ordered structures in the heterogeneous Sb-Sn alloys.

CONCLUSIONS

1. Spiral structures formed by different alloy phases are observed during electrodeposition of silver-tin alloys from thiocyanate-pyrophosphate electrolytes. The phase analysis shows that the structures are formed by the phases Ag₃Sn and Sn.
2. Depending on the electrolysis conditions during deposition of Ag-Sb alloys it is possible to obtain structures with different level of spatio-temporal organization.
3. The pyrophosphate-tartrate electrolytes for the deposition of Sb-Sn alloys is developed for deposition of alloy coatings appropriate for investigation of their phase heterogeneity and properties.

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ЕЛЕКТРООТЛАГАНЕ И СТРУКТУРА НА БИНАРНИ СПЛАВИ ОТ СРЕБРО, КАЛАЙ И АНТИМОН

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(Резюме)

Възможно ли е да се получат периодични пространствено-времени структури при отлагане на сплавите Ag-Sb и Ag-Sn от нецианидни електролити? Да се намерят подходящите електролити, при които да се получат сплавни покрития от Sb-Sn в широк диапазон от състав на компонентите – това са въпросите, на които е необходимо да се отговори в настоящето изследване. Установено е, че спиралните структури, получени от различни фази на сплавта се наблюдават при електроотлагане на сплав Ag-Sn от тиоцианатно-пирофосфатни електролити. Фазовият анализ показва, че структурите са съставени от фазите Ag₃Sn и Sn.

В зависимост от условията на електроотлагане на сплавта Ag-Sb от тиоцианатни е възможно получаването на структури с различно ниво на самоорганизация. Определени са състави на пирофосфатно-тартаратни електролити за отлагане на сплави Sb-Sn, при които е възможно получаването на хетерогенни покрития за последващо изследване на техният фазов състав