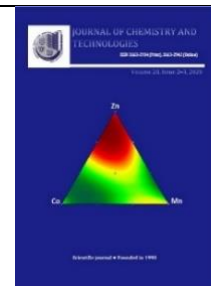




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### ALKALINE ELECTROLYTE ELECTRODEPOSITION OF Pb-Sn(TiO<sub>x</sub>) ALLOY

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#### Annotation

In this work, the production of thermal and electrolytic triple alloy Pb-Sn (TiO<sub>x</sub>) is investigated and some properties of the obtained material are considered. Conclusions are made on the advantage of the electrolytic method in comparison with the thermal one. An alkaline tin and lead electrolyte containing potassium metatitanate has been developed. According to the criteria of the maximum content of titanium, dissipative power and surface quality, its optimal composition is determined: KOH – 100–150 g/l, SnCl<sub>2</sub> – 16 g/l, (CH<sub>3</sub>COO)<sub>2</sub>Pb – 75 g/l, K<sub>2</sub>TiO<sub>3</sub> – 0.2 g/l, glycerol – 50–60 g/l. The optimal conditions for electrolysis are a temperature of 20–30 °C, current density  $i_k = 20$  mA/cm<sup>2</sup>; the ratio of the cathode and anode surfaces is not less than 1 : 2. The passivated coatings photocatalytic activity research results together with their anti-corrosion tests data and surface morphology analysis confirmed their high quality. The obtained alloy can be used as a corrosion-resistant coating, as a substrate for photo- and electroactive electrodes based on valve metal oxides, etc.

**Keywords:** K<sub>2</sub>TiO<sub>3</sub>; Pb-Sn alloy; electrolysis mode; electrodeposition; PbO<sub>2</sub>; SnO<sub>2</sub>.

### ЕЛЕКТРООСАДЖЕННЯ СПЛАВУ Pb-Sn(TiO<sub>x</sub>) З ЛУЖНОГО ЕЛЕКТРОЛІТУ

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#### Анотація

У даній роботі досліджено отримання термічного та електролітичного потрійного сплаву Pb-Sn(TiO<sub>x</sub>) та розглянуті деякі властивості отриманого матеріалу. Зроблено висновки щодо переваги електролітичного методу у порівнянні з термічним. Розроблений лужний електроліт луження-свинцювання, що містить калію метатитанат. За критеріями максимального вмісту титану, розсіювальної здатності та якості поверхні визначений його оптимальний склад: KOH – 100–150 г/л, SnCl<sub>2</sub> – 16 г/л, (CH<sub>3</sub>COO)<sub>2</sub>Pb – 75 г/л, K<sub>2</sub>TiO<sub>3</sub> – 0.2 г/л, гліцерол – 50–60 г/л. Оптимальними умовами електролізу є температура 20–30 °C, густина струму  $i_k = 20$  mA/cm<sup>2</sup>; співвідношення поверхонь катоду та аноду не менше 1 : 2. Результати дослідження фотокаталітичної активності пасивованих покриттів у поєднанні з даними їх антикорозійних випробувань та аналізу морфології поверхні підтвердили їх високу якість. Отриманий сплав може бути використаний як корозійностійке покриття, як підложка для фото- та електроактивних електродів на основі оксидів вентильних металів тощо.

**Ключові слова:** K<sub>2</sub>TiO<sub>3</sub>; сплав Pb-Sn; режим електролізу; електроосадження; PbO<sub>2</sub>; SnO<sub>2</sub>.

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**ЭЛЕКТРООСАЖДЕНИЕ СПЛАВА Pb-Sn(TiO<sub>x</sub>) ИЗ ЩЕЛОЧНОГО ЭЛЕКТРОЛИТА**Екатерина А. Плясовская<sup>1</sup>, Олег Б. Гирин<sup>2</sup>, Виктор Ф. Варгалюк<sup>1</sup><sup>1</sup>Днепропетровский национальный университет имени Олеся Гончара, просп. Гагарина, 72, Днепро, 49010, Украина<sup>2</sup>ГВУЗ «Украинский государственный химико-технологический университет», Днепро, Украина**Аннотация**

В данной работе исследовано термическое и электролитическое получение тройного сплава Pb-Sn(TiO<sub>x</sub>) и рассмотрены некоторые свойства полученного материала. Сделаны выводы о преимуществе электролитического метода в сравнении с термическим. Разработан щелочной электролит лужения-свинцевания, содержащий метатитанат калия. По критериям максимального содержания титана, рассеивающей способности и качества поверхности определен его оптимальный состав: КОН – 100–150 г/л, SnCl<sub>2</sub> – 16 г/л, (СН<sub>3</sub>СОО)<sub>2</sub>Pb – 75 г/л, K<sub>2</sub>TiO<sub>3</sub> – 0.2 г/л, глицерин – 50–60 г/л. Оптимальными условиями электролиза являются температура 20–30 °С, плотность тока  $i_k = 20$  А/см<sup>2</sup>; соотношение поверхностей катода и анода не меньше 1:2. Результаты исследования фотокаталитической активности пассивированных покрытий в сочетании с данными коррозионных испытаний и анализом морфологии поверхности подтвердили их высокое качество. Полученный сплав может быть использован в качестве коррозионностойкого покрытия, подложки для фото-и электроактивных электродов на основе оксидов вентильных металлов и т.д.

*Ключевые слова:* K<sub>2</sub>TiO<sub>3</sub>; сплав Pb-Sn; режим электролиза; электроосаждение; PbO<sub>2</sub>; SnO<sub>2</sub>

**Introduction**

Tin-lead alloy coatings are used in many industries. For example, as a protective layer during etching of printed circuit boards, or during long-term storage of products, etc [1–8]. But it is also important that a mixture of the oxides of these metals is widely spread as photo- and electroactive materials for the production of anodes used in water purification and electrochemical synthesis of organic and inorganic materials, and the best known and most effective additive to PbO<sub>2</sub> and PbO is titanium (IV) oxide [9;10]. As a rule, the deposition of doped PbO<sub>2</sub> and SnO<sub>2</sub> is carried out by chemical and electrochemical methods on an inert base (Ti, Pt, etc.) [11–13]. And one of the current problems connected with such oxide electrodes is cracking of the working layer that leads to poor performance. It is known [14] that when creating an active oxide layer on the surface of a material capable of reproducing the working layer during oxidation, the electrodes get rid of the cracking problem and their service life is significantly extended.

