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СИНТЕЗ ЭВТЕКТИЧЕСКИХ СПЛАВОВ Sn – Ag И Sn – Ag – Cu БЕЗЭЛЕКТРОЛИЗНЫМ ОСАЖДЕНИЕМ ИЗ ПИРОФОСФАТНЫХ РАСТВОРОВ

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Легкоплавкие сплавы $Sn_{94,7}Ag_{5,3}$ и $Sn_{94,0}Ag_{4,8}Cu_{1,2}$ востребованы в качестве припоев в сборке изделий электронной техники. Разработан простой метод безэлектролизного осаждения таких сплавов (в мас. %) из водных пирофосфатных растворов. Метод основан на восстановлении ионов Ag(I) и Cu(II) порошком олова. Фазовый состав сплава $Sn_{94,7}Ag_{5,3}$ включает кристаллические фазы β-Sn, Ag_3Sn, а фазовый состав сплава $Sn_{94,0}Ag_{4,8}Cu_{1,2}$ – β-Sn, Ag_3Sn, Cu_6Sn_5, что соответствует составу эвтектик. Определено, что плавление бинарного и тройного сплавов начинается при температуре 200 °С и происходит в две стадии. Это обусловлено структурой частиц, ядро которых состоит из олова, а оболочкой которых является сплав Sn – Ag или Sn – Ag – Cu. Установлено, что медь, соосаждаемая в сплав, участвует в контактном вытеснении ионов Ag(I).

Ключевые слова: контактное вытеснение; сплав; олово; серебро; медь; эвтектика; пирофосфатный электролит; фазовый состав; побочные процессы.

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SYNTHESIS OF Sn – Ag AND Sn – Ag – Cu EUTECTIC ALLOYS BY ELECTROLESS DEPOSITION FROM PYROPHOSPHATE SOLUTIONS

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To obtain low-melting alloys (in wt. %) $Sn_{94.7}Ag_{5.3}$ and $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ used as solders for microassembly of electronic devices, simple method of electroless deposition from pyrophosphate solutions has been developed. The method is based on the reduction of Ag(I) and Cu(II) ions with tin powder as a reducing agent. $Sn_{94.7}Ag_{5.3}$ and $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ alloys include crystalline phases of β-Sn, Ag_3Sn and β-Sn, Ag_3Sn, Cu_6Sn_5 respectively, which corresponds to the phase composition of the eutectics. It has been revealed that binary and ternary alloys begin to melt at a temperature of 200 °C, but the melting occurs in two stages. This is due to the structure of particles with tin core and Sn – Ag or Sn – Ag – Cu alloy shell. It has been found that copper co-deposited into the alloy participates in the contact displacement of Ag(I) ions.

Keywords: contact displacement; alloy; tin; silver; copper; eutectic; pyrophosphate electrolyte; phase composition; side processes.

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Introduction

Eutectic alloys containing tin, silver and copper (SAC) are widely used in microassembly of electronic devices due to the low melting temperature (217–221 °C), resistance to thermal cycling in a wide temperature range (from −75 to +160 °C), good compatibility with a number of metal coatings [1]. For example, SAC of different compositions are used for mounting power transistor crystals and for the replacement of FTO/ITO in solar cell assembly [2; 3]. The compositions of SAC alloys in demand in electronics are the following (in at. %): SAC-305 ($Sn_{95.7}Ag_{3.3}Cu_{0.1}$), SAC-405 ($Sn_{94.7}Ag_{4.4}Cu_{0.9}$) and SAC-396 ($Sn_{94.9}Ag_{3.3}Cu_{1.8}$). The alloys include crystalline phases of β-tin, Ag_3Sn, Cu_6Sn_5 [1; 2; 4; 5]. Depending on the assembly technology alloys are used in the form of blanks (foil, wire), coatings, powders [1; 4; 5].

Alloy blanks are obtained by melting of high-purity metals in the required quantities [6]. SAC alloys coatings can be electrochemically formed in aqueous solutions as the result of layer-by-layer metal plating or co-reduction of Ag(I), Cu(II), Sn(II) [7]. However, the layer-by-layer metal deposition requires subsequent heat treatment to homogenise the composition of the alloy. The simultaneous electrochemical reduction of Ag(I), Cu(II), Sn(II) is characterised by a low reproducibility of the alloy composition as the result of a number of side processes. They involve the reduction of Cu(II) and Ag(I) with Sn(II) in the bulk of solution due to a large difference in electrode potentials of the metals and Sn(II, IV) hydrolysis followed by the inclusion of resulting oxo- and hydroxocompounds of tin into the growing coating.

Ultra- and nanostructured powder alloys commonly used as catalysts can be obtained by co-reduction of Ag(I), Cu(II), Sn(II) in aqueous and non-aqueous solutions using ethanol or ethylene glycol as the solvents containing sodium borohydride as the reducing agent in the presence of stabilisers (for example, polyvinylpyrrolidone) [8–11]. As it is shown in the work [12] the synthesis of SAC using microemulsion allows one to obtain powders consisting of 10 nm particles. Resultant alloys are characterised by the melting temperature equal to 183.6 °C that is lower as compared to the eutectic alloy.

