

INFLUENCE OF THE COMPOSITION AND STRUCTURE OF HYDROXYL-CONTAINING SURFACTANTS ON THE PROCESS OF ELECTROCHEMICAL TIN-BISMUTH ALLOY DEPOSITION

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Abstract: The possibility of electrochemical deposition of tin–bismuth alloy with an increased tin quota which is in demand for microassembly in electronics was revealed. Modification of the acid EDTA electrolyte with hydroxyl-containing surfactants differing in the length of hydrocarbon chain and the number of hydroxyl groups provided the deposition of Sn–Bi alloys with tin content 36.0–63.0 wt.% in the presence of 1,4-butyndiol (BD), and up to 80.0 wt.% using polyvinyl alcohol (PVA-10) or a product of processing a mixture of alkylphenols with ethylene oxide (OP-10). The reasons for different surfactants action were found. PVA-10 and OP-10, unlike BD, slow down the diffusion of Bi(III) ions by 3–4 times. All surfactants accelerate the diffusion of Sn(II) ions, which is especially noticeable in the case of BD. This effect of BD is due to its complexation with Sn(II) ions instead of EDTA, as a result of which the diffusion of positively charged particles to the cathode is accelerated.

Keywords: electrodeposition, tin–bismuth alloy, hydroxyl contacting surfactant, cyclic voltammetry.

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Introduction

Tin-bismuth alloys containing 54.0–61.0 wt.% bismuth have a melting point of 138–139 °C. They are obtained in the form of powders, blanks, coatings, and widely used for assembling electronic products due to their fusibility and a number of physical and chemical properties [1–3]. Sn–Bi alloys are used for step soldering, for the assembly of liquid crystal display panels, temperature-sensitive devices. However, due to their low ductility, they cannot be used in the assembly of devices operating under thermal cycling conditions [4, 5].

The method of Sn–Bi alloy electrochemical deposition from aqueous solutions makes it possible to control the thickness of coatings and provides their growth only on conductive elements. When tin is deposited together with bismuth or some other metals, the coatings are growing more fine-grained and less porous compared to pure tin

layers. Moreover, the alloying prevents tin whiskers formation and polymorphic transformation $\beta\text{-Sn} \rightarrow \alpha\text{-Sn}$ (tin plague) at temperatures below 13.2 °C [6].

It is difficult to control the ratio of tin and bismuth in the alloy during electrochemical deposition from aqueous solutions due to the significant difference in the values of electrode potentials of these metals, which are: $E^0(\text{Sn}^{2+}/\text{Sn}^0) = -0.136 \text{ V}$, $E^0(\text{Bi}^{3+}/\text{Bi}^0) = +1.21 \text{ V}$. Another problem is the tendency for Sn(II) and Bi(III) ions to hydrolyze in aqueous solutions at $\text{pH} > 1$. This causes the instability of electrolytes and the inclusion of hydrolysis products in the coatings. As a result, the functional properties of coatings and the quality of assembly deteriorate [7, 8].

Several methods are used to control alloy formation in the processes of electrochemical deposition. One of them is the introduction of ligands into the solution, ensuring the formation

of stable complex compounds with the ions of more noble metal and the shift of its electrode potential to the region of more negative values. In case of Sn–Bi deposition ethylenediamine tetraacetic acid (EDTA) can fulfill such function, due to the formation of more stable complex compounds with Bi(III) ions: $K_s(\text{BiEDTA}^-) = 1,15 \cdot 10^{28}$; $K_s(\text{SnEDTA}^{2-}) = 1,9 \cdot 10^{18}$ [9, 10].

One more method is based on the introduction of surfactants into electrolytes, which selectively influence the conditions for the reduction of metal ions and the growth of metal coating. Thus, surfactants usually promote the formation of fine-grained and close-packed coatings, owing to the diffusion control of metal ions reduction, and an increase in the overvoltage of hydrogen evolution. The action of surfactants mostly is due to their adsorption on the surface of the cathode, which, firstly, affects its charge and, secondly, limits the growth of metal particles. It is important to note that some surfactants can play a role of ligand for one of the metal ions [11].

For electrochemical deposition of Sn–Bi alloy coatings, both sulfate and methanesulfonate solutions with $\text{pH} < 2$ are used, including tin(II) sulfate or methane

sulphonate, $\text{Bi}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (or Bi_2O_3) and surfactants [12–15]. Gelatin, polyethylene glycol, polyoxyethylene lauryl ether (POELE), tetramethylbutylphenyl]- ω -hydroxydeca (oxyethylene) (Triton 100), benzylalcohol, OP-7, OP-10, OP-20 are used as surfactants [16–18]. A number of authors introduce hydroquinone and formalin into solutions to suppress Sn(II) oxidation [14, 17–19]. Only one work provides information on the introduction of citric acid and EDTA into the electrolyte as ligands for Sn(II) and Bi(III) ions to control the composition of the Sn–Bi alloy [20].