It is logical to use a lead-tin alloy as such a base material. Both thermal and electrochemical methods for producing lead-tin alloys are well known. Electrodeposition of tin-lead alloy proceeds without complications as these metals have fairly close standard potentials, furthermore, they are emitted at the cathode from simple salts solutions with approximately equal overvoltage. Therefore, depending on their ion concentration ratio in the electrolyte, alloys with a wide range of their content in the coating can be obtained [8; 15; 16]. The deposition of lead-tin alloys is

mostly carried out from acidic solutions, but alkaline tin and lead electrolytes are also known. The incorporation of titanium into tin-lead coatings is a complex issue. Thermal fusion is hindered by a large difference in the melting temperatures of the metals ( $t_{\text{melt}}(\text{Sn}) = 231.9$  °C;  $t_{\text{melt}}(\text{Pb}) = 327.4$  °C;  $t_{\text{melt}}(\text{Ti}) = 1665$  °C [17]). In our previous works we showed that a material containing titanium compounds in matrix tin can be obtained electrochemically from alkaline solutions with the addition of potassium metatitanate [14; 18]. The fusion of this material with lead under certain conditions made it possible to obtain a triple alloy Pb-Sn (TiO<sub>x</sub>), but the maximum proportion of tin in it was 17 %, in addition, the fusion process almost did not allow to influence the obtained material composition in a controlled manner [19]. From all these aspects, electrochemical methods have proven to be more effective. A triple Pb-Sn(TiO<sub>x</sub>) alloy was obtained from a combined alkaline tin and lead electrolyte with the addition of K<sub>2</sub>TiO<sub>3</sub>.

In this work, the production of thermal and electrolytic triple alloy Pb-Sn (TiO<sub>x</sub>) is investigated and some properties of the obtained material are considered.

**Materials and methods**

For the preparation of the combined tin-lead electrolyte traditional alkaline electrolytes for tinning and lead plating were taken as a basis [15; 18]. We have chosen electrolytes of the following compositions. Tinning electrolyte: tin(II) chloride 40 g/l; potassium hydroxide 84 g/l. Lead plating electrolyte: lead 80 g/l (in terms of metal); potassium hydroxide 150 g/l; glycerin

60 g/l. The alkaline concentrate of potassium metatitanate was prepared according to the method [20]. The concentration of titanium compounds in the electrolyte and the resulting precipitate was controlled spectrophotometrically, according to the method [21]. All working solutions were made of the reagents of a grade not lower than "chemically clean" on double-distilled water.

The electrochemical studies were performed in a standard three-electrode cell using a potentiostat ПИ-50-1, a programmer ПП-8, and a digital USB oscillograph. The working electrodes were: a platinum plate with an area of 2 cm<sup>2</sup>, a copper plate with an area of 10 cm<sup>2</sup>, a steel plate with a working surface of 10 cm<sup>2</sup>. The auxiliary electrode was a lead plate with an area of 10 to 30 cm<sup>2</sup>. The reference electrode was a saturated silver-silver chloride electrode; all the values of potentials in the article are given in relation to a silver chloride electrode.

The surface morphology of the coatings was examined using a scanning electron microscope PEM-106И, operating in a secondary image acquisition mode. The maximum residual pressure in the microscope column (in the gun area) did not exceed  $6.7 \cdot 10^{-4}$  Pa, the gun current was 115 mA.

## Results and discussion

*Optimization of the combined electrolyte composition and electrolysis conditions.* The problem with creating a combined electrolyte was that these electrolytes of tinning and lead plating contained incompatible anions. Thus, alkaline tinning electrolytes are usually prepared on the basis of chlorides or sulphates of tin (II), and the corresponding lead compounds are insoluble. Also, the solubility of plumbates is limited, and dilution can lead to the precipitation of insoluble precipitates of lead (II) hydroxides [15]. But the choice of glycerate lead electrolyte provided a

positive result. Glycerate complexes of lead (II) are stable and can compete with the formation of hardly soluble chlorides and hydroxides [22]. Also, to avoid the aforementioned dilution problem, the concentration of alkali and glycerol in the combined lead-tin electrolyte was increased to the concentration of alkali in the plumbate electrolyte.

As a result, the following intervals of component concentrations in the combined electrolyte were investigated: KOH – 100–150 g/l, SnCl<sub>2</sub> – 8–32 g/l, (CH<sub>3</sub>COO)<sub>2</sub>Pb – 25–100 g/l, K<sub>2</sub>TiO<sub>3</sub> – 0.2 g/l, глицерол – 50–60 g/l. The electrolyte was time-stable in these concentration ranges. The combined electrolyte retains its transparency for a long time (more than a week) at a volume ratio of plumbate and stannate electrolytes from 1 : 4 to 4 : 1, respectively. The introduction of potassium metatitanate in millimolar amounts leads to turbidity of the solution after a few hours.

Electrodeposition of the alloy was performed at a current density  $i = 20$  mA / cm<sup>2</sup> without stirring the electrolyte. The optimal value of  $i$  was determined during studies of the combined electrolyte dissipative power (DP) in the Hull angular cell. At current densities greater than this value, intensive growth of dendrites was observed. At a temperature of the electrolyte above 30 °C, the coating became porous, and at 50 °C the adhesion of the coating to the base became unsatisfactory both in the case of steel cathodes, and copper or platinum ones.

DP was also determined in the Herring-Bloom cell. Alkaline electrolyte coatings were selected for comparison: tinning, tinning with the addition of potassium metatitanate, tinning - lead plating, and, tinning - lead plating with the addition of potassium metatitanate for the volume ratio of plumbate and stannate electrolytes 3 : 2. The results are given in table 1.

Table 1

Dissipative power values of alkaline electrolytes

Type of coating	Sn	Sn(TiO <sub>x</sub> )	Sn-Pb	Pb-Sn(TiO <sub>x</sub> )
DP, %	64	73	75	87

As can be seen from Table 1, the addition of potassium metatitanate to the electrolyte in all cases increases the dissipative power of alkaline electrolytes. For the tinning electrolyte DP increases by 9 %, for the tinning - lead plating electrolyte - by 12 %.

