

Condensed Matter and Interphases

Kondensirovannye Sredy i Mezhfaznye Granitsy
<https://journals.vsu.ru/kcmf/>

Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9262>

Electrocrystallisation of Cu-Sn-TiO₂ composite coatings in sulphuric acid electrolytes

A. A. Kasach¹✉, D. S. Kharytonau², I. M. Zharskii¹, I. I. Kurilo¹

¹Belarusian State Technological University
13a Sverdlova st., Minsk 220006, Belarus

²Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
8 Niezapominajek, Krakow 30-239, Poland

Abstract

The aim of the article is to determine the peculiarities of electrochemical production of Cu–Sn–TiO₂ composite coatings in sulphuric acid electrolytes with intermittent agitation under stationary and pulsed modes of electrolysis.

Linear voltammetry and static and pulsed chronopotentiometry were used to study the kinetic features of electrocrystallisation of Cu–Sn–TiO₂ composite coatings in a sulphuric acid electrolyte with intermittent agitation. When the electrolyte was stirred, the cathodic potential shifted towards electropositive values. It was shown that after switching the agitation off, the value of the cathodic potential at which the copper-tin alloy forms at a cathodic current density of -0.013 A/cm^2 was reached within 70 s and when using pulsed electrolysis, it was reached within 80 s. Scanning electron microscopy established that the most homogeneous and uniform Cu–Sn–TiO₂ coatings were formed when pulsed electrolysis was used.

Intermittent agitation of the sulphuric acid electrolytes led to the formation of ordered multilayer structures consisting of microlayers of the Cu–Sn alloy and copper due to the intermittent elimination of diffusion limitations for the discharge of copper(II) ions when agitation was switched on, which resulted in suppression of the process of the underpotential deposition of tin.

Keywords: Electrocrystallisation, Formation of alloys, Composite coating, Pulsed electrolysis, Structure

Funding: This research was funded by the Ministry of Education of the Republic of Belarus as part of the State Research Programme “Mechanics, metallurgy, and diagnostics in machinery construction” (2016–2020), subprogramme “Electroplating”, order No. 4.1.28 “Electrochemical composite coatings based on tin alloys with photocatalytic properties” (2019–2020, state registration number 20212333).

For citation: Kasach A. A., Kharytonau D. S., Zharskii I. M., Kurilo I. I. Electrocrystallisation of Cu–Sn–TiO₂ composite coatings in sulphuric acid electrolytes. *Condensed Matter and Interphases*. 2022;24(2): 220–226. <https://doi.org/10.17308/kcmf.2022.24/9262>

Для цитирования: Касач А. А., Харитонов Д. С., Жарский И. М., Курило, И. И. Электрокристаллизация композиционных покрытий Cu–Sn–TiO₂ в сернокислых электролитах. *Конденсированные среды и межфазные границы*. 2022;24(2): 220–226. <https://doi.org/10.17308/kcmf.2022.24/9262>

✉ Aliaksandr A. Kasach, e-mail: kasach2018@bk.ru

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1. Introduction

Electrochemical copper and tin alloys are characterised by high hardness, wear resistance, and corrosion resistance [1, 2]. Alloys containing up to 20 wt% of Sn (yellow bronzes) are used as protective and decorative coatings, as well as a sublayer before chrome plating [3, 4]. Recently, these alloys have attracted a wide attention due to their antibacterial activity against many Gram positive and Gram negative bacteria [5–8]. Unlike copper coatings, which are characterised by low wear resistance, fade quickly in the air, and lose their decorative appearance, copper-tin alloys are less susceptible to wear and corrosion [9, 10].