This manuscript focuses on the use of surfactants to control the composition and morphology of Sn–Bi alloy obtained by the electrochemical deposition. The purpose of the work is the analysis of the possibility to control the composition of this alloy by introducing into the electrolyte surfactants which contain hydroxyl groups and differ in the number of these groups and the length of the hydrocarbon chain. To deposit the Sn–Bi alloy 1,4-butyndiol (BD), polyvinyl alcohol (PVA-10), and a product of processing a mixture of mono- and dialkylphenols with ethylene oxide (OP-10) were chosen as surfactants. Their formulas are presented in Fig. 1.

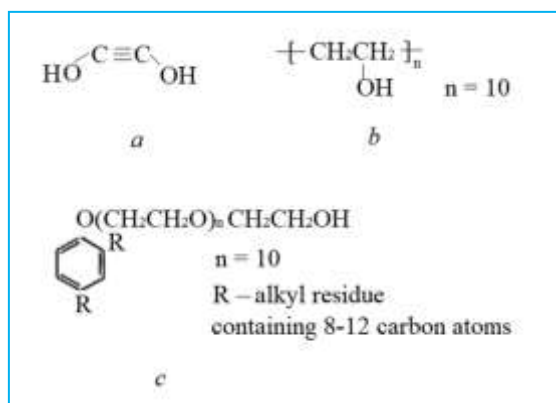


Fig. 1. Substances used as surfactants in the electrolyte for Sn–Bi alloy electrodeposition: *a* – BD, *b* – PVA-10, *c* – OP-10

The choice of these surfactants is determined by the presence of hydroxyl groups in their composition, which makes it possible

for them to act as a ligand for Sn(II) and Bi(III) ions and form corresponding complex compounds that differ in stability.

Experimental part

Tin–bismuth alloy was obtained by joint electrochemical reduction of Sn(II) and Bi(III)

from the electrolyte of the following composition (mol/dm^3): tin(II) sulphate – 0.02

and bismuth(III) nitrate – 0.005 as metal issues; sodium chloride – 0.014 to increase the solution electroconductivity; hydrochloride acid to pH 1.0 to prevent hydrolysis of tin and bismuth compounds; EDTA – 0.02 to bind Bi(III) into stronger bidentate complex compounds compared with similar Sn(II) complexes and thus bring the values of electrode potentials of these metals closer. BD, PVA-10 or OP-10 were added to the electrolyte in an amount of 0.01 mol/dm³ to study the effect of these surfactants. Note, that the introduction of EDTA suppresses Sn(II) hydrolysis up to pH 10, owing to the formation of bidentate complexes Sn(EDTA)²⁻, SnHEDTA⁻, SnH₂EDTA [10, 21].

Electrodeposition of Sn–Bi coatings was carried out in the galvanostatic mode at a current density (j) varying in the range of 1–6 mA/cm² and at a temperature of 20 °C. A further increase in the current density caused the growth of dendrites. A copper plate covered with chemically deposited Ni–P barrier layer 4 μm thick was used as a cathode. Platinum anodes were placed on both sides of the cathode at a distance of 5 cm. The ratio of the working areas of the cathode and anodes was 6:1.

Electrochemical study of the processes of Sn(II) or/and Bi(II) ions reduction in the presence of surfactants and in their absence was carried out by the method of cyclic voltammetry (CV) using PGstat Autolab (Russia) with software Nova 2.1 in a standard three-electrode cell for electrochemical investigation with a graphite rod as the working electrode, Ag/AgCl reference electrode and a platinum auxiliary electrode, at a potential scan rate of 20 mV/s, at 20 °C. The walls of the graphite rod were hermetically isolated with polymer stable in an acid media. Isolation was needed to keep the working square constant. The working surface of graphite rod was prepared by careful polishing, washing and drying. All solutions were deaerated with argon before and during the measurements.

Diffusion coefficients of Sn(II) ($D_{\text{Sn(II)}}$) and Bi(III) ($D_{\text{Bi(III)}}$) ions in the solutions containing Sn(II) and/or Bi(III) in the presence of the surfactants or in their absence, were calculated by the equation of Berzin–Dalahaya based on the diffusion current densities of Sn(II) and Bi(III) reduction (j_d) at different potential sweep rates ranging from 3 to 100 mV:

$$j_d = 3,423 \cdot 10^5 n^{3/2} C \sqrt{\nu} \sqrt{D},$$

where n is the number of electrons required to reduce metal ions, ν – is the rate of a potential sweep.