In addition, the stability of the electrolyte itself is significantly affected by temperature. Table 2

shows the dependence of the combined electrolyte appearance on temperature for the volume ratio of plumbate and stannate electrolytes 3 : 2, but these patterns were observed in all the studied volume ratios of lead plating and tinning electrolytes.

Table 2

Influence of temperature on the appearance of the combined electrolyte					
Type of electrolyte	Consistency of the electrolyte at temperature, °C				
	20	30	40	50	60
Combined, plumbate-stannate	transparent	transparent	transparent	slight turbidity	black precipitate
-/- with the addition 0.2 g/l $K_2TiO_3$	transparent	transparent	cloudy light	cloudy dark	black precipitate

It is determined that the combined electrolyte is very sensitive to the ratio of the cathode to anode area. Satisfactory quality of the coating is obtained only with a ratio of the cathode to anode area not less than 1: 2 respectively.

When optimizing the electrolyte composition, the factor of the titanium content in the coating also had to be taken into account. The

optimization of the potassium metatitanate volume concentration in the combined electrolyte was not performed, as we relied on data from the previous works [14;18]. After dissolving the electrolytic precipitate in concentrated nitric acid, the titanium content was determined spectrophotometrically. The results are given in Table 3.

Table 3

Concentration of titanium ( $C_s$ ) in coatings Pb-Sn( $TiO_x$ ), obtained from the combined alkaline electrolytes of tinning – lead plating. Content of  $K_2TiO_3$  in the electrolyte  $C_v = 0.2$  g/l

Volume ratios of lead plating - tinning electrolytes	1 : 4	2 : 3	3 : 2	4 : 1
Correlation Pb : Sn in terms of mol-eq	1.00 : 4.36	1.23 : 2.00	2.75 : 2.00	7.35 : 2.00
$C_s$ , mg/cm <sup>2</sup>	$1.7 \cdot 10^{-2}$	$38.9 \cdot 10^{-2}$	$60.9 \cdot 10^{-2}$	$44.6 \cdot 10^{-2}$

As can be seen from Table 3, the maximum amount of Ti is observed at the ratios of the electrolytes of lead-plating and tinning 3 : 2 respectively. The amount of titanium in the electrolyte with a ratio of 1: 4 is close in values to that in the coating Sn( $TiO_x$ ) [14].

The analysis of SEM images presented in Fig. 1 gives grounds to assert the fundamental morphological difference of the coating surfaces obtained in the combined electrolyte with

different ratio of lead plating and tinning electrolytes. Thus, the coating surface obtained at the ratio of these electrolytes of 1 : 4 was characterized by the heterogeneity of grain aggregates in both size and shape. Against the background of grain aggregates with an average size of 3-4  $\mu$ m, much larger grain conglomerates with an average size of 5-6  $\mu$ m can be seen (see Fig. 1a), while anisotropic (10 x 2  $\mu$ m) formations are clearly displayed.

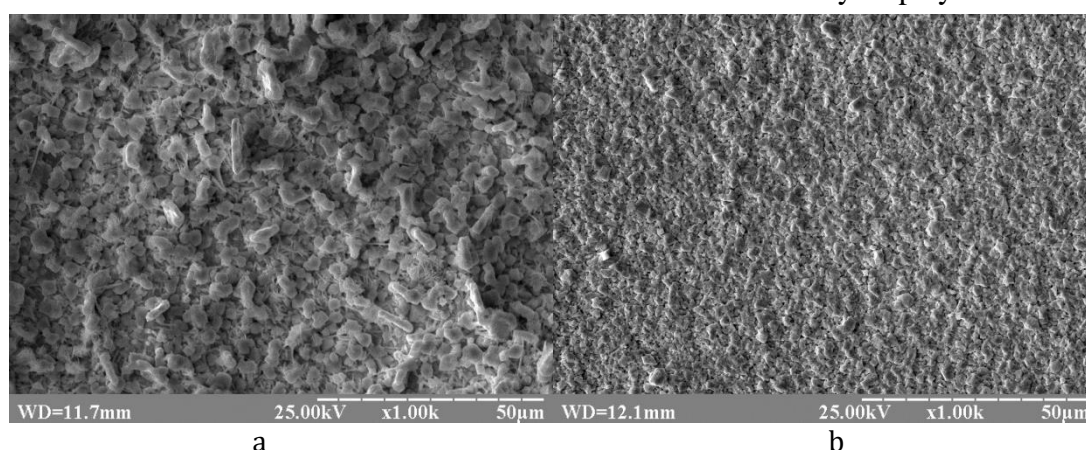


Fig. 1. SEM images (x1000) of the electrodeposited alloy Pb-Sn( $TiO_x$ ) surface, obtained in the combined electrolyte at  $i = 20$  mA/cm<sup>2</sup> with the ratio of lead plating and tinning electrolytes a) 1 : 4 and b) 4 : 1

In contrast to this structural inhomogeneity, the coatings obtained in the combined electrolyte with a ratio of lead plating and tinning electrolytes 4 : 1, had a homogeneous and finer structure with

an average grain aggregate size of 1.5-2  $\mu$ m (see Fig. 1b). Such a significant diminution of the grain aggregates of approximately the same size indicates an increase in the specific surface area of

the samples with the increase in the proportion of lead plating electrolyte in the combined electrolyte.

On the basis of the received data it is possible to draw a conclusion that increasing the proportion of the lead plating electrolyte in the combined electrolyte leads both to the formation of a more homogeneous surface structure and to the reduction in size of the electrolytic sediment grain conglomerates, that improves the quality of the obtained alloys.

The diminution of the electrodeposited alloy structure in the lead-tin system with the increase of the lead plating electrolyte proportion in the combined electrolyte can be explained on the basis of the ideas about the electrochemical phase formation of metals and alloys through the stage of supercooled liquid state [23]. According to the concept [24–26], during electrochemical deposition of a metal or alloy in an aqueous medium on a solid cathode, a strongly supercooled metallic liquid is formed in the form of many liquid clusters of atoms, which are released avalanche-like in different places of the cathode.

