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## Effect of electrolyte composition on the electrodeposition of Cu-Sb alloys from methanesulfonate-tartrate electrolytes

*The electrochemical processes of deposition and dissolution of Cu and Sb separately or together from acid methanesulfonate-tartrate electrolytes are investigated by cyclic voltammetric technique.*

*The influence of different parameters of the electrodeposition process, such as current density, temperature, electrolyte composition and acidity on the antimony content, phase composition and morphology of the coatings is shown. The increase in current density leads to an increase in the antimony content in the alloy, as well as to an increase in the deposition rate of the alloy. The antimony content decreases with the rise in temperature, as expected. The increase in D(-)-tartaric acid concentration in the electrolyte leads to a slight increase in antimony content.*

*The possibility of deposition of compact bright Cu-Sb coatings with up to 52 wt. % Sb and compressive internal stress from the investigated electrolytes is shown.*

*At high antimony content the deposition of multiphase heterogeneous coatings with ordered spatial distribution of the different alloy phases on the cathodic surface can be observed. The phenomena and the observed structures are very similar to those observed during electrodeposition of some other silver alloys, such as Ag-Sn, Ag-Sb, Ag-Bi and Ag-In.*

**Key words:** copper-antimony alloy, electrodeposition, ordered structures

### 1. INTRODUCTION

The high corrosion resistance, high metallic lustre and wide range of applications of Sb and its alloys make their electrodeposition of practical importance [1]. For example the addition of Sb to Cu improves the physico-mechanical properties of Cu coatings, as well as their corrosion resistance [2]. Up to 5% Sb in the coatings give them decorative appearance [3]. Ammoniacal [4], cyanide [5], tartrate-cyanide [2,5,6], sulphate-tartrate [7], polyphosphate [8] and pyrophosphate baths [3] were proposed for Cu-Sb deposition. Cu-Sb alloys with low antimony content are deposited from most of these electrolytes. Some of the electrolytes suffer from shortcomings such as frequent corrections of Sb concentration, toxicity etc. Recently, a procedure for single potential deposition of crystalline Cu<sub>2</sub>Sb layers from aqueous solutions at room temperature was developed [9, 10]. This compound is a promising anode material for lithium-ion rechargeable batteries. The use of citric acid as a complex forming agent increases the solubility of antimony salts and shifts the reduction potentials of copper and antimony toward each other, enabling the direct deposition of the intermetallic compound at pH 6. Electrodeposition of Cu<sub>2</sub>Sb directly onto conducting substrates represents a facile synthetic method for the synthesis of high quality samples with excellent electrical contact to a substrate, which is critical for further battery testing.

The present study shows the possibility of deposition of compact semi-bright Cu-Sb coatings with up to 52 wt. % Sb from acid methanesulfonate-tartrate electrolytes.

### 2. EXPERIMENTAL

The composition of the investigated electrolyte is given in Table 1.

Table 1

Components	Composition, g (cm <sup>3</sup> ) dm <sup>-3</sup>
CuSO <sub>4</sub> · 5H <sub>2</sub> O	16
K-SbO-C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 0.5H <sub>2</sub> O	18
Methansulphonic acid (70%)	20
D(-)C <sub>4</sub> H <sub>6</sub> O <sub>6</sub>	96

The cyclic voltammetry (CV) experiments, as well as the anodic linear sweep voltammetry (ALSV) measurements were performed in a 100 cm<sup>3</sup> three-electrode glass cell at room temperature without agitation of the electrolyte. The vertical working electrode (area 0.5 cm<sup>2</sup>) and the two counter electrodes were made of platinum. A saturated calomel (SCE) reference electrode was used.

The experiments were carried out by means of a computerized PAR 263A potentiostat/galvanostat using the Soft Corr II software. The sweep rate was varied from 5 to 1000 mV s<sup>-1</sup>.

The coatings were deposited in a glass cell of 125 cm<sup>3</sup>. Distilled water and *pro analisi* grade reagents were used. Copper anode 5 x 1 cm was used. Coatings were deposited on 0.3 mm thick stainless steel substrates of dimensions 2 x 1 cm. Prior to deposi-

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tion, the substrates were electrochemically degreased and pickled according to a standard procedure. The coatings are deposited at 20 °C unless it is stated otherwise, without agitation of the electrolyte.