To obtain binary powder alloys such as Sn − Cu or Sn − Ag with a required composition and properties close to the eutectic, the method of contact displacement (CD) has been developed [12; 13]. This method is based on the reduction of more noble metal ions such as Cu(II) or Ag(I) with an active metal powder, which is tin:

$$2Ag^{+} + Sn^{0} \rightarrow Sn^{2+} + 2Ag^{0},$$
$$Cu^{2+} + Sn^{0} \rightarrow Sn^{2+} + Cu^{0}.$$

The aim of this work was to synthesise Sn − Ag and Sn − Ag − Cu powder alloy, similar in composition to SAC, using the reaction of Ag(I) and Cu(II) ions reduction with tin in pyrophosphate solutions, and to identify side processes that can affect the composition of the alloys.

The choice of the CD solution was based on the known recommendations on the composition of electrolytes for electrodeposition of Ag, Cu and Cu – Ag alloy coatings [14–17]. Thus, for the synthesis of powdery binary and ternary alloys with low melting temperatures, the authors of this manuscript used a pyrophosphate solution in which Cu(II) and Ag(I) ions are bound into $CuP_2O_7^{2-}$ ($K_{stab} = 10^{8.80}$), $Cu(P_2O_7)_2^{6-}$ ($K_{stab} = 10^{12.57}$), $Ag(P_2O_7)_2^{7-}$ ($K_{stab} = 10^{3.74}$) complex ions [18]. The possibility of Cu(II) and Ag(I) reduction in pyrophosphate solutions with tin and its oxidation with the formation of $[Sn(P_2O_7)]^{2+}$ ($K_{stab} = 10^{14}$) complex ions has been shown previously in the work [19]:

$$2Ag(P_2O_7)_2^{7-} + Sn^0 \rightarrow 2Ag^0 + Sn(P_2O_7)^{2-} + 3P_2O_7^{4-}, \tag{1}$$

$$Cu(P_2O_7)_2^{6-} + Sn^0 \rightarrow Cu^0 + Sn(P_2O_7)^{2-} + P_2O_7^{4-}. \tag{2}$$

Materials and methods

The pyrophosphate aqueous solution used for CD includes 0.005 5 mol · dm^{-3} $AgNO_3$, 0.001 6 mol · dm^{-3} $CuSO_4$, 0.125 mol · dm^{-3} $K_4P_2O_7$, 0.003 mol · dm^{-3} NH_3 (pH 10.0). In order to provide the content of silver in the alloy to be 6–8 times higher than copper quota, the concentration of Ag(I) in the solution was 3.4 times greater than that of Cu(II). To study the CD in the Ag^+/Sn and Cu^{2+}/Sn binary systems, solutions with only Ag(I) or only Cu(II) were used.

Ag(I) and Cu(II) ions were reduced with tin powder (99.9 wt. % Sn, particle size 10–20 μm) in the described above solutions for 2–20 min, after which the resulting powder was separated from the solution by decantation, washed with distilled water in argon current and dried at 20 °C in argon atmosphere.

The morphology of the surface of powder particles, the shape of the particles, and their sizes were studied using scanning electron microscopes (SEM) LEO-1420 and LEO-1455VP (*Carl Zeiss*, Germany). The elemental composition of the alloys was determined by X-ray microanalysis using scanning electron microscope LEO-1420 with energy dispersive X-ray (EDX) analyser Rontec (*Carl Zeiss*) and spectrometer Elvax Light SDD (*Elvatech*, Ukraine). Synthesis of the alloy powders and the analysis of their compositions were carried out at least 5 times, the mean square error of determination was 3 %. X-ray diffraction (XRD) analysis was performed with X-ray diffractometer DRON-3 (*Innovation center «Bourevestnik»*, Russia) using CuK_α radiation. Joint Committee on Powder Diffraction Standards card files were used for phase identification.

The melting points of alloy powders were determined by differential scanning calorimetry in the inert atmosphere (nitrogen) using thermal analyser Netzsch STA 449C (Germany), the heating rate was 10 K/min, weight of powders 0.03 g.

In order to reveal processes accompanying the CD reaction used for the alloy synthesis a change in the values of open circuit potentials (OCP) during the treatment of copper, silver or tin foil (99.9 wt. %, area 0.25 cm^2) working electrodes in the solutions with different composition were analysed. Measurements were carried out in three-electrode cell using Autolab PGSTAT204 (*Metrohm*, Netherlands) potentiostat with saturated Ag/AgCl reference electrode and platinum auxiliary (counter) electrode. Before the analysis, copper or tin working electrodes were treated in 5 % hydrochloric acid solution, while silver electrode was treated in 5 % ammonia solution to remove oxides from their surface, followed by washing with distilled water. OCP measurements were carried out in the solutions of the full composition, as well as in the solutions free of one or both of the metal ions to be reduced.