During the electrochemical deposition of a lead-tin system alloy with the increased concentration of lead ions in the combined electrolyte, the alloy crystallizes in the form of a solid substitution solution based on lead doped with tin. The formation of this type of solution is explained by the fact that in this case the Hume-Rosery rule is fulfilled, according to which for the formation of alloys in the form of solid substitution solutions it is necessary that the atomic radii of interacting metals differ by no more than 15%. In this case, the difference between the radii of Pb atoms (0.1935 nm) and  $\beta$ -Sn (0.1862 nm) is only 4 %.

Since with the increasing degree of supercooling during electrodeposition of metal / alloy, its structure becomes finer [27], and the degree of supercooling of lead exceeds the same value for tin by 1.5 times, increasing the concentration of the solvent metal (Pb) in a lead-

tin system alloy will lead to the formation of a finer structure than at a decreased concentration of it, as observed experimentally.

Additional diminution of the electrodeposited alloy Pb (Sn) structure is also possible by means of its doping with titanium. As shown in [28], when interacting in the process of electrodeposition of the elements that differ significantly in valence, the occurrence of intermetallic compounds in the alloy structure is likely. Such intermetallics must be additional centers of the heterogeneous crystallization of the liquid clusters of the alloy atoms or their combinations in the supercooled liquid state.

Within this work some properties of Pb-Sn(TiO<sub>x</sub>) coatings were also investigated.

*Photocatalytic properties.* On the surface of the triple alloy Pb-Sn (TiO<sub>x</sub>) in air or as a result of artificial oxidation, a film of oxides of lead, tin and titanium should form, mostly in the maximum oxidation states. According to many studies (for example, [29; 30]) combinations of these oxides show significant catalytic, electrocatalytic and photocatalytic properties. The latter are most characteristic of the materials containing TiO<sub>2</sub>, and are a very popular area of modern research [11–13]. That is why we first tested the photocatalytic behavior of Pb-Sn (TiO<sub>x</sub>)-electrodes by the example of a model reaction of hydrogen peroxide decomposition. The oxidation of the surface of all the electrodes took place in air at room temperature during the day. The photodegradation was performed in H<sub>2</sub>O<sub>2</sub> solution, initial and current concentrations of which were set permanganatometrically according to the method described in [31] at UV irradiation on oxide catalysts of different nature. . The initial peroxide concentration values varied in the range of 0.04–0.05 mol/l. Without UV irradiation the fraction of decomposed H<sub>2</sub>O<sub>2</sub> did not exceed 2–3 % per hour. The fraction of decomposed H<sub>2</sub>O<sub>2</sub> without catalyst, but under UV irradiation, was 10–12 % per hour, the results in tables 4, 5 are given less these values.

Table 4

**H<sub>2</sub>O<sub>2</sub> (mass %), decomposed for 1 h under the action of UV radiation on materials**

Material	Sn	Sn-Ti	Sn-Pb
Part of H <sub>2</sub> O <sub>2</sub>	7.2	15.3	8.6

Table 5

**H<sub>2</sub>O<sub>2</sub> (mass %), decomposed for 1 h under the action of UV radiation on Pb-Sn(TiO<sub>x</sub>)-electrodes obtained at different volumetric ratios of electrolytes**

Volume ratios of plumbate and stannate electrolytes	1 : 4	2 : 3	3 : 2	4 : 1
Part of H <sub>2</sub> O <sub>2</sub>	14.0	18.1	23.1	25.6

As can be seen from Table 4 and 5, the materials containing oxidized titanium are naturally more photocatalytically active than unmodified samples. As for the Pb-Sn ( $\text{TiO}_x$ ) alloy, the decomposed part of  $\text{H}_2\text{O}_2$  increases gradually with the increase in the amount of lead in the combined electrolyte. This can be due to both the high oxidizing properties of lead (VI) oxide formed on the surface and the increase in the specific surface area of the material (see Fig. 1).

**Electrochemical properties.** The anodic behavior of a tin electrode in alkaline solutions with the addition of potassium metatitanate was studied quite carefully in the works [10–11], but no data were available on the behavior of a lead electrode under similar conditions. Based on Fig. 2, we can say that complete passivation of the lead electrode is not achieved at the anodic potential scan (Fig. 2, curve 1). The introduction of 1 mmol / l of potassium metatitanate into the electrolyte reduces the peak of the anodic dissolution of lead almost 5 times, which indicates an intensive interaction between  $\text{Pb}^{2+}$  and  $\text{TiO}_3^{2-}$ , possibly with the formation of a hardly soluble compound that blocks the electrode surface. But the high solubility of oxygen-containing compounds of lead in alkalis does not allow to form a stable passive film on the surface of the lead electrode, as can be seen from the comparison of curves 1 and 2 (Fig. 2).

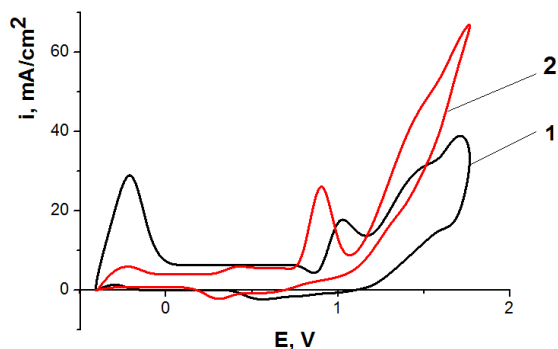


Fig. 2. Voltamperograms registered on Pb-electrodes: 1 – in 0.5 mol / l KOH solution; 2 – in 0.5 mol / l KOH solution +  $1 \cdot 10^{-3}$  mol/l  $\text{K}_2\text{TiO}_3$ .  $V = 20 \text{ mV} / \text{s}$ .