The Cu and Sb percentage in the coatings depending on the electrolysis conditions was determined by X-ray fluorescence analysis (Fischerscope XDAL). The rate of deposition of the alloy (the thickness of the deposited coatings) was determined on the basis of XRF measurements. The surface morphology of the coatings was studied by optical and scanning electron microscopy (SEM). The phase analysis was performed by means of a Philips PW 1050 diffractometer at 2 $\theta$  angles from 10° to 95° with Cu $K_{\alpha}$  irradiation and scintillation detector.

The internal stress,  $IS$ , was monitored with the apparatus constructed by Stalzer [11] operating on the principle of the one-sided galvanized bendable cathode. The cathodes for this measurement were 10 cm long, 1 cm wide, 0.3 mm thick and their backsides were lacquer-insulated. The alloy was deposited along 7 cm of the plate, dipped in the electrolyte (400 cm<sup>3</sup>). During electrodeposition, the cathode is bending in a specific direction depending on whether the induced internal stress is compressive or tensile. A sensor detects the deviation and compensates it through an electric feedback system. The force needed for compensation and hence the value of the internal stress is deduced from the electrical signal. The latter is transferred through a suitable interface to a computer for monitoring and processing. The method permits *in situ* monitoring of the internal stress during electrodeposition.

### 3. RESULTS AND DISCUSSION

#### 3.1. CV measurements

The hydrogen evolution in the absence of Cu and Sb in the electrolyte starts at about -300 mV (Figure 1, curve 1). In the absence of Sb, copper deposition starts at 0 V (curve 2). One cathodic maximum is registered at about -450 mV and the copper dissolution reaction starts at about 0 mV and reaches its maximal rate at a potential of 380 mV. Two cathodic peaks are registered on the voltammetric curve during electrodeposition of antimony (curve 3) - one cathodic maximum at -630 mV and a second cathodic maximum at -400 mV during the reverse scan. The first peak could be attributed to deposition of antimony from tartrate complex on platinum and the second one is probably due to deposition of antimony on antimony and for this reason the peak is shifted to less negative potentials as compared to the second peak. The CV curve obtained using Sb working electrode confirms this suggestion - the maximum of antimony depo-

sition peak appears at about -410 mV. The positions of the antimony peaks offer the opportunity for co-deposition with copper.

One antimony dissolution maximum is observed in the anodic cycle at about 130 mV. It is more negative than the copper dissolution potential in this electrolyte. In this system, copper is a more positive element than antimony. The electrodeposition of the alloy is of regular type according to Brenner [12].

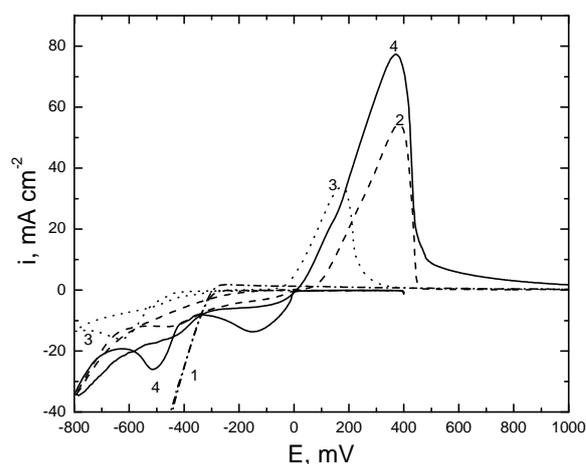


Fig.1. Cyclic voltammetric curves: 1 (· · ·) - supporting electrolyte; 2(- - -) - electrolyte with Cu; 3(· · ·) - electrolyte with Sb; 4(—) - electrolyte with Cu and Sb; sweep rate 25 mV s<sup>-1</sup>

In the presence of both metals in the electrolyte (curve 4), 3 cathodic peaks are registered when scanning in negative direction. The first peak (deposition of pure copper) is shifted to less negative potentials (-140mV) as compared to the peak in the antimony-free electrolyte (-450 mV). It seems that antimony depolarises copper deposition. On the other hand tartaric acid forms complexes with both metals, hence only a part of tartaric acid is complexed with copper and another part with antimony and this could be the reason for the higher and depolarized copper peak. The latter assumption is more probable, because the increase in tartaric acid concentration in the electrolytes containing only copper or antimony lead to decreased height and a shift of the copper and antimony deposition peaks to more negative potentials (Figure 2a and b). This effect is more strongly pronounced at antimony.