The coatings morphology was studied by scanning electron microscopy using LEO 1420. Metal content in the coatings was determined by the energy dispersive X-ray microanalysis (EDX) with the help of Rontec attachment to LEO-1420 microscope.

X-ray diffraction (XRD) analysis was fulfilled using X-ray diffractometer DRON-3 (Russia) at CoK_α radiation. JCPDS card files were used for phase identification.

The melting points of Sn–Bi alloys were determined by differential scanning calorimetry (DSC) in the inert atmosphere (nitrogen) using thermal analyzer Netzsch STA449 Jupiter, the heating rate was 10 K/min.

Results and discussion

Influence of surfactants in the electrolyte on the processes of Sn(II) and Bi(III) electrochemical reduction.

The processes of Sn(II) and Bi(III) ions electroreduction from the electrolyte containing one of the surfactants or without it were studied using the CV method. The cathode branch of CV curve corresponding to Sn(II) reduction from the electrolyte in the absence of surfactants, demonstrates the beginning of the

process at –0.320 V (Fig. 2).

The curve has a plateau of the maximum diffusion current density (j_d) of –57 mA/cm² starting at the potential $E_d = -0.410$ V (Fig. 2, Table 1). Hydrogen begins to release at –0.450 V. Sn(II) reduction from the solution containing the BD occurs at less negative potential equal to –0.160 V; diffusion current density (j_d) equal to –66 mA/cm² is achieved at $E_d = -0.240$ mV; the process of H(I)

reduction begins at the potential of -0.300 V (Fig. 2, Table 1). The depolarization effect of Sn(II) reduction in the presence of BD can be explained as follows. In the basic solution containing EDTA at pH 1 a number of complex ions can be formed such as SnEDTA^{2-} , SnHEDTA^- , SnH_2EDTA [10]. The stability of ions in this row decreases by several orders of

magnitude. Apparently, in the presence of BD, partial destruction of complex Sn(II) ions with EDTA occurs as a result of competitive complexation. The formation of bidentate complex Sn(II) ions with di- or triatomic alcohols is a known fact described in the works [22–24].

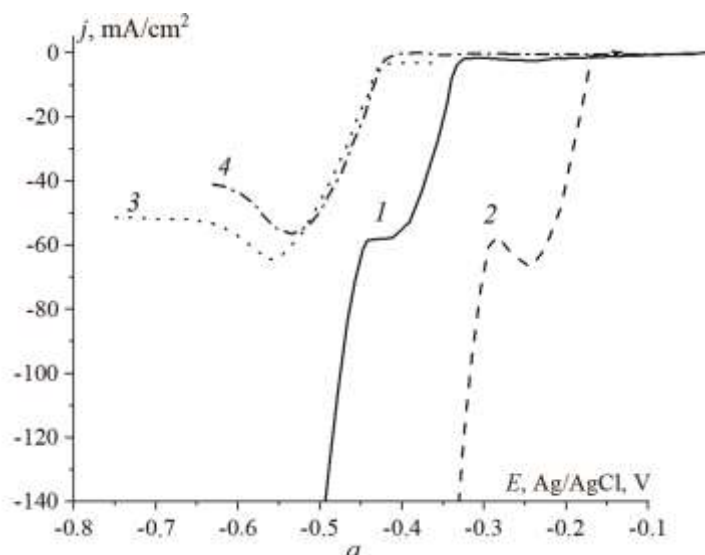


Fig. 2. CV curves for graphite electrode in the electrolyte containing Sn(II) ions in the absence of Bi(III), recorded at the potential scan rate 20 mV/s and at a temperature of 20 °C: composition of solutions (mol/dm³): 1 – tin(II) sulphate – 0.02; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; 2, 3, 4 – the same solutions additionally containing 0.01 mol/dm³ of a surfactant such as BD, PVA-10, OP-10 respectively

Table 1. Some characteristics of cathodic scans of CV curves for electrolytes containing Sn(II) and/or Bi(III) ions in the presence of surfactants and in their absence

Surfactant	Reduction start potential (E_0), V	E_d , V	j_d , mA/cm ²
Reduction of Sn(II) from the solution containing (mol/dm ³): tin(II) sulphate – 0.02; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; a surfactant – 0.01			
–	–0,320	–0,410	–57,0
BD	–0,160	–0,240	– 66,0
PVA-10	–0,410	–0,570	–64,0
OP-10	–0,430	–0,540	–55,0
Reduction of Bi(III) from the solution containing (mol/dm ³): bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; a surfactant – 0.01			
–	–0,144	–0,200	–0,7
BD	–0,144	–0,288	–0,4
PVA-10	–0,188	–0,245	–2,4
OP-10	–0,200	–0,244	–2,2
Join reduction of Sn(II) и Bi(III) from the solution containing (mol/dm ³): tin(II) sulphate – 0.02; bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; a surfactant – 0.01			