The tin-lead thermal alloy also did not show the ability to passivate in alkaline media, and the maxima of active dissolution of lead and tin are maintained at the dissolution potentials of individual substances. Introduction to this alloy of titanium compounds changes the nature of current-voltage dependences. In previous works of our laboratory with the thermal alloy Pb-Sn- $\text{TiO}_x$ , electrochemical studies were performed to determine the ability of the alloy to form strong oxide films on the surface. Similar studies were

performed for the electrolytic alloy. In Fig. 3 the current-voltage curves recorded in a 0.5 molar solution of KOH on an electrolytic alloy Pb-Sn- $\text{TiO}_x$  are shown.

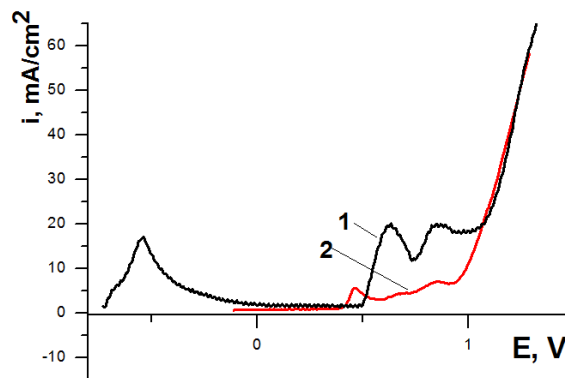


Fig. 3. Voltamperograms registered in 0.5 mol / l KOH solution on an electrolytic alloy Pb-Sn( $\text{TiO}_x$ ): 1 – on a freshly precipitated alloy; 2 – upon re-registration.  $V = 20 \text{ mV} / \text{s}$ .

In 0.5 mol / l KOH solution for thermal alloy, a significant part of passive area and peaks of active anodic and transpassive oxidation were observed. As can be seen, the passivation area in the range of potentials from  $-0.2$  to  $0.5 \text{ V}$  is also present on the electrolytic alloy. Curve 2 on Fig. 3 was recorded on the same surface that has already passed to  $E = 1.2 \text{ V}$ . In this case, the peak of active dissolution is not observed at all, and the peaks in the transpassive area are reduced by 3–3.5 times. This indicates the formation of an insoluble in alkali oxide film on the surface of the alloy.

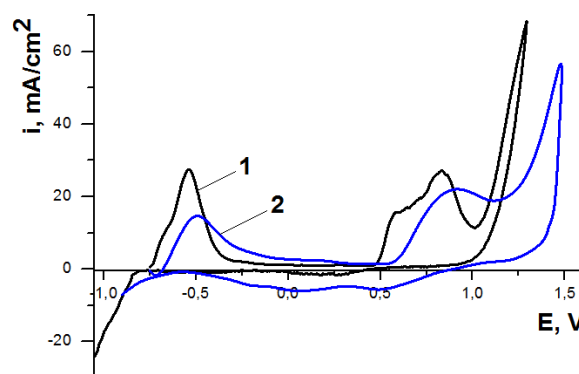


Fig. 4. Voltamperograms registered in 0.5 mol / l KOH solution on the alloy Pb-Sn- $\text{TiO}_x$ : 1 – obtained electrolytically; 2 – obtained thermally.  $V = 20 \text{ mV} / \text{s}$

When comparing the cyclic curves obtained on thermal and electrolytic alloys (Fig. 4), there is a coincidence of the general shape of the curve and the location of the main areas. The reason for the discrepancies can be related to the method of obtaining the alloy, as well as to the different quantitative ratio of components in it.

**Corrosion tests.** To test the ability of the alloy to form strong oxide films on the surface, corrosion



tests of a passivated sample Pb-Sn ( $\text{TiO}_x$ ) were performed. The alloy was precipitated from a combined electrolyte with a ratio of lead plating and tinning electrolytes 3: 2 respectively, with the addition of 0.2 g / l of potassium metatitanate, because according to our previous studies, it is from this solution that a coating is obtained with the maximum amount of titanium compounds and with a high quality of sediments, which has a high adhesion to the base.

The formation of the oxide layer on the coating took place under standard conditions in air for one hour. The corrosion test was performed in an acetic acid medium (boiling solution 31.2 g/l  $\text{CH}_3\text{COOH}$  1 g/l  $\text{Na}_2\text{S}$ , 60 s). This is due to the fact that similar tests have previously been performed for passivated samples of Sn ( $\text{TiO}_x$ ) obtained by different methods, and it is possible to compare the results [14; 18]. For Pb-Sn ( $\text{TiO}_x$ )-electrodes passivated in the air during the day, the phenomenon of self-regeneration of oxide surface after mechanical damage was observed. A similar phenomenon was observed on the passivated Sn( $\text{TiO}_x$ ) electrode. It can be assumed that the addition of potassium metatitanate is the cause of self-healing of oxide layer mechanical damage in composite materials, probably due to the formation of the corresponding galvanic couple.

In addition to direct corrosion tests, the method of self-activation curves practically grounded in [32] was used to compare the properties of oxide layers that were electrochemically formed by anodizing lead-based alloys in alkaline solutions. Self-activation was performed according to the method described in [32]. The method is designed for the express analysis of oxide layer corrosion resistance and is generally able to characterize this value for metals and alloys of different nature. Passivation was performed in 0.5 mol / l KOH solution for 60 s at a potential of 1.2 V, which corresponds to the area of oxygen evolution on Pb-Sn ( $\text{TiO}_x$ ) (Figs. 2, 4). The results are shown in Fig. 5.

Compared with the undoped Pb-Sn alloy, Pb-Sn ( $\text{TiO}_x$ ) self-activation time increased by 31 %. In contrast to the thermal alloy, under the same conditions of passivation [19], the self-activation time of the electrodeposited alloy increases sharply. For the thermal alloy it was 50 s, and for the electrolytic – 950 s. This can be explained by the higher content of tin in the electrolytic alloy, which could not be introduced into the thermal alloy.