In corroboration with the assumption about the influence of the tartaric acid is the fact that the third cathodic peak, observed at -516 mV (Figure 1, curve 4), is higher and depolarised with about 110 mV as compared to the peak in the copper free electrolyte.

A very small cathodic hump is observed at -380 mV. At this potential probably a copper-antimony alloy coating is deposited.

In the anodic part of the cyclic voltammetric curve only one electrochemical reaction is registered. The dissolution of the coating starts at potentials between this of pure copper and pure antimony dissolution. There is no maximum registered, that could be ascribed to the pure antimony phase, i.e. antimony is probably combined in alloy phases with copper. Another possibility is that pure antimony in the coating is covered by copper due to a replacement reaction when the system passes over the potential range of the antimony dissolution reaction during the anodic sweep.

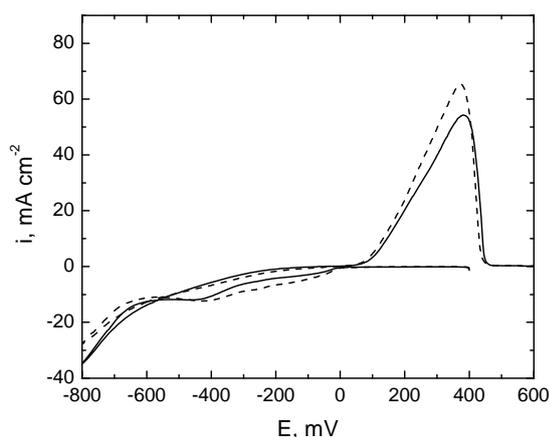


Fig. 2a. CV curves in copper electrolyte: 1 (---) with  $24 \text{ g dm}^{-3}$  tartaric acid; 2 (—) with  $96 \text{ g dm}^{-3}$  tartaric acid

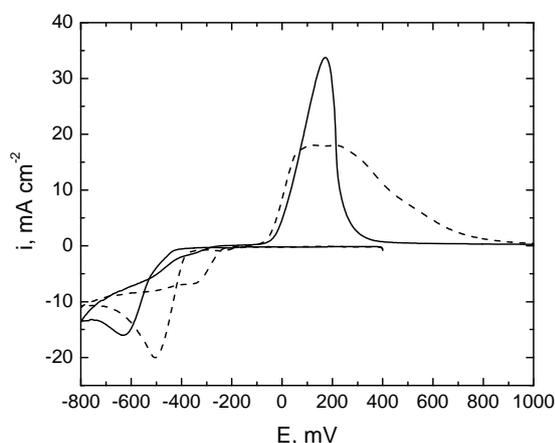


Fig. 2b. CV curves in antimony electrolyte: 1 (---) with  $24 \text{ g dm}^{-3}$  tartaric acid; 2 (—) with  $96 \text{ g dm}^{-3}$  tartaric acid

To verify this assumption anodic linear sweep voltammetry measurements were performed in solution containing only tartaric acid and MSA. Even in this case a separate peak corresponding to antimony dissolution is not observed, the dissolution of the coating begins at potentials of pure copper dissolution. Such a peak is observed when dissolution of Cu-Sb alloy is performed in electrolyte containing

$200 \text{ g dm}^{-3}$  tartaric acid. Possibly this amount of tartaric acid as a complex forming agent for antimony is sufficient to depolarize the dissolution of some excess amount of antimony in the coating strongly enough to enable the appearance of a separate antimony dissolution peak.

### 3.2. Composition and deposition rate of Cu-Sb alloy

It is possible to obtain semi bright compact coatings from the investigated electrolyte with antimony content of up to about 52 wt %. The influence of the current density on the antimony percentage in the coatings is shown in Figure 3. Each point of the curve represents the average of at least nine measurements in three different heights of the electrodes. The antimony content in the coatings sharply increases depending on the current density up to  $0.5 \text{ A dm}^{-2}$ . At higher current densities the antimony content in the coatings slightly increases. In alkaline ammonium-tartrate electrolytes the antimony content in the coatings doesn't exceed 7 wt. %, while in cyanide-tartrate electrolytes it is possible to obtain brittle or spongy coating with a wide range of antimony contents [4].