Sulphuric acid electrolytes can be used for electrochemical production of yellow bronzes [11–13]. This type of electrolyte is characterised by low toxicity. What is more, wastewater generated as a result of their application is easily regenerated and disposed. In sulphuric acid electrolytes, the process of alloy formation can occur at potentials with higher positive values than those of the standard electrode potential of the Sn²⁺|Sn⁰ system (–0.136 V) [13, 14]. In order to obtain homogeneous and fine-grained coatings, special organic additives are added to sulphuric acid electrolytes: thiourea [14], quaternary ammonium salts [15], gelatin [16], synthanol, etc. [17]. Among the disadvantages of sulphuric acid electrolytes used for the deposition of Cu-Sn alloys are their low covering and scattering power, as well as narrow intervals of cathodic current densities providing for homogeneous and shiny coatings [15]. In [15], it was found that pulsed electrolysis with a relative current pulse duration of 1.5 and a frequency of 66.7 Hz allows expanding the working range of cathodic current densities, at which semi-shiny yellow bronze coatings are formed, almost by four times. The formation of copper and tin alloys in sulphuric acid electrolytes occurs if the duration of the cathodic current pulse exceeds the value of the transition time of the discharge process of copper(II) ions. The modification of the Cu-Sn matrix by TiO₂ nanoparticles hardens it and improves the antibacterial properties of coatings [18]. In [19] it was shown that the introduction of TiO₂ nanoparticles in the amount of 1 to 10 g/dm³ into the sulphuric acid electrolyte at a deposition potential of –0.05 V leads to the production

of composite electrochemical coatings (CECs) containing between 0.17 and 1.72 wt% of TiO₂. The potentiostatic electrolysis ensures the formation of coatings with homogeneous distribution of the alloy components. In industry, galvanostatic electrolysis is mainly used for electrochemical deposition of metals and alloys since using potentiostatic modes on an industrial scale is difficult. In the case of galvanostatic electrolysis, electrolyte stirring significantly influences cathodic polarisation, which, in turn, can affect the quantitative composition of the formed Cu-Sn alloy.

The aim of the work was to determine the peculiarities of the electrochemical production of Cu-Sn-TiO₂ composite coatings in sulphuric acid electrolytes with intermittent agitation under the stationary and pulsed modes of electrolysis.

2. Experimental

An electrolyte of the following composition was used for the electrochemical deposition of Cu-Sn coatings, g/dm³: CuSO₄·5H₂O – 40; SnSO₄ – 40; CS(NH₂)₂ (thiourea) – 0.005; H₂SO₄ – 100. The electrolysis was carried out without agitation of the electrolyte at a cathodic current density of 0.013 A/cm². When obtaining the Cu-Sn-TiO₂ CEC, TiO₂ nanoparticles (Degussa aeroxide P25) in the amount of 5 g/dm³ were introduced into the basic composition. In order to deagglomerate the particles in the electrolyte for the CEC application, it was sonicated for 20 min using a UP 200 Ht homogenizer (Hielscher Ultrasonics GmbH, Teltow, Germany). To maintain the TiO₂ particles in suspension, during the precipitation process of the CEC the electrolyte was agitated intermittently with a magnetic stirrer every 5 min for 10 s (stirring rate of 400 rpm). The electrolysis was carried out using both stationary and pulsed modes. When using stationary electrolysis, the cathodic current density was 0.013 A/cm². The parameters of pulsed electrolysis: relative pulse duration – 1.5; pulse frequency – 66.7 Hz; cathodic density of the pulse current – 0.0225 A/cm². The parameters of stationary and pulsed modes of electrolysis used in the work were selected based on the results of previous studies [15] and provided high-quality and homogeneous yellow bronze coatings. The cathodes were pieces of copper-foiled dielectric. M0 copper was used for

the anodes. The dimension of the working surface of the electrodes was 6 cm².

Cathodic polarisation curves and chronopotentiograms of copper electrode in electrolytes used for the application of the Cu-Sn alloy and CECs based on it were taken in a standard three-electrode cell using an Elins P40X potentiostat/galvanostat (Electrochemical Instruments, Russia). The polarisation curves of the copper electrode were taken at a linear potential sweep rate of 1 mV/s. A saturated silver/silver chloride electrode was used as the reference and a M0 copper plate was used as the counter electrode. The values of electrode potentials were recalculated in the scale of the standard hydrogen electrode. To obtain reliable results, all electrochemical studies were carried out at least three times.