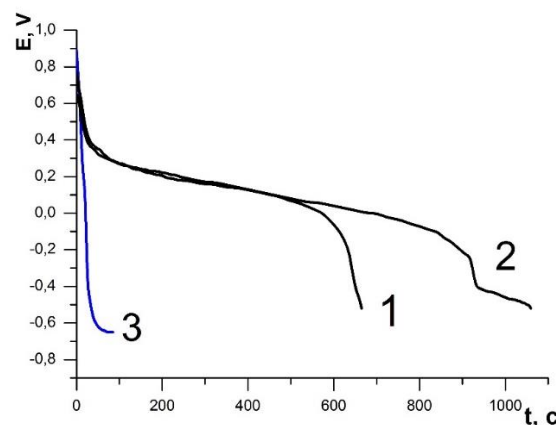


Fig. 5. Self-activation curves registered in 0.5 mol / l KOH solution: 1 – on a Pb-Sn electrode; 2 – on an electrodeposited Pb-Sn ( $\text{TiO}_x$ ) electrode; 3 – on a thermal alloy Pb-Sn( $\text{TiO}_x$ )

## Conclusions

A combined lead plating and tinning electrolyte was created on the basis of alkaline electrolytes of tinning and lead plating with the addition of potassium metatitanate. According to the criteria of the maximum content of titanium, dissipative power and surface quality, its optimal composition was determined: KOH – 100–150 g/l,  $\text{SnCl}_2$  – 16 g/l,  $(\text{CH}_3\text{COO})_2\text{Pb}$  – 75 g/l,  $\text{K}_2\text{TiO}_3$  – 0.2 g/l, glycerol – 50–60 g/l. The optimal conditions for electrolysis are a temperature of 20–30 °C, current density  $i_k = 20 \text{ mA/cm}^2$ ; the ratio of the cathode and anode surfaces not less than 1 : 2.

The research results of the passivated coatings photocatalytic activity in combination with their anti-corrosion tests data and the surface morphology analysis confirmed their high quality.

## Bibliography

- [1] Effect of heating rates and Zn-addition on the thermal properties of Pb-Sn alloy / A. Alnakhli, B. Hassan, M. Abdulhafiz, M. A. Al-Hajji // International journal of advanced research. – 2020. – 5(3). – P. 20–27.
- [2] Arefi-Rad M. R. Pb-doped SnS nano-powders: Comprehensive physical characterizations / M. Reza. Arefi-Rad, H. Kafashan // Optical Materials. – 2020. – V. 105. – 109887.
- [3] Interfacial behaviors of Sn-Pb, Sn-Ag-Cu Pb-free and mixed Sn-Ag-Cu/Sn-Pb solder joints during electromigration / F. Wang, D. Li, S. Tian [et al.] // Microelectronics Reliability. – 2017. – 73. – P. 106–117.
- [4] Sekimoto H. Effect of Aqueous Antimony Species on Corrosion of Pb-Sn-Ca Alloy in Copper Electrowinning / H. Sekimoto, S. Sugawara, J. Nosaka // Materials transactions. – 2020. – 61(8). – P. 162–163.
- [5] Mechanical properties of Pb/Sn, Pb/In and Sn-In solders / W. K. Jones, Y. Liu, M. Shah, R. Clarke // Soldering and Surface Mount Technology. – 1998. – 10(1). – P. 37–41.
- [6] Zhengxi H. The Internal stress and binding force of carbon nanotubes / Pb-Sn composite coatings / H. Zhengxi, J. Xiaohua // Advances in Engineering Research (AER). – 2017. – Vol. 143. – P. 675 – 680.