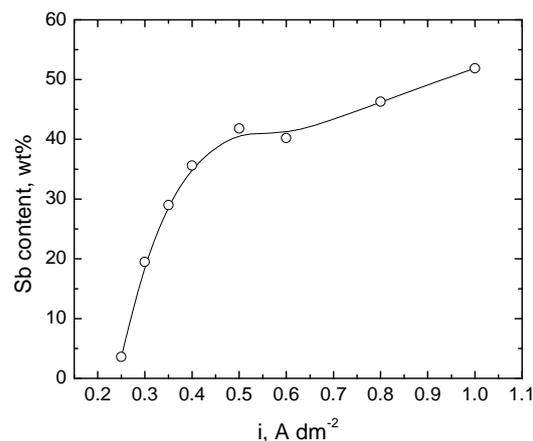


Fig. 3. Effect of the current density on the antimony content in the coatings

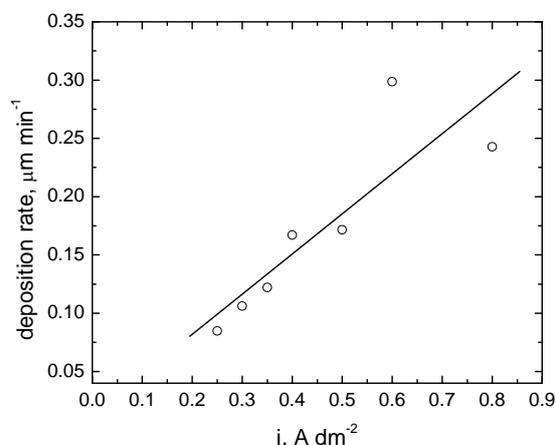
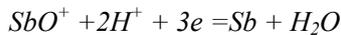


Fig. 4. Effect of the current density on the deposition rate of the Cu-Sb coatings

The dependence of the deposition rate of the Cu-Sb coatings on the current density is almost linear (Figure 4). The deposition rate varies between 0.08 and 0.32  $\mu\text{m}$  per minute depending on the current density. Each point of the curve represents the average of at least nine measurements in three different heights of the electrodes. Current densities of up to 1  $\text{A}\cdot\text{dm}^{-2}$  can be applied in the unstirred alloy electrolyte.

### 3.3. Influence of tartaric acid and methanesulphonic acid on antimony content in the coatings

The increase in tartaric acid concentration leads to slight increase in antimony content in the coatings (Figure 5). This increase could be due to 2 reasons. The antimony deposition in the strong acid electrolyte runs through the following reaction:



The increased acidity of the electrolyte could favour the antimony deposition, although the change of the pH-value of the strong acid electrolyte is not so substantial (from 0.89 down to 0.74).

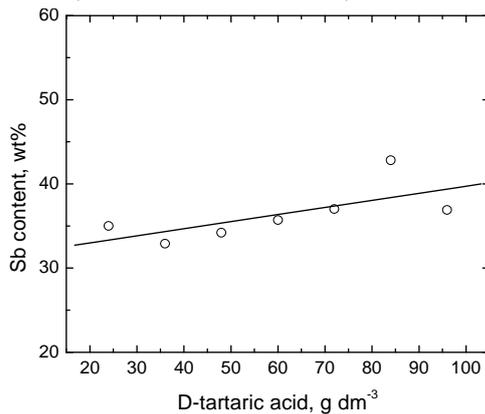


Fig.5. Effect of the tartaric acid on the antimony percentage in the coatings,  $0.6 \text{ A dm}^{-2}$

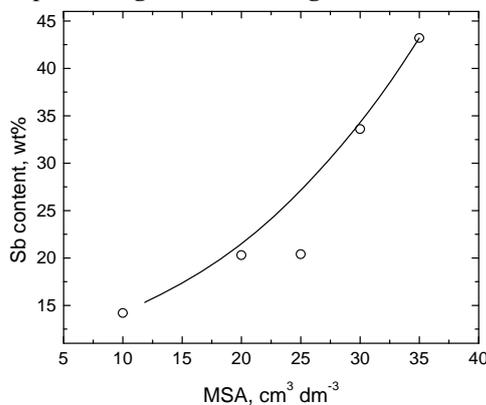


Fig.6. Effect of MSA on the antimony percentage in the coatings;  $0.6 \text{ A dm}^{-2}$

On the other hand tartaric acid forms relatively strong complexes with both metals and inhibits their

deposition, so that some combined effect of both factors could be the reason for this behaviour.