–	–0,515	–0,554	–69
BD	–0,493	–0,545	–60
PVA-10	–0,527	–0,571	–64
OP-10	–0,527	–0,574	–65

The reduction of Sn(II) in the presence of PVA-10 or OP-10 begins at more negative potentials equal to –0.410 and –0.430 V, than in the solution in the absence of a surfactant. The plateaus of the limiting diffusion current are also shifted to the region of lower potentials. Thus, in the case of solutions with PVA-10 and OP-10 j_d equals to –64 and –55 mA/cm², and it is achieved at –0.570 V and –0.540 V, respectively. The potentials of hydrogen evolution in solutions with PVA-10 and OP-10 are shifted to the negative region, compared to a solution without a surfactant.

The different effect of BD, PVA-10, and OP-10 on the reduction of Sn(II) indicates a dissimilarity in mechanisms of their action. As follows from the data systematized in the review on acidic tin plating solutions [25] PVA-10, and OP-10 impede the delivery of Sn(II) ions through the Helmholtz layer owing to their adsorption on the cathode surface, that increases

the overvoltage of Sn(II), as well as H(I) reduction. The BD operates differently. Its molecules can be involved in the formation of positively charged complex ions with Sn(II) such as SnBD(H₂O)₂²⁺ or Sn(BD)₂²⁺, which are smaller compared to complexes with EDTA. The smaller size and positive charge favor the delivery of these ions to the cathode thus facilitating the reduction of Sn(II).

This assumption is confirmed not only by a shift in the potentials for the onset of Sn(II) reduction and the start of the limiting diffusion current to higher values (see Table 1, Fig. 2) but also by the experimental data for determining the diffusion coefficients (Table 2). These data indicate an increase in the rate of Sn(II) ions diffusion by 1.4 times at the addition of BD into the initial electrolyte containing EDTA. When PVA-10 and OP-10 are introduced into the electrolyte, the diffusion coefficient of Sn(II) ions also increases, but to a much lesser extent.

Table 2. Diffusion coefficients of Sn(II) and Bi(III) ions in solutions in the presence and absence of surfactants

Surfactant	$D, \text{cm}^2 \cdot \text{s}^{-1} \cdot 10^6$	
	Sn(II)	Bi(III)
	Solution contains (mol/dm ³): tin(II) sulphate – 0.02; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; a surfactant – 0.01	Solution contains (mol/dm ³): bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; a surfactant – 0.01
–	1,660	4,947
BD	2,341	2,658
PVA-10	2,143	1,791
OP-10	2,035	1,284

In the case of a solution containing Bi(III) ions in the absence of Sn(II) and regardless of the presence or absence of BD, the reduction of Bi(III) begins at the potential of –0.144 V which is greater than for the reduction of Sn(II). Two “shoulders” are observed on the cathode scans starting at $E_d = -(0,200-0,288)$ V and $E_{d2} = -(0,303-0,362)$ V (Fig. 3). It is known that usually the reduction of Bi(III) is a one-step process [20, 26–29]. The reason for the “two-stage” process of Bi(III) reduction is a high

strength and high size of BiEDTA[–] complex ions [26, 30], as a result of which their delivery to the cathode and destruction occur gradually. It is also known that during long-term operation of bismuth plating electrolytes in the EDTA absence, polynuclear aqua hydroxo complexes of Bi(III) are formed as a result of Bi(III) ions hydrolysis [31]. This is a reason for the appearance of a shoulder on the cathode scan of CV curves, similar to that observed in the case of solutions containing EDTA.

When adding BD to the bismuth plating solution together with EDTA, the value j_d of diffusion current density in both shoulders becomes about 1.8 times smaller, and it is reached at more negative potential.

In the case of solutions containing PVA-10 or OP-10 the start of Bi(III) reduction is

shifted to more negative potentials of -0.188 and -0.200 V, accordingly. One broadened peak is observed on the cathode scans at $E_d -0.245$ V and -0.244 V with the diffusion current density equal to 2.2 and 2.4 mA/cm² respectively, that exceeds currents observed in the surfactant absence (see Table 1).