- [7] Bakour Z. Electrochemical Corrosion of Pb-Sn and Pb-Sb Alloys for Lead-Acid Battery Applications / Z. Bakour, A. Dakhouche // *Acta Physica Polonica A*. – 2018. – 134(1). – P. 103–105.
- [8] Hu Z. Corrosion resistance of Pb–Sn composite coatings reinforced by carbon nanotubes / Z. Hu, X. Jie, G. Lu // *Journal of Coatings Technology and Research*. – 2010. – 7(6). – P. 809–814.
- [9] Electrochemical reduction of CO<sub>2</sub> to Formic Acid on Pb-Sn Alloy Cathode / P. Widiatmoko, I. Nurdin, H. Devianto, B. Prakarsa, H. Hudoyo // *IOP Conference Series Materials Science and Engineering*. – 2020. – 823:012053.
- [10] Yang Z. P-block metal-based (Sn, In, Bi, Pb) electrocatalysts for selective reduction of CO<sub>2</sub> to formate / Z. Yang, F. E. Oropeza, K. H. L. Zhang // *APL Materials*. – 2020. – 8(6):060901.
- [11] Bagheri S. N. Titanium dioxide as a catalyst support in heterogeneous catalysis / S. N. Bagheri, N. M. Julkapli // *Scientific World Journal* – 2014. – Vol. 214. – P. 3–10.
- [12] Hintshoa N. Photo-catalytic activity of titanium dioxide carbon nanotubeno-composites modified with silver and palladium nanoparticles / N. Hintshoa, L. Petrika, A. Nechaeva // *Applied Catalysis B: Environmental*. – 2014. – Vol. 157. – P. 273–283.
- [13] Salomatina S. V. Structure and catalytic activity of poly (titanium oxide) doped by gold nanoparticles in organic polymeric matrix / E. V. Salomatina, A. S. Loginova, S. R. Ignatov // *Inorg. Organomet. Polym.* – 2016. – Vol. 26. – P. 1280 – 1291.
- [14] Plyasovskaya K. Research into corrosion and electrocatalytic properties of the modified oxide films on tin / K. Plyasovskaya, V. Vargalyuk, I. Sknar [et al.] // *Eastern European Journal of Enterprise Technologies*. – 2017. – 5 (12-89). – P. 39–45.
- [15] Ильин В. А. Лужение и свинцевание / В.А. Ильин – М.: Машгиз. –1971. – 46 с.
- [16] Hu Z. Study of Polyacrylic Acid Dispersing Pb-Sn-CNTs Composite Plating Solution / Z. Hu, X. Jie // *5th International Conference on Advanced Design and Manufacturing Engineering*. – 2015. – 978-94-6252-113-1.
- [17] Физические величины. Справочник. / А. П. Баби́чев, Н. А. Бабушкина, А. М. Братковский [и др.]; Под ред. И. С. Григорьева, Е. З. Мейлихова. — М.: Энергоатомиздат, 1991. – 1232 с.
- [18] Варгалюк В. Ф. Электроосаждение олова в присутствии K<sub>2</sub>TiO<sub>3</sub> / В. Ф. Варгалюк, Е.А. Плясовская, Е. И. Нестер // *Вісн. Дніпропетр. ун-ту. Сер.: Хім.* – 2016. – Т. 24, № 1. – С. 7 – 12.
- [19] Сплав Pb-Sn з добавками сполук титану / А.Г. Пашина, А.Я. Ріттер, К.А. Плясовська, В.Ф. Варгалюк. – 2018. – Матеріали II всеукраїнської наукової конференції «Теоретичні та експериментальні аспекти сучасної хімії та матеріалів» 10 квітня 2018, Дніпро. – С. 71.
- [20] А. с. СССР, МКИ G 23 N 5/32. Способ приготовления щелочного электролита / Б.Ф. Ляхов, В.Н. Кудрявцев, А.Т. Ваграмян (СССР). – № 393370; опубл. 24.12.75, Бюл. № 33. – 23 с.
- [21] Марченко Э. Фотометрическое определение элементов / Э. Марченко. –1971. – М.: Мир. – 501 с
- [22] Рахманкулов Д. Л. Физические и химические свойства глицерина / Д. Л. Рахманкулов, Б. Х. Кимсанов, Р. Р. Чанышев. – М.: Химия, 2003. – 200 с.
- [23] Girin O. B. Mechanism of liquid phase formation in metals during electrodeposition / O. B. Girin, V. P. Khlyntsev // *Elektronnaya Obrabotka Materialov*. – №3. – P. 13–18.
- [24] Girin O. B. Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 1 / O. B. Girin // *Surf. Eng. Appl. Electrochem.* – 2017. – V. 53, №2. – P. 137–143.
- [25] Girin O. B. Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 2 / O. B. Girin // *Surf. Eng. Appl. Electrochem.* – V. 53, №3. – P. 233–239.
- [26] Girin O. B. Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 3 / O. B. Girin // *Surf. Eng. Appl. Electrochem.* – 2017 – V. 53, №4. – P. 339–344.
- [27] Girin O. B. Mechanism of structure formation in electrolytic coatings / O. B. Girin, G. M. Vorob'ev // *Russian metallurgy. Metally*. – 1987. – № 4. – P. 148–152.
- [28] Girin O. B. (2020). Electrochemical phase formation of metals and alloys at chemically identical solid or liquid cathode: part 1 – metals. / O. B. Girin, D. G. Korolyanchuk, // *Surf. Eng. Appl. Electrochem.* – 2020. – V. 56, № 1. – P. 28–40.
- [29] Velichenko A. B. Electrodeposition of PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials from suspension electrolytes / A. B. Velichenko, V. A. Knysh, T. V. Luk'yanenko, N. N. Nikolenko // *Theor. Exp. Chem.* – 2016. – Vol. 52. – P. 127–131.
- [30] Influence of preparation methods on the structure and catalytic performance of SnO<sub>2</sub>-doped TiO<sub>2</sub> photocatalysts / M. Huang, S. Yu., B. Lin [et al.] // *Ceramics Int.* – 2014. – Vol. 40(8). – P. 13305–13312.
- [31] Аналитическая химия. Химические методы анализа / Под ред. О. М. Петрухина. – М.: Химия, 1992. – 400 с.
- [32] Головкин Д. А. Самоактивация оловянного электрода, модифицированной анодной обработкой в щелочном растворе / Д. А. Головкин, Е. А. Беляновская // *Вопросы химии и химической технологии*. – 1999. – № 1. – С. 84 – 86.

## References

- [1] Alnakhlani, A., Hassan, B., Abdulhafiz, M., Al-Hajji, M. A. (2020). Effect of heating rates and Zn-addition on the thermal properties of Pb-Sn alloy. *International journal of advanced research*, 5(3), 20–27. <http://dx.doi.org/10.21474/IJAR01/3478>
- [2] Arefi-Rad, M. R., Kafashan, H. (2020). Pb-doped SnS nano-powders: Comprehensive physical characterizations. *Optical Materials*, 105, 109887. <http://dx.doi.org/10.1016/j.optmat.2020.109887>
- [3] Wang, F., Li, D., Tian, S., Zhang, Z., Wang, J., Yan, C. (2017). Interfacial behaviors of Sn-Pb, Sn-Ag-Cu Pb-free and mixed Sn-Ag-Cu/Sn-Pb solder joints during electromigration. *Microelectronics Reliability*, 73, 106–117. <http://dx.doi.org/10.1016/j.microrel.2017.04.031>
- [4] Sekimoto, H., Sugawara, S., Nosaka, J. (2020). Effect of Aqueous Antimony Species on Corrosion of Pb–Sn–Ca Alloy in Copper Electrowinning. *Materials transactions*, 61(8), 162–163. <http://dx.doi.org/10.2320/matertrans.M-M2020831>
- [5] Jones, W. K., Liu, Y., Shah, M., Clarke R. (1998). Mechanical properties of Pb/Sn, Pb/In and Sn-In solders. *Soldering and Surface Mount Technology*, 10(1), 37–41. <http://doi.org/10.1108/09540919810203847>
- [6] Zhengxi, H., Xiaohua, J. (2017). The Internal stress and binding force of carbon nanotubes / Pb-Sn composite