The influence of the concentration of methanesulphonic acid in the electrolyte on the antimony content in the coatings is much stronger than the influence of tartaric acid. The increase in methanesulphonic acid concentration from 10 to 35  $\text{cm}^3 \text{ dm}^{-3}$  leads to an increase in the antimony content of three times (Figure 6). This confirms the assumption that the acidity of the electrolyte exerts a strong effect on the percentage of the deposited alloy.

### 3.4. Effect of the concentration of antimony in the electrolyte and of the temperature on the antimony content in the coatings

An increase of the antimony concentration in the electrolyte leads surprisingly to a decrease in its content in the coating (Figure 7). This behaviour could be connected with the results of the CV-experiments and the effect of the pH-value of the electrolyte and possibly it is due to some rearrangement of the complexes of both metals in the electrolyte when the concentration relations are changed, but the effect needs more detailed studies to be explained.

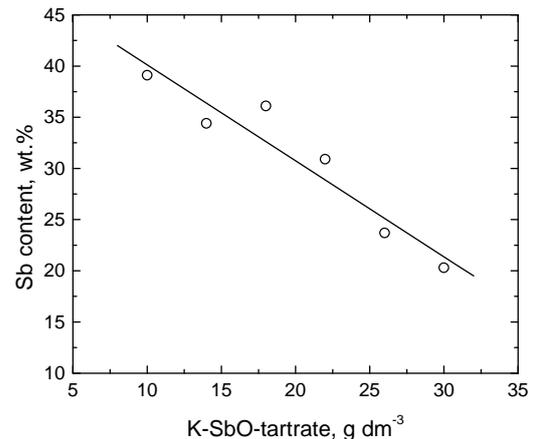


Fig.7. Effect of the antimony concentration,  $0.6 \text{ A dm}^{-2}$

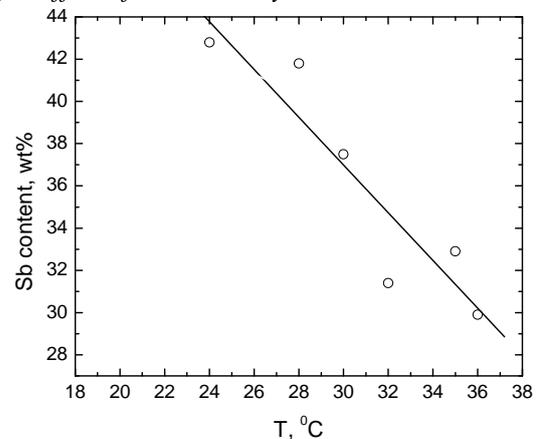


Fig.8. Effect of temperature on antimony content in the coatings deposited at  $0.6 \text{ A dm}^{-2}$

As expected, the rise in temperature leads to decrease in antimony (less noble element) content (Figure 8). Similar results were obtained by Yurinskaia and Popov [7] in sulfate-tartrate electrolytes, but the coatings obtained from their electrolyte contain up to 10 wt. % antimony. The linear dependence shows a slope of about 1 wt. % Sb per °C when the deposition temperature is increased.

### 3.5. Phase composition

At low antimony content in the alloy (up to 10 wt. %) only the copper phase ( $\alpha$ -phase) is present in the coatings (Figure 9). At higher antimony contents three phases are registered in the alloy: Cu,  $\text{Cu}_2\text{Sb}$  ( $\eta$ -phase) and pure Sb. The phase composition does not depend on the antimony content in the range 10-50 wt. % Sb, in contrast to the coatings obtained in alkaline cyanide-tartrate by E. Raub [4]. He found that at antimony content from 0 to 13.8 wt. % only the copper phase is present in the alloy. From 13.8 to 43.2 wt. % Sb the  $\epsilon$ -phase ( $\text{Cu}_3\text{Sb}$ ), from 43.2 to 58 wt. % Sb – the  $\zeta$ -phase ( $\text{Cu}_{10}\text{Sb}_3$ ), and from 58 to 100 wt. % Sb – the  $\zeta + \eta$  phases are registered. Pure antimony phase appears at copper content up to 42%.