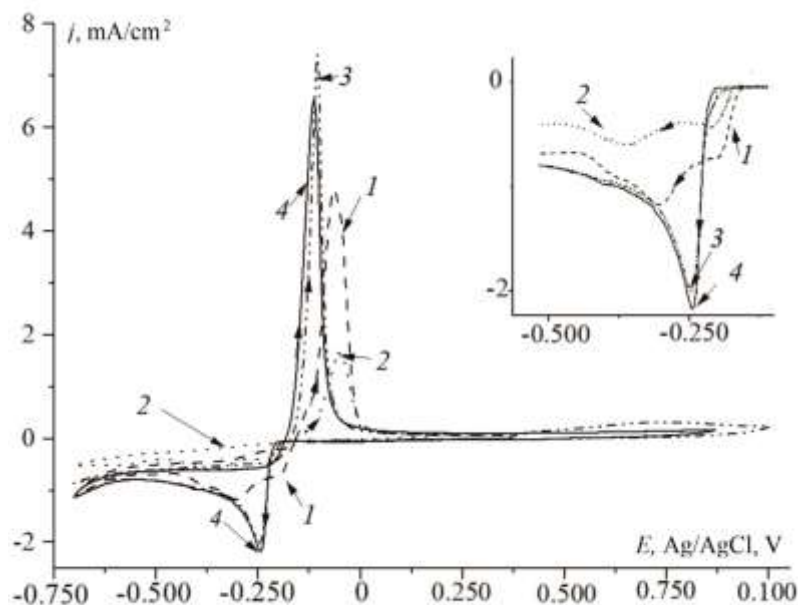


Fig. 3. CV curves for graphite electrode in the electrolyte containing Bi(III) ions in the absence of Sn(II), recorded at the potential scan rate 20 mV/s and at a temperature of 20 °C:

composition of solutions (mol/dm³): 1 – bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloric acid to pH 1.0; 2, 3, 4 – the same solutions additionally containing 0.01 mol/dm³ of a surfactant such as BD, PVA-10, OP-10 respectively

Nevertheless, diffusion coefficients of Bi(III) ions are almost 3–4 times less than in the solution in the absence of surfactants. The revealed fact can be explained by the complexity of the structure and stability of the BiEDTA[−] complex ion surrounded by oligomers PVA-10 or OP-10. Their molecules have a fairly long hydrocarbon chain, several functional groups, and are effectively adsorbed on the surface of cathode affecting its charge. Bi(III) has eight coordinate bonds: two Bi–N bonds, four Bi–O bonds with one of the EDTA molecules; two Bi–O bonds with a second EDTA molecule. The assumption about the delayed destruction of BiEDTA[−] complex ions is based on data from the works [26, 31].

Note that the reduction of Sn(II) ions is accompanied by the release of hydrogen which, in the absence of a surfactant, becomes clearly

visible at potentials lower than -0.45 V. In contrast to this, the reduction of H(I) in solutions containing only bismuth ions does not occur up to -0.700 V. Therefore, the overvoltage of hydrogen evolution on the surface of bismuth films is greater than on the surface of freshly deposited tin.

The fact of two-stage complex Bi(III) ions reduction from solutions in the absence of a surfactant or in the presence of BD and at the same time, large values of $D_{\text{Bi(III)}}$ give reason to assume that the destruction of BiEDTA[−] ions and electron transfer are the slowest stages. The single-stage reduction of Bi(III), low values of $D_{\text{Bi(III)}}$, and increased values of the current density j_d in the case of solutions containing PVA-10 and OP-10 additives, indicate that these surfactants, unlike BD, promote a decrease in the electron transfer overvoltage.

On the cathode scans of CV curves, characterizing the simultaneous Sn(II) and Bi(III) reduction from the solutions, regardless of the presence of surfactants in them, one maximum is observed (Fig. 4).

The process of simultaneous reduction

begins at more negative potentials compared to E_0 of Sn(III) reduction. The potentials of the diffusion currents are also smaller varying in the range of $-(0.545-0.574)$ V. Their shift is maximum in the presence of BD and minimum in the case of PVA-10 and OP-10.