Results and discussion

The elemental analysis has evidenced that the content of metals in the synthesised binary and ternary alloys exhibits only a little change with an increase in the CD duration from 2 to 20 min (see table). After 2 min of the CD process Sn − Ag − Cu ternary alloy contains 5.5 wt. % Ag and 0.3 wt. % Cu. As the CD duration increases up to 15 min the quota of copper in the alloy reaches 1.2 wt. %. Silver content in the binary Sn – Ag alloy is 4.0–6.6 wt. %, while the copper quota in the binary Sn – Cu alloy is 0.3–0.5 wt. %, which is 13.3 times less than the silver content in Sn – Ag alloy. The latter fact can be explained by a significant difference in the values of K_{stab} of $Ag(P_2O_7)_2^{7-}$ and $Cu(P_2O_7)_2^{6-}$ complex ions [18].

The data provide an evidence that in the absence of Cu(II) or Ag(I) in the solution, the rate of Ag(I) and Cu(II) reduction is close to the simultaneous Ag(I) and Cu(II) reduction.

According to the results of X-ray diffraction analysis Sn – Ag alloy includes crystalline phases of β-Sn and Ag_3Sn (fig. 1, *c*). Two crystalline phases of β-Sn and Cu_6Sn_5 have been identified in the Sn – Cu alloy (fig. 1, *b*). The ternary alloy includes crystalline phases of Ag_3Sn and Cu_6Sn_5 intermetallics and β-Sn (fig. 1, *a*). It should be noted that oxides were not detected by X-ray phase analysis. In the case of initial tin powder an oxide layer thickness does not exceed 2 nm and cannot be detected by XRD analysis.

**Elemental composition of Sn – Ag – Cu, Sn – Ag,
Sn – Cu alloys, wt. %**

CD duration, min	Sn	Ag	Cu
Sn – Ag – Cu			
2	94.2 ± 0.9	5.5 ± 0.1	0.3 ± 0.1
5	94.2 ± 0.9	5.1 ± 0.1	0.7 ± 0.1
7	94.1 ± 0.9	5.1 ± 0.1	0.8 ± 0.1
10	94.2 ± 0.8	5.0 ± 0.1	0.8 ± 0.1
15	94.0 ± 0.9	4.8 ± 0.1	1.2 ± 0.1
Sn – Ag			
2	96.0 ± 0.8	4.0 ± 0.1	–
7	93.4 ± 0.9	6.6 ± 0.1	–
10	94.7 ± 0.9	5.3 ± 0.1	–
20	95.3 ± 0.9	4.7 ± 0.1	–
Sn – Cu			
2	99.5 ± 0.9	–	0.5 ± 0.1
7	99.6 ± 0.9	–	0.4 ± 0.1
10	99.7 ± 0.9	–	0.3 ± 0.1
20	99.6 ± 0.8	–	0.4 ± 0.1

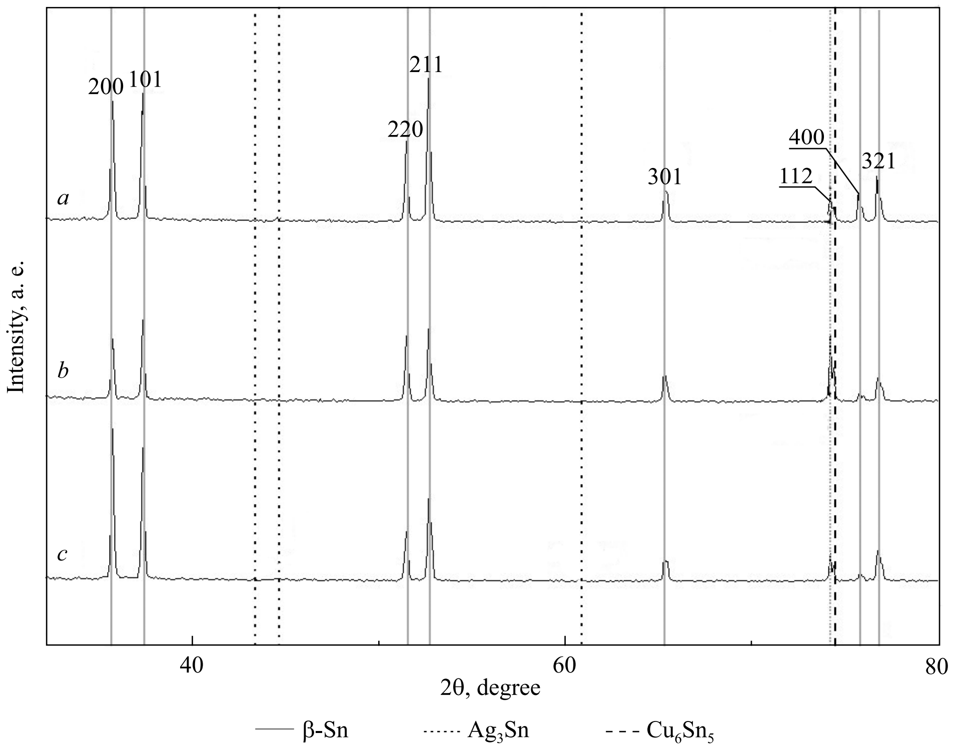

Fig. 1. XRD-pattern of the powders:
a – $Sn_{94.0}Ag_{4.8}Cu_{1.2}$; *b* – $Sn_{99.5}Cu_{0.5}$; *c* – $Sn_{94.7}Ag_{5.3}$

It has been revealed that the melting of binary and ternary alloys occurs in two stages. The first stage starts at 200 °C, that is consistent with the data given in literature [1], the second stage begins at 226 °C (fig. 2). The latter fact can be explained by the peculiarities of the structure of particles, the thin core of which consists of tin, while their shell consists of an alloy of tin with silver or tin with silver and copper.