- coatings. *Advances in Engineering Research (AER)*, 143, 675 – 680.
- [7] Bakour, Z., Dakhouche, A. (2018). Electrochemical Corrosion of Pb-Sn and Pb-Sb Alloys for Lead-Acid Battery Applications. *Acta Physica Polonica A*, 134(1), 103–105. <http://doi.org/10.12693/APhysPolA.134.103>
- [8] Hu, Z., Jie, X., Lu, G. (2010). Corrosion resistance of Pb-Sn composite coatings reinforced by carbon nanotubes. *Journal of Coatings Technology and Research*, 7(6), 809–814. <http://doi.org/10.1007/s11998-010-9269-y>
- [9] Widiatmoko, P., Nurdin, I., Devianto, H., Prakarsa, B., Hudoyo, H. (2020). Electrochemical reduction of CO<sub>2</sub> to Formic Acid on Pb-Sn Alloy Cathode. *IOP Conference Series Materials Science and Engineering*, 823:012053. <http://doi.org/10.1088/1757-899X/823/1/012053>
- [10] Yang, Z., Oropeza, F. E., Zhang, K. H. L. (2020). P-block metal-based (Sn, In, Bi, Pb) electrocatalysts for selective reduction of CO<sub>2</sub> to formate. *APL Materials*, 8(6):060901
- [11] Bagheri, S. N., Julkapli, N. M. (2014). Titanium dioxide as a catalyst support in heterogeneous catalysis. *Scientific World Journal*, 214, 3–10. <https://doi.org/10.1155/2014/727496>
- [12] Hintshoa, N., Petrika, L., Nechaeva, A. (2014). Photocatalytic activity of titanium dioxide carbon nanotubenano-composites modified with silver and palladium nanoparticles. *Applied Catalysis B: Environmental*, 157, 273–283. <https://doi.org/10.1016/j.apcatb.2014.03.021>
- [13] Salomatina, S. V., Loginova, A. S., Ignatov, S. R. (2016). Structure and catalytic activity of poly (titanium oxide) doped by gold nanoparticles in organic polymeric matrix. *Inorg. Organomet. Polym.*, 26, 1280–1291. <https://doi.org/10.1007/s10904-016-0409-4>
- [14] Plyasovskaya, K. Vargalyuk, V., Sknar, I., Cheremysynova, A., Sigunov, O., Karakurkchi, A. (2017). Research into corrosion and electrocatalytic properties of the modified oxide films on tin. *Eastern European Journal of Enterprise Technologies*, 5(12–89), 39–45. <https://doi.org/10.15587/1729-4061.2017.109710>
- [15] Ilin, V.A. (1971). [Tinning and leading], Moscow, USSR: Mashgiz. (in Russian).
- [16] Hu, Z., Jie, X. (2015). Study of Polyacrylic Acid Dispersing Pb-Sn-CNTs Composite Plating Solution. *5th International Conference on Advanced Design and Manufacturing Engineering*, 978-94-6252-113-1. <https://doi.org/10.2991/icadme-15.2015.401>
- [17] Babichev, A. P., Babushkina, N. A., Bratkovskiy, A. M. (1991). [Physical quantities. Directory]. In I. S. Grigoreva, E. Z. Meylihovala (Ed.). Moscow, USSR: Energoatomizdat. (in Russian).
- [18] Varghaljuk, V. F., Plyasovskaya, K. A., Nester, E. I. (2016). [Electrodeposition of tin in presence of K<sub>2</sub>TiO<sub>3</sub>]. *Visnik Dnipropetrovs'kogo universitetu. Seriâ Himiâ – Bulletin of Dnipropetrovsk university. Series Chemistry*, 24(1), 7–12. (in Russian). <https://doi.org/10.15421/081602>
- [19] Pashina, A. G., Ritter, A. Ya. Varghaljuk, V. F., Plyasovskaya, K. A. (2018). [Pb-Sn alloy with additives of titanium compounds]. *Teoretichni ta eksperimentalni aspekti suchasnoyi himiyi ta materialiv – Theoretical and experimental aspects of modern chemistry and materials*, 71. (in Ukrainian).
- [20] Lyahov, B.F., Kudryavtsev, V.N., Vagramyan, A.T. USSR Patent No. 393370. Moscow, USSR. (in Russian).
- [21] Marchenko, E. M. (1971). [Photometric determination of elements]. Moscow, USSR: Mir. (in Russian).
- [22] Rahmankulov, D. L., Kimsanov, B. H., Chanyishev R. R. (2003). [Physical and chemical properties of glycerin]. Moscow, Russia: Khimiya. (in Russian).
- [23] Girin, O. B., Khlyntsev, V. P. (2000). Mechanism of liquid phase formation in metals during electrodeposition. *Elektronnaya Obrabotka Materialov*, 3, 13–18.
- [24] Girin, O. B. (2017). Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 1. *Surf. Eng. Appl. Electrochem.*, 53, 2, 137-143. <https://doi.org/10.3103/S1068375517020041>
- [25] Girin, O. B. (2017). Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 2. *Surf. Eng. Appl. Electrochem.*, 53, 3, 233-239. <https://doi.org/10.3103/S1068375517030048>
- [26] Girin O. B. (2017). Further evidence of phase formation through a liquid state stage in metals being electrodeposited: part 3. *Surf. Eng. Appl. Electrochem.*, 53, 4, 339-344. <https://doi.org/10.3103/S1068375517040056>
- [27] Girin, O. B., Vorob'ev, G. M. (1987). Mechanism of structure formation in electrolytic coatings. *Russian metallurgy. Metally*, 4, 148-152.
- [28] Girin, O. B., Korolyanchuk, D. G. (2020). Electrochemical phase formation of metals and alloys at chemically identical solid or liquid cathode: part 1 – metals. *Surf. Eng. Appl. Electrochem.*, 56, 1, 28-40. <https://doi.org/10.3103/S1068375520010068>
- [29] Huang, M., Yu., S., Lin, B., Dongn, L., Zhang, F., Fan, M., Wang, L., Yu, J., Deng, Ch. (2014). Influence of preparation methods on the structure and catalytic performance of SnO<sub>2</sub>-doped TiO<sub>2</sub> photocatalysts. *Ceramics Int.*, 40, 13305–13312. <https://doi.org/10.1016/j.ceramint.2014.05.043>
- [30] Velichenko, A. B., Knysh, V. A., Luk'yanenko, T. V., Nikolenko, N. N. (2016). Electrodeposition of PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials from suspension electrolytes. *Theor. Exp. Chem.*, 52, 127–131. <https://doi.org/10.1007/s11237-016-9461-y>
- [31] Petrukhyna, O. M. (1992). [Analytical chemistry. Chemical methods of analysis]. Moscow, Russia: Khimiya. (in Russian).
- [32] Golovko, D. A., Belyanovskaya, E. A. (1999). [Self-activation of a tin electrode modified by anodic treatment in an alkaline solution]. *Voprosy khimii i khimicheskoi technologii – Issues of Chemistry and Chemical Technology*, (1), 84–86 (in Russian). 31996–32002 <https://doi.org/10.1039/C8RA05345F>