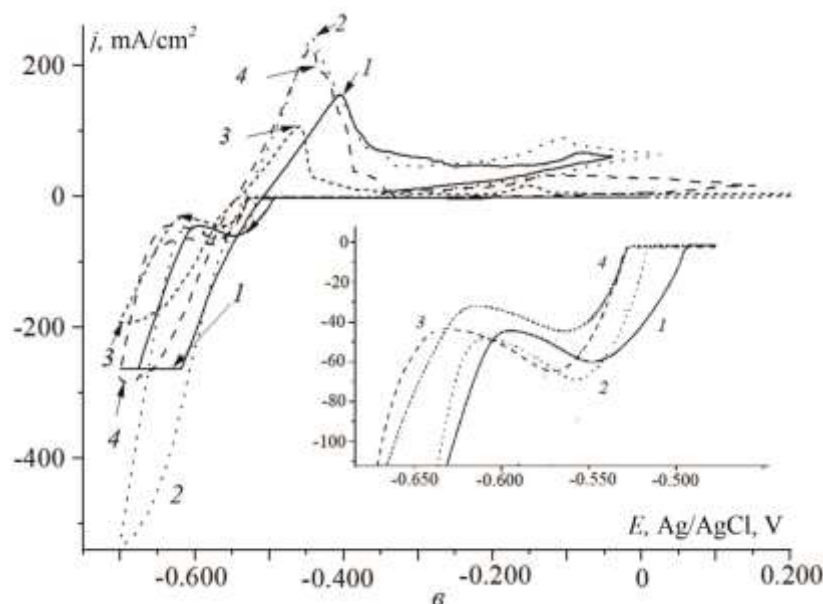


Fig. 4. CV curves for graphite electrode in the electrolyte containing Bi(III) and Sn(II) ions, recorded at the potential scan rate 20 mV/s and at a temperature of 20 °C: composition of solutions (mol/dm³): 1 – tin(II) sulphate – 0.02; bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0; 2, 3, 4 – the same solutions additionally containing 0.01 mol/dm³ of a surfactant such as BD, PVA-10, OP-10 respectively

Diffusion current densities of the simultaneous Sn(II) and Bi(III) reduction are of the same order as in the case of tin(II) electrochemical reduction in the presence of surfactants. However, in their absence, the current of joint Sn(II) and Bi(III) reduction is approximately 20% greater than j_d Sn(II). The shift in polarization curves to the region of more negative potentials indicates the effect of overpolarization inherent to simultaneous reduction of both metals regardless of the presence of surfactants in the solution.

The revealed effect of overpolarization is probably due to the adsorption of complex bismuth(III) ions on the cathode, which affects the charge of its surface [11, 31].

Anodic scans of CV curves, regardless of the presence of surfactants in the Sn–Bi alloy plating solution, are characterized by the presence of two maxima. The first broadened maximum (see Fig. 4) is in the potential range from -0.520 to -0.350 V. It is caused by the

two-stage oxidation of the reduced tin and/or solid solutions of bismuth in tin [32, 33]. The second maximum is associated with the oxidation of bismuth. Some differences in the positions of the anodic peaks, their width and the density of anodic current are determined by a diversity in metal ratios in the alloy, tin concentration in its solid solution in bismuth.

Composition, morphology and thermal behavior of Sn–Bi alloys.

EDX analysis data indicate that Sn–Bi alloy obtained in the absence of a surfactant in the electrolyte contains 10.0–23.0 wt.% of tin. The introduction of BD into the electrolyte ensures a gain of tin content in Sn–Bi alloy to 36.0–63.0 wt.%. In the presence of PVA-10 or OP-10 in the electrolyte, tin quota in the alloy reaches 24.0–80.0 wt.%. In the case of all electrolytes studied, the content of tin in coatings rises within the specified limits with increasing current density. The current efficiency of both metals reduction is in the

range of 10–68%. It decreases with rising current density due to the intensified hydrogen ions reduction.

The results of XRD analysis of the alloy coatings containing 55–80 wt.% of tin indicate the presence of crystalline β -Sn, Bi and solid solution of tin in bismuth (Fig. 5, *a*) [34].

The intensity of peaks belonging to the solid solution of tin in bismuth noticeably diminishes with a rise of tin quota in the coatings. Thus, the intensity of these peaks is five times lower in the case of $\text{Sn}_{77}\text{Bi}_{23}$ coatings in comparison with $\text{Sn}_{55}\text{Bi}_{45}$ coatings of the same thickness (see Fig. 5, *a*, curve 2).