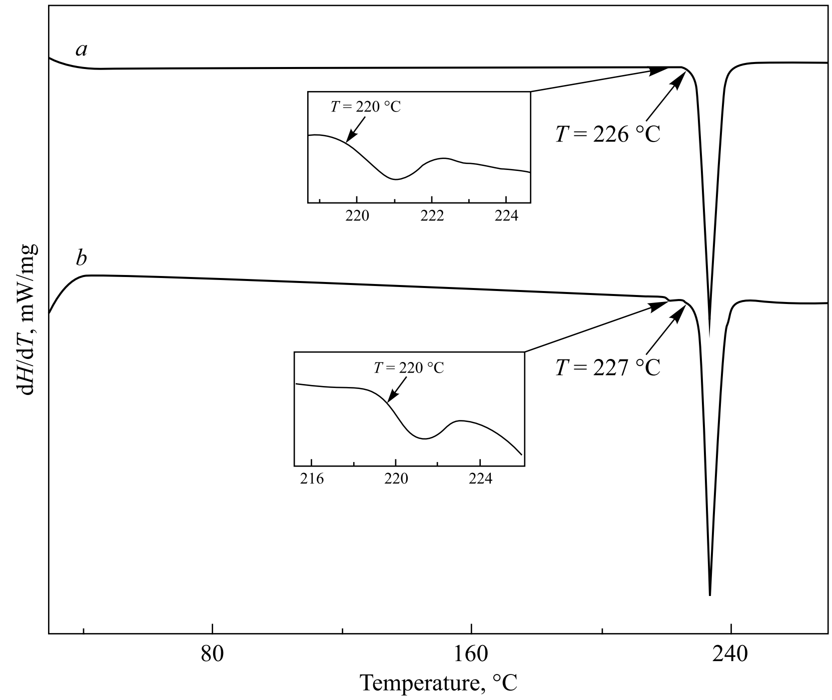

Fig. 2. Differential scanning calorimetry curve for $Sn_{94.7}Ag_{5.3}$ (*a*) and $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ (*b*) alloys

SEM study showed that tin powder consists of spherical or oval particles ranging in size from 0.4 up to 25 µm with rather smooth surface, on which there are the single, sparsely located tubercles having 0.3–0.5 µm in diameter (fig. 3, *a*). Tin particles do not change their shape and size during the treatment in pyrophosphate solution containing Ag(I) ions, but the surface of particles becomes more rough within the nano-scale (fig. 3, *b*, *e*). The microprobe analysis (fig. 4), as well as SEM images obtained in the compositional mode (fig. 5), indicate that during the CD a thin discontinuous silver-containing film is formed on the surface of tin particles, with the uneven distribution of silver over the surface. According to the results of elemental analysis, the concentration of silver on the surface of tin particles ranges from 2 to 30 wt. % (see fig. 4, *a*). This is consistent with the XRD data, evidencing that the reduced silver incorporates into the Ag_3Sn crystalline phase.

The treatment of tin powder in pyrophosphate solution containing Cu(II) ions does not affect the shape and size of the initial particles, but their surface becomes covered with uniformly distributed low-contrast nuclei having 70–100 nm in size (fig. 3, *d*), which consist of Cu_6Sn_5 intermetallic compound according to XRD analysis.