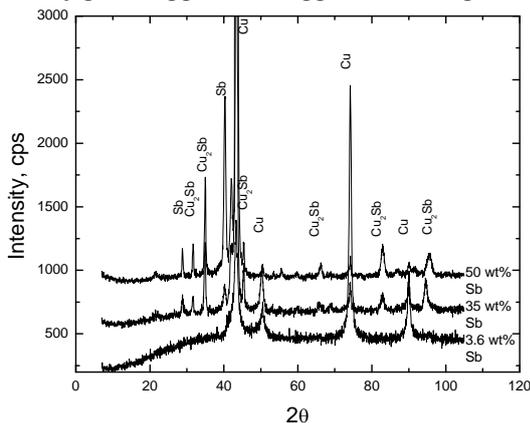


Fig. 9. X-ray diffractograms of Cu-Sb alloy coatings with different antimony content

### 3.6. Internal stress

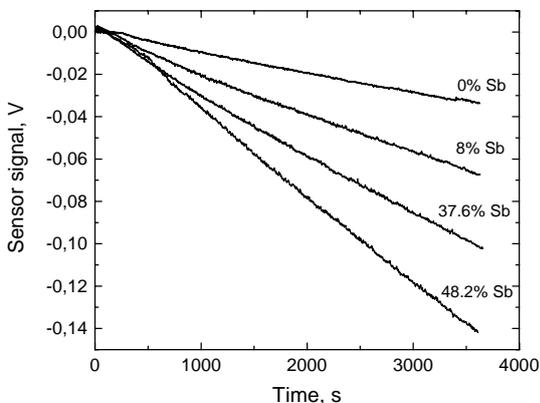
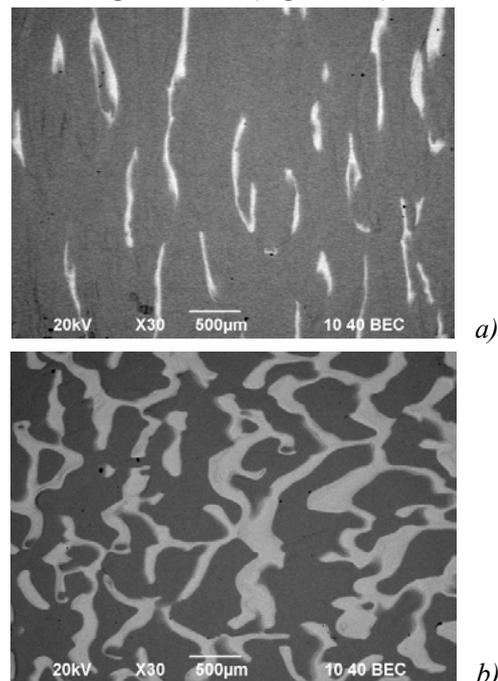


Fig. 10. Sensor signal vs. time curves at different current densities – 0.2, 0.5, 0.6, 0.9  $\text{A dm}^{-2}$ , respectively

Compressive internal stress was registered in the pure copper coatings deposited from the alloy electrolyte (Figure 10). The stress in the coating is proportional to the slope of the sensor signal vs. time curve. The linearity shows that the stress values are constant during the deposition time. The co-deposition of antimony leads to an increase in the compressive stress. After reaching the saturation limit of the copper lattice with Sb, the next antimony-richer phase should be formed in the deposit. According to the XRD experiments at higher Sb contents the  $\text{Cu}_2\text{Sb}$  phase is registered and the IS measurements show compressive stress in the presence of this phase in the coatings.

### 3.7. Surface morphology

The co-deposition of Sb leads to deposition of semi-bright coatings. At room temperature in the current density interval between 0.2 and 1.0  $\text{A dm}^{-2}$  heterogeneous multiphase coatings can be deposited, with an ordered spatial distribution of the different phases on the surface of the cathode. Under certain conditions the different phases could self-organize themselves in ordered vertical structures, as shown in Figure 11a. The phase heterogeneity of the alloy is well visible. Antimony forms island structures on copper (bright areas on Figure 11a) similar to the bismuth islands on copper substrates [13, 14]. The antimony content in these bright areas is in the range from 45 to 70 wt. %, while the dark areas are composed mainly of copper (antimony content is about 1-2.2 wt. %). The structure of the antimony rich phases and the copper-rich phases is completely different (Figure 11c d). The increase in current density (i.e. increased antimony content in the coatings) leads to coalescence of antimony-rich areas and formation of very interesting structures (Figure 11b).