The morphology, qualitative, and quantitative compositions of the formed coatings were studied using a JSM-5610 LV scanning electron microscope (Jeol Ltd.) equipped with a JED-2201 energy dispersion X-ray (EDX) analyser. The accelerating voltage for surface imaging and elemental analysis was 20 kV.

3. Results and Discussion

To assess the effect of electrolyte mixing on the kinetic features of electrodeposition of coatings, polarisation curves of the copper electrode in electrolytes used for the application of Cu-Sn (Fig. 1, curve 1) and Cu-Sn-TiO₂ (Fig. 1, curves 2, 3) were obtained. In the used electrolytes, the process of copper and tin codeposition could occur in the range of cathodic potentials from 0.0 to -0.136 V, i.e., at potentials corresponding to the process of underpotential deposition of Sn [14]. When 5 g/dm³ of TiO₂ was introduced into the studied electrolyte within the potential range of -0.01–(-0.06) V, the cathodic polarisation curves of the copper electrode shifted towards negative values and the cathodic current density decreased and reached 4±1.5 mA/cm² at a potential of -0.04 V, which indicated the inhibition of the process of the reduction of copper(II) ions. The agitation of the electrolyte used to deposit Cu-Sn-TiO₂ had a depolarising effect (Fig. 1, curve 3) due to a decrease in the diffusion limitations for the discharge of copper(II) ions. Codeposition of tin and copper was possible when the discharge of

copper(II) ions occurred at the limiting diffusion current [14]. Mechanical mixing of the electrolyte helped to remove the diffusion limitations for the discharge of copper(II) ions, however, it did not provide a uniform mass transfer over the volume of the cell and the area of the cathode [19]. This, in turn, led to the formation of either copper coatings or Cu-Sn coatings with a low tin content. Thus, constant agitation of electrolyte prevented the formation of Cu-Sn coatings corresponding to the composition of yellow bronze. Therefore, the electrolyte should be agitated intermittently to obtain Cu-Sn-TiO₂ CECs.

Fig. 2 shows the chronopotentiograms of the copper electrode during the deposition of the Cu-Sn alloy (Fig. 2a, curve 1) and the Cu-Sn-TiO₂ CEC (Fig. 2a, curve 2). The introduction of TiO₂ particles of the modifying phase into the electrolyte led to a slight shift of the *E*-*t*-dependency towards the electronegative values. The authors of [19] suggested that the increase in electrode polarisation during the deposition of the Cu-Sn-TiO₂ CEC may be due to the adsorption of the modifying phase particles on the surface of the growing precipitate, which, in turn, may reduce the active area of electrode involved in the electrochemical reaction. When the agitation of the electrolyte was switched on (*t* = 300 s), the cathodic potential shifted towards positive values from -0.07 to 0.07–0.10 V. After the magnetic stirrer was turned off (*t* = 310 s),

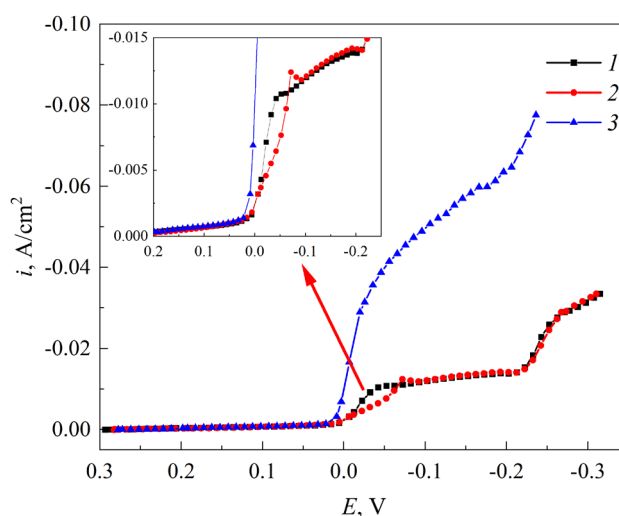


Fig. 1. Cathodic polarisation curves of the copper electrode in electrolytes used for the application of Cu-Sn (curve 1) and Cu-Sn-TiO₂ (curve 2, 3); 1, 2 – without stirring the electrolyte; 3 – mechanical stirring