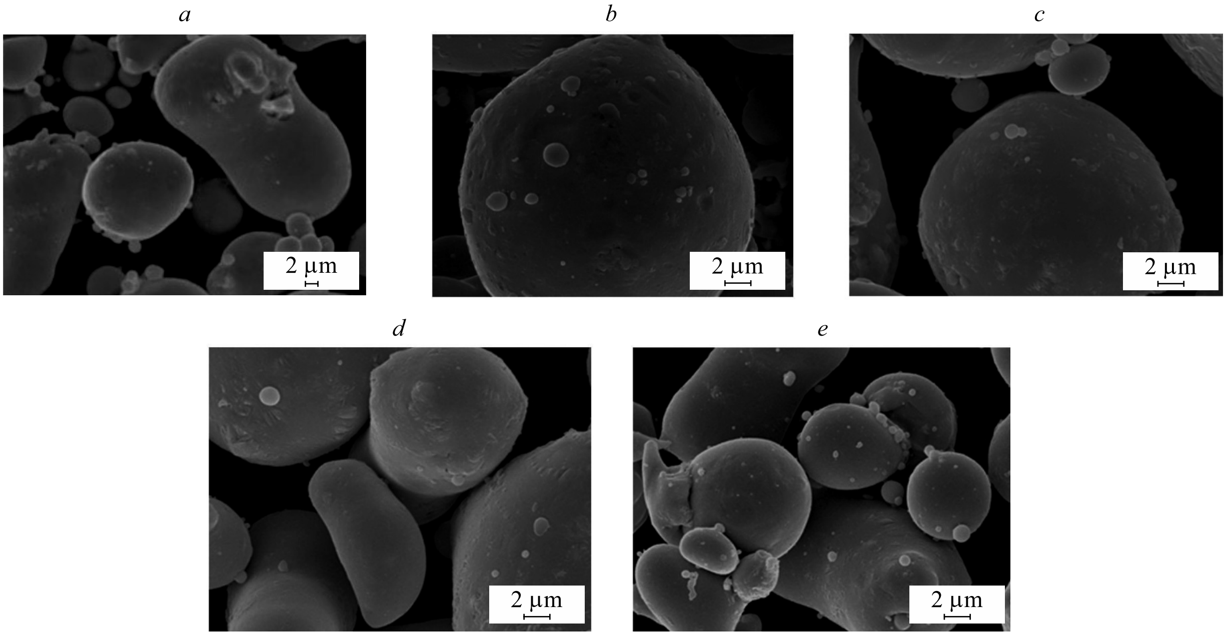

Fig. 3. SEM images of powders:
a – Sn; *b*, *e* – $Sn_{94.7}Ag_{5.3}$; *c* – $Sn_{94.0}Ag_{4.8}Cu_{1.2}$; *d* – $Sn_{99.5}Cu_{0.5}$.
Duration of tin powder treatment in pyrophosphate solutions:
a – 2 min; *b* – 15 min; *c*, *d*, *e* – 20 min

The surface of tin grains becomes nanorough already within 2 min of the treatment in pyrophosphate solution containing both Ag(I) and Cu(II) ions, just as it happens during the processing in the solution with only Ag(I) ions. Further, with an increase in the treatment time to 20 min, the surface morphology of the particles does not change (fig. 3, *c*). In addition, contrast particles with a diameter of 0.2–0.3 μm appear, during the CD of Ag(I) ions (see fig. 4, *b*). At the same time, low-contrast nanoparticles 70–100 nm in size are observed on tin surface, which are similar to those formed during the treatment of tin powder in Cu(II) containing pyrophosphate solution (see fig. 4, *b*).