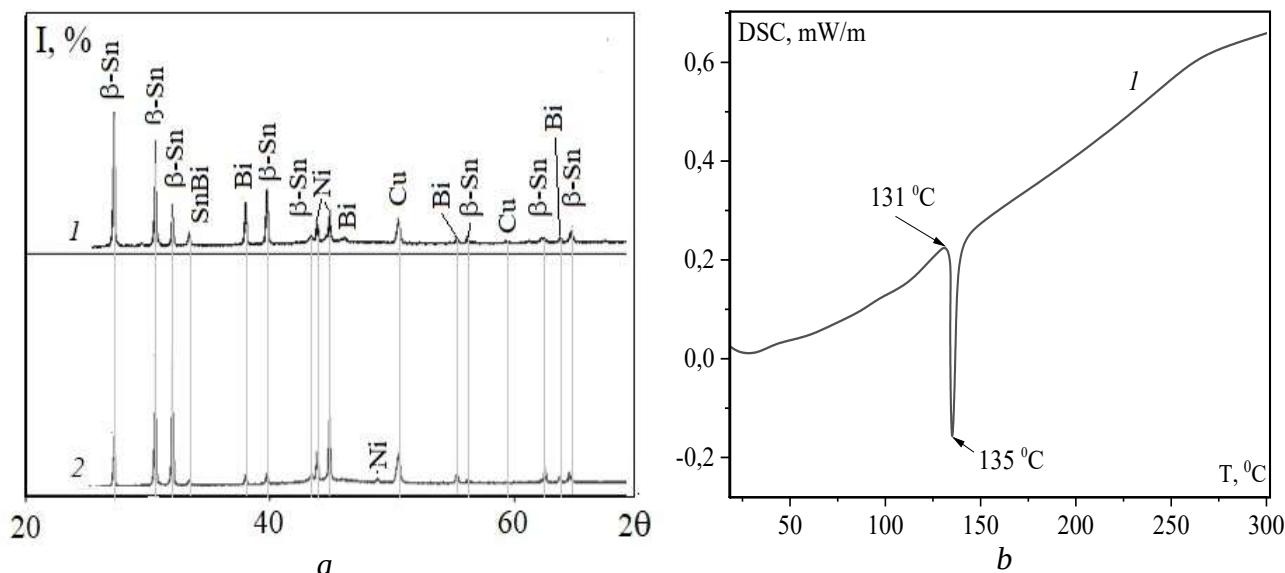


Fig. 5. Data on XRD (*a*) and DSC analyses (*b*) of Sn–Bi coatings $1.5 \pm 0.1 \mu\text{m}$ thick deposited at $j = 5 \text{ mA/cm}^2$ from the solutions containing (mol/dm³): tin(II) sulphate – 0.02; bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0, and 0.01 mol/dm³ of BD (1, $\text{Sn}_{55}\text{Bi}_{45}$ alloy) or PVA-10 (2, $\text{Sn}_{77}\text{Bi}_{23}$ alloy)

Thermal analysis of the $\text{Sn}_{55}\text{Bi}_{45}$ alloy demonstrates that its melting begins at 131 °C and occurs most intensely at 135 °C (Fig. 5, *b*).

The introduction of BD, PVA-10 and OP-10 into solutions for Sn–Bi alloy electrodeposition causes a change in the coatings morphology (Fig. 6). The most fine-grained coatings are deposited in a solution without a surfactant (see Fig. 6, *a*). They consist of spherical, loosely packed particles 0.6–0.8 μm in size, partially assembled into aggregates up to 3.0 μm in length. There are many pores of different shape and size within 0.2–1.0 μm .

Sn–Bi coatings obtained in a solution with BD consist of tightly fused grains of irregular shape and sizes ranging from 1 μm to 5 μm . The grain boundaries are difficultly distinguished. The quantity of pores is significantly less than

in coatings deposited in the absence of a surfactant, but their size equals to 0.2–1.0 μm as in the case of coatings obtained from the solution in the absence of surfactants (see Fig. 6, *b*).

Sn–Bi coatings deposited from the solution containing PVA-10 consist of dendrites and needles mainly not exceeding 3 μm in size. Coatings formed in the presence of OP-10 include plate-like polygonal crystals 6.0–8.0 μm in length, which are tightly fused together. The pores between them are 1–3 μm in size. Some needle-like particles are also observed on the surface (see Fig. 6, *c*). The formation of dendrites, large lamellar crystallites, and needles in the solutions with PVA-10 and OP-10 confirms the fact of diffusion difficulties during the joint reduction of Sn (II) and Bi (III).