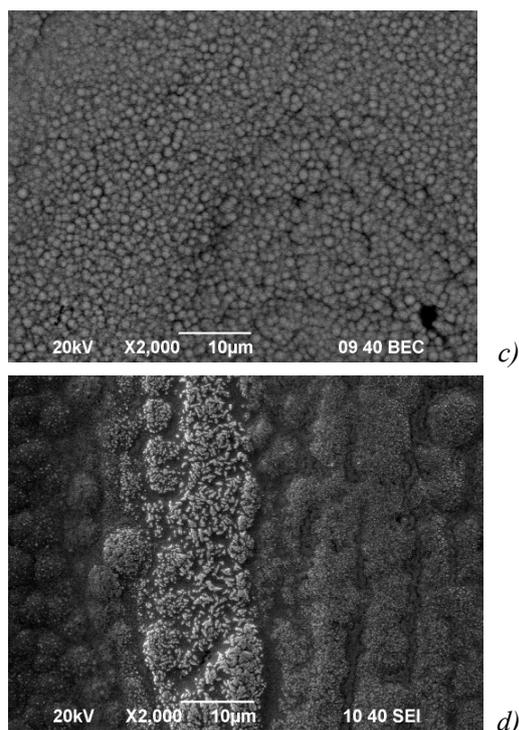


Fig.11. SEM micrograph of an Cu-Sb alloy coating deposited at: a)  $0.4 \text{ A dm}^{-2}$ ; b)  $0.8 \text{ A dm}^{-2}$ ; c) dark area; d) bright area

Ordered structures are observed not only on the surface of the coatings. The cross-section of a Cu-Sb coating on a flat copper substrate shows a lamellar structure (Figure 12). The antimony content in the bright lamellas is about 60-70 wt. % and in dark ones – about 3 wt. %.

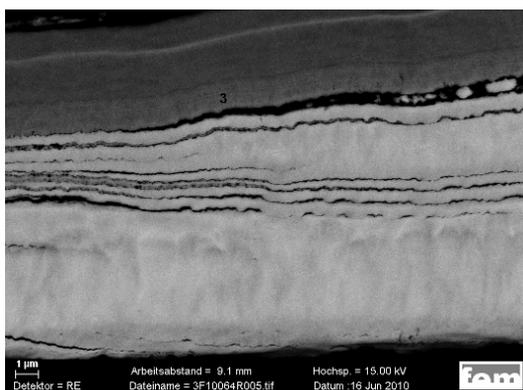


Fig.12. Cross-section of a Cu-Sb alloy coating;  $0.6 \text{ A dm}^{-2}$

Ordered structures are observed not only on the surface of the coatings. The cross-section of a Cu-Sb coating on a flat copper substrate shows a lamellar structure (Figure 12). The antimony content in the bright lamellas is about 60-70 wt. % and in dark ones – about 3 wt. %.

#### 4. CONCLUSION

Semi-bright compact copper-antimony alloys can be deposited from the investigated acid tartrate electrolyte with antimony content up to 52 wt. % depending on the applied current density. At certain experimental conditions heterogeneous coatings with a spatial distribution of phases with different antimony content are deposited. The different phases could spontaneously organize themselves in periodic ordered structures combining in this way their properties forming a new composite material.

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## IZVOD

### UTICAJ SASTAVA ELEKTROLITA NA TALOŽENJE Cu-Sb LEGURA IZ METANSULFONAT-TARTARAT ELEKTROLITA

*Elektrohemijski procesi taloženja i rastvaranja Cu i Sb odvojeno ili zajedno iz rastvora metansulfonat-tartarat elektrolita su predmet istraživanja pomoću ciklično-voltametrijske tehnike. Uticaj različitih parametara procesa taloženja, kao što su gustina struje, temperatura, sastav i kiselost elektrolita, na faze sastava i morfologiju depozita su prikazani. Povećanje gustine struje dovodi do povećanja sadržaja antimona u leguri, kao i do procenta depozicije legure. Sadržaj antimona opada sa povećanjem temperature. Povećanje procenta D(-)-vinske kiseline u elektrolitu dovodi do blagog povećanja sadržaja antimona u leguri.*

*Mogućnost taloženja kompaktnih, sjajnih Cu-Sb legura do 52% mas. Sb je prikazan.*

*Sa visokim sadržajem antimona u višefaznim heterogenim slojevima može se posmatrati prostorni raspored različitih faza legure na katodnim površinama. Pojave i posmatrane strukture su veoma slične onima koje su posmatrane tokom taloženja nekih legura srebra, kao što su Ag-Sn, Ag-Sb, Ag-Bi i Ag-In.*

**Ključne reci:** bakar-antimon legura, elektrodepozicija, uređene strukture