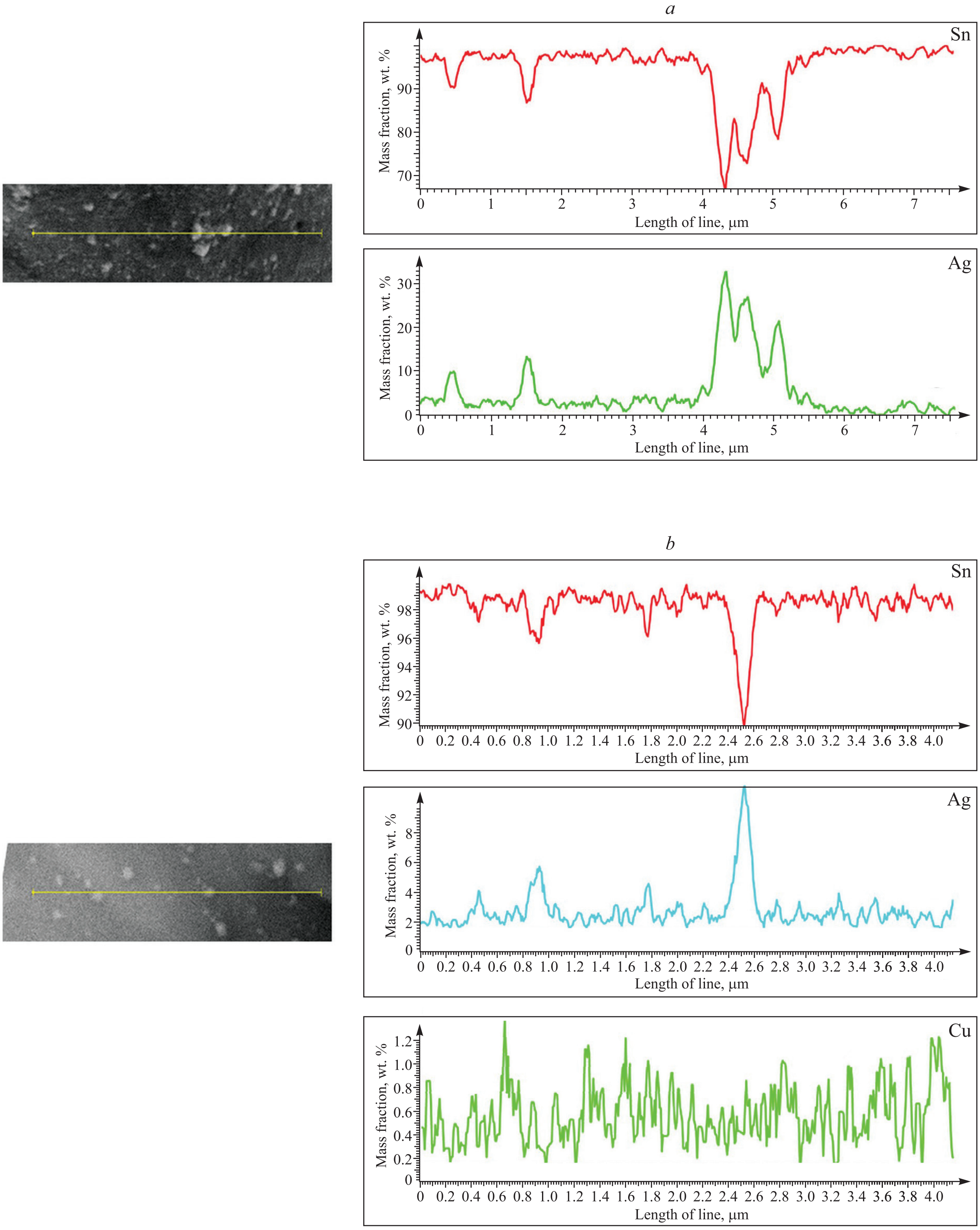

Fig. 4. Local elemental analysis of alloys along the scanning line:
a – $Sn_{94.7}Ag_{5.3}$; *b* – $Sn_{94.0}Ag_{4.8}Cu_{1.2}$

The local elemental analysis using EDX evidenced that the appearance of copper-containing particles on the tin surface does not affect the distribution of silver over the surface. Copper is distributed on the surface of tin particles more evenly than silver (see fig. 4, *b*; fig. 5, *f*, *j*). The entire picture does not change with an increase in the treatment duration in this solution up to 20 min. A parallel reduction of Ag(I) and Cu(II) ions on the tin surface occurs, and it ends at the stage of the formation of thinnest film of disparate nanoparticles of two intermetallic compounds on the surface of tin grains.

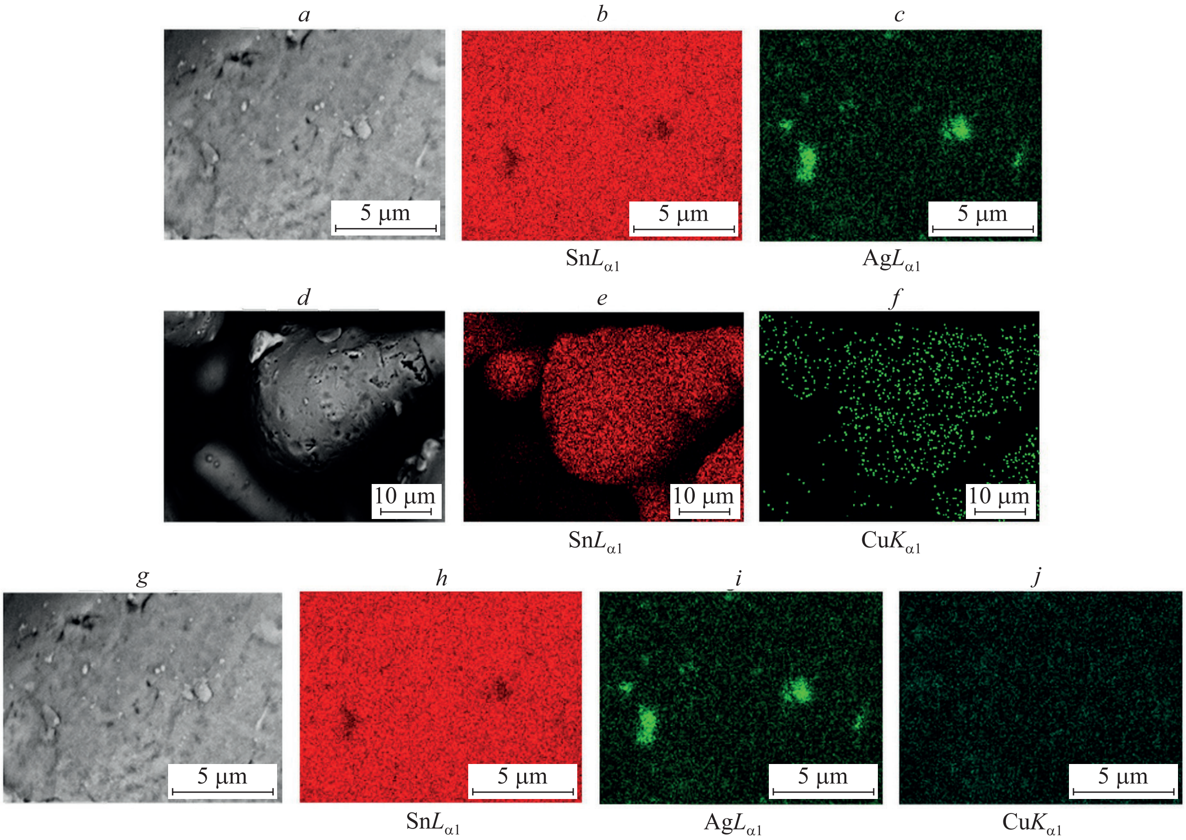

Fig. 5. SEM images of the alloy powders
$Sn_{94.7}Ag_{5.3}$ (*a* – *c*), $Sn_{99.6}Cu_{0.5}$ (*d* – *f*), $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ (*g* – *j*)
in topographic mode (*a*, *d*, *g*) and in compositional mode (*b*, *c*, *e*, *f*, *h* – *j*)