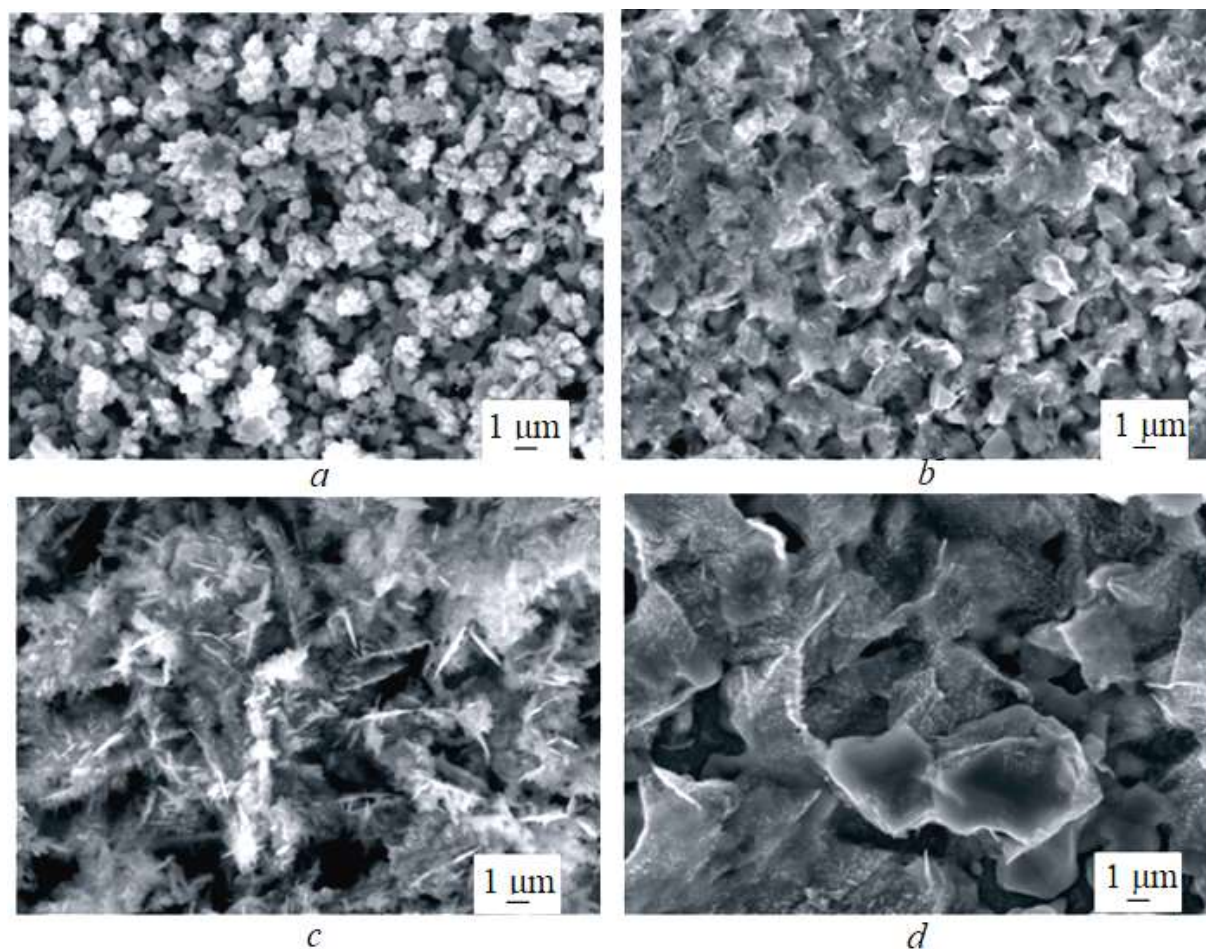


Fig. 6. SEM photographs of Sn–Bi coatings $1.5 \pm 0.1 \mu\text{m}$ thick deposited at a current density 6 mA/cm^2 from the solutions containing (mol/dm^3): tin(II) sulphate – 0.02; bismuth(III) nitrate – 0.005; sodium chloride – 0.014; EDTA – 0.02; hydrochloride acid to pH 1.0, and 0.01 mol/dm^3 of a surfactant: *a* – surfactant is absent; *b*, *c*, *d* – with the additives of BD, PVA-10, and OP-10 respectively

Conclusions

The process of electrochemical deposition of a tin–bismuth alloy from the acidic electrolyte with the addition of EDTA as a ligand in the presence of surfactants containing hydroxyl groups and differing in the number of these groups and the length of the hydrocarbon chain, that are BD, PVA-10 or OP-10 was investigated. It has been shown that, regardless of the presence of a surfactant in the electrolyte, the simultaneous reduction of SnEDTA^{2-} and BiEDTA^- ions occurs with an effect of overpolarization, which may be due to the adsorption of negatively charged ions of the second metal on the cathode.

It is determined that the introduction of all the studied surfactants into the electrolyte causes an increase in the quota of tin in the tin–

bismuth alloy from 10.0–23.0 wt.% in the absence of an additive to 36 wt.% with the introduction of BD and up to 80 wt.% in the presence of PVA-10 and OP-10. All three surfactants accelerate the diffusion of tin ions, which is most noticeable in the case of the BD additive, but they strongly slow down the diffusion of bismuth ions. The surfactants with the extended hydrocarbon chain, such as PVA-10 and OP-10 have a particularly strong retarding effect.

In the presence of BD in the electrolyte the potential of the beginning Sn(II) reduction and the plateau of the limiting diffusion current are shifted to the region of higher values, while oligomer surfactants, on the contrary, shift these potentials to the region of more negative values.

This fact indicates that BD, unlike PVA-10 and OP-10, affects the thermodynamic characteristics of the reducing Sn(II) ions. Apparently, in the presence of BD, partial destruction of complex tin(II) ions with EDTA occurs as a result of competitive complexation, the stability of complex ions decreases, and

such complexes as $\text{SnBD}(\text{H}_2\text{O})_2^{2+}$ or $\text{Sn}(\text{BD})_2^{2+}$ appear. Their charge changes from negative to positive and thus, their delivery to the cathode is accelerated that is confirmed by the experimentally discovered increase in the diffusion coefficient of tin ions.

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