Along with the main CD reactions (1) and (2), several side processes occur during the synthesis of the alloys in pyrophosphate electrolyte that involve: (i) copper oxidation due to its ability to reduce Ag(I) ions as evidenced by the calculated values of electrode potentials under conditions used $(Cu(P_2O_7)_2^{6-}/Cu^0) = -0.16$ V, $E(Ag(P_2O_7)_2^{7-}/Ag^0) = 0.34$ V); (ii) tin oxidation in alkaline media according to data of the works [20; 21]; (iii) passivation of freshly deposited copper due to its oxidation with oxygen dissolved in the water with the formation of slightly soluble pyrophosphates [22]:

$$Cu^0 + 2Ag(P_2O_7)_2^{7-} \rightarrow 2Ag^0 + Cu(P_2O_7)_2^{6-} + 2P_2O_7^{4-}, \quad (3)$$

$$2Sn + 4H_2O + P_2O_7^{4-} \rightarrow Sn_2P_2O_7\downarrow + 4OH^- + 2H_2, \quad (4)$$

$$2Cu + O_2 + P_2O_7^{4-} + 2H_2O \rightarrow Cu_2P_2O_7\downarrow + 4OH^-. \quad (5)$$

To detect these side processes, the dependences of the OCP on the duration of tin, copper and silver working electrodes treatment in the solutions of different composition were studied (fig. 6).

The OCP of the copper working electrode in the supporting solution free of Cu(II) and Ag(I) ions increases by 0.023 V (from –0.328 to –0.305 V) during 300 s, after which it remains unchanged (see fig. 6, *a*, curve *4*). In the Cu(II)-containing solution the OCP similarly increases by 0.024 V from –0.316 to –0.292 V (see fig. 6, *a*, curve *3*). The increase in the OCP of copper electrode in the supporting solution and in Cu(II)-containing solution can be explained by the oxidation of copper with the formation of slightly soluble pyrophosphates (reaction (5)) or copper oxides blocking the copper surface. It explains the invariance of the OCP value after 300 s processing. The OCP of copper electrode in solutions containing only Ag(I) ions (see fig. 6, *a*, curve *2*) or both Ag(I) and Cu(II) ions (see fig. 6, *a*, curve *1*) decreases by 0.05 V during the first 20 s. This effect is due to the occurrence of the CD (reaction (3)). Then OCP of copper electrode increases and approximately at 100 s after the immersion acquires the value of the initial potential; further slight increase of electrode potential is observed as the result of copper surface passivation.

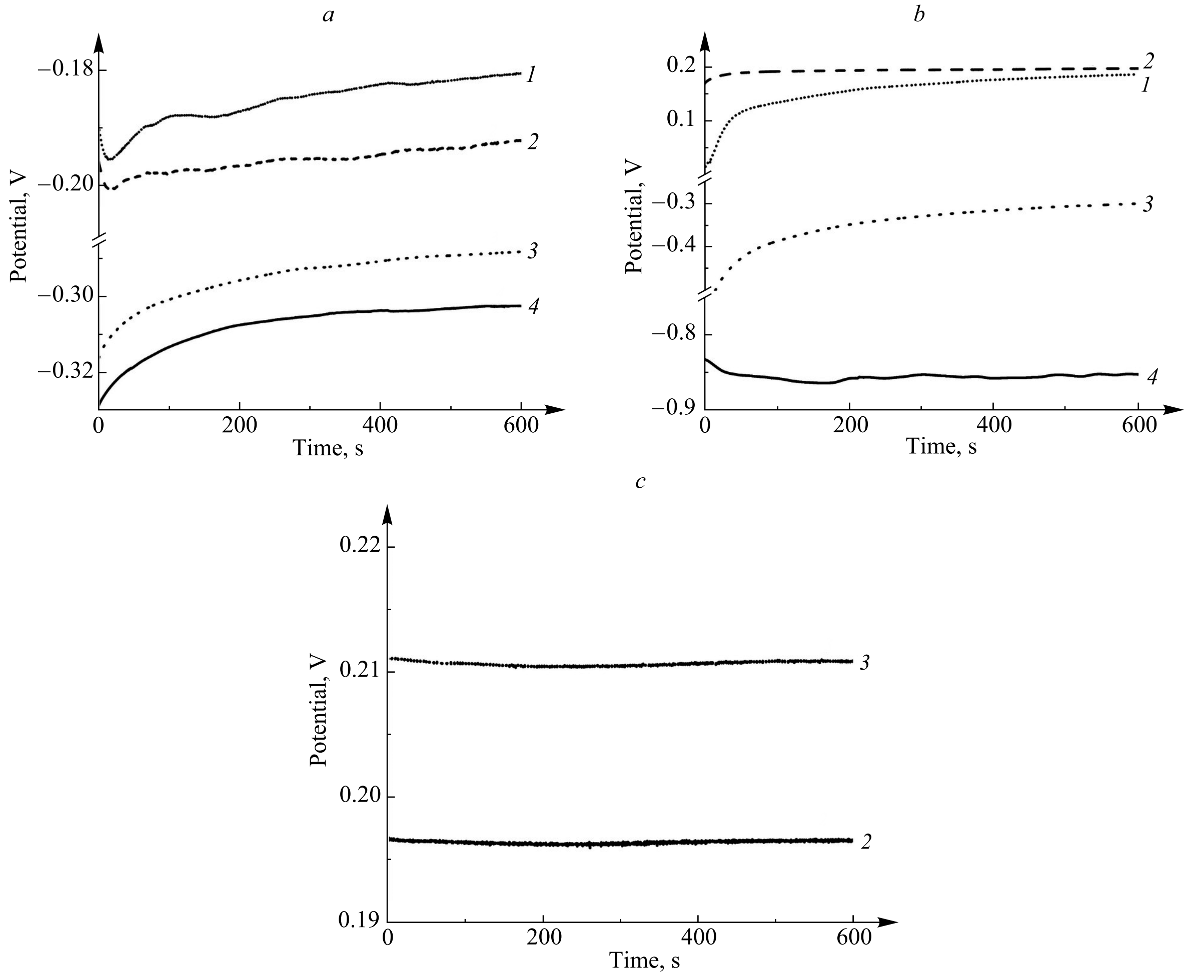

Fig. 6. Time dependence of OCP (electrodes: *a* – Cu, *b* – Sn, *c* – Ag).
The time scale corresponds to the duration of treatment in the solutions:
1 – Ag(I) and Cu(II); *2* – Ag(I); *3* – Cu(II); *4* – supporting solution

The OCP of tin electrode in the supporting solution (see fig. 6, *b*, curve *4*) decreases by 0.020 V within 40 s, that can be due to reactions of tin with pyrophosphate ions (reaction (4)) and oxygen dissolved in the solution. After tin electrode treatment for 40 s in the supporting solution, the OCP ceases to change, that can be addressed to passivation of tin surface with the formation of Sn(II, IV) oxides. The treatment of tin electrode in Cu(II) containing solution for 200 s results in the increase in OCP by 0.220 V due to the reaction (2) (see fig. 6, *b*, curve *3*). In contrast, OCP of tin rises by 0.022 V within 4 s treatment in the solution containing Ag(I) and Cu(II) ions (see fig. 6, *b*, curve *1*), the latter can be attributed to the simultaneous occurrence of reactions (1) and (2).

In the solution containing Ag(I) ions OCP of tin changes only by 0.022 V during the first 60 s (see fig. 6, *b*, curve *1*). It follows that CD reaction in the Sn/Cu^{2+} system proceeds more intensively in comparison with the Sn/Ag^{+} system. The simultaneous presence of Cu(II) and Ag(I) ions in the solution suppresses the reduction of Cu(II) ions with tin powder.

The OCP of silver electrode in the solutions of different composition does not change with processing time. This fact indicates that CD does not occur in the Ag/Cu^{2+} system (see fig. 6, *c*, curves *2*, *3*) and silver surface remains not passivated.

An additional experiment was undertaken to reveal the reason of passivation of copper and tin surfaces. Copper and tin foils were treated in 5 % solution of hydrochloric acid and then immersed in the pyrophosphate solution free from Cu(II) and Ag(I) ions for 20 min. Then the foils were rinsed in distilled water and air-dried. XRD analysis of the foils surface did not reveal the presence of $Cu_2P_2O_7$, $Sn_2P_2O_7$, as well as oxides of Sn(II or IV) or silver, that may be due to the formation of too thin films not detected by this method of analysis.

Conclusions

Simple method of obtaining powders of binary Sn – Ag and ternary Sn – Ag – Cu alloys has been developed, using the reaction of Ag(I) and Cu(II) contact displacement with tin in pyrophosphate solutions. It has been established that simultaneous reduction of Ag(I) and Cu(II) from their complex pyrophosphate compounds with tin powder ensures the formation of $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ alloy containing β-Sn, Ag_3Sn, Cu_6Sn_5 crystalline phases. The contact displacement of Ag(I) with tin powder in pyrophosphate solution yields a powder of $Sn_{94.7}Ag_{5.3}$ alloy consisting of β-Sn, Ag_3Sn phases which corresponds to the eutectic Sn − Ag alloy.

The melting of binary and ternary alloy powders occurs in two stages, the first stage starts at 200 °C, while the second one begins at 226 °C. The reason of two-stage melting is the heterogeneous structure of particles consisting of tin core and Sn − Ag or Sn − Ag − Cu alloy shell.

It was found that the process of $Sn_{94.7}Ag_{5.3}$ and $Sn_{94.0}Ag_{4.8}Cu_{1.2}$ alloys formation is accompanied by contact displacement of Ag^+ ions with copper freshly deposited on the surface of tin particles.

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