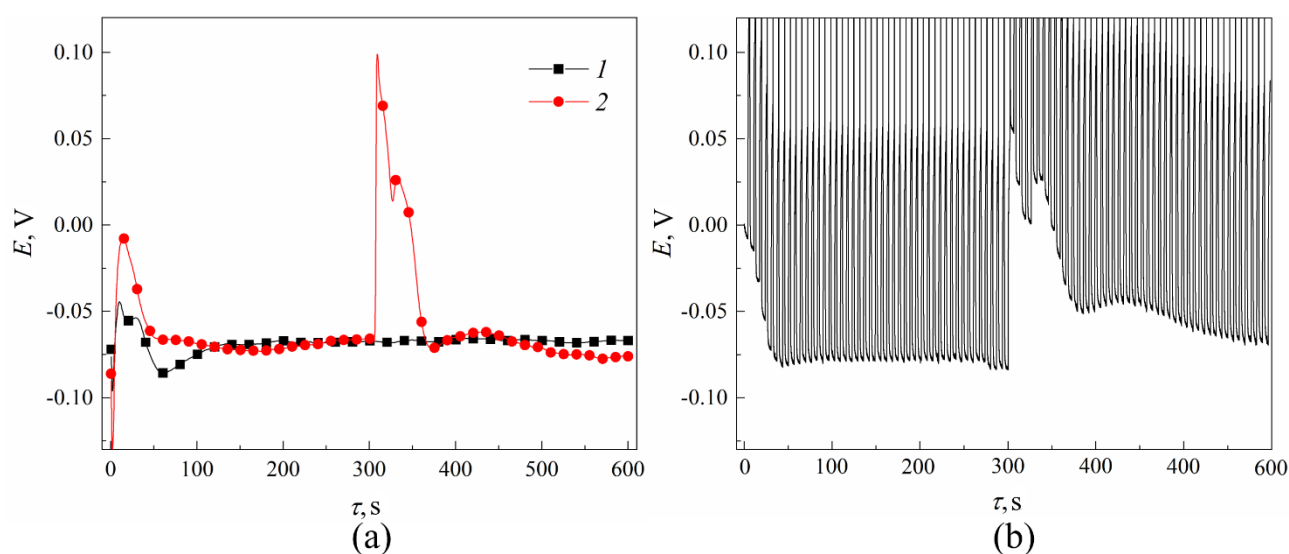


Fig. 2. Chronopotentiograms of the copper electrode in electrolytes used for the application of Cu-Sn (*a*, curve 1) and Cu-Sn-TiO₂ (*a*, curve 2; *b*). Electrolysis mode: *a* – stationary; *b* – pulsed

there was a gradual increase in the cathodic polarisation of the electrode, which was due to the contribution of the diffusion overvoltage. The value of the cathodic potential corresponding to the formation of the Cu-Sn alloy was reached 60 seconds after the magnetic stirrer was turned off. When using pulsed electrolysis (Fig. 2b), it took longer for the constant value of the cathodic potential to be reached (70–80 s) after mixing was switched off, which was due to the relaxational effect of the pause.

Fig. 3 shows micrographs of the obtained Cu-Sn and Cu-Sn-TiO₂ coatings. Under stationary conditions, at a cathodic current density of 0.013 A/cm² (Fig. 3a), fine-grained and homogeneous Cu-Sn coatings were formed. The introduction of TiO₂ nanoparticles into the electrolyte led to the formation of rough and less uniform coatings (Fig. 3b, c). The surface of the Cu-Sn-TiO₂ CEC included globules whose size

varied between 5 and 20 μm. Coatings obtained by pulsed electrolysis (Fig. 3c) were characterised by a more uniform and smoother structure.

The table presents data on the elemental composition of the obtained coatings. The cathodic current density of 0.013 A/cm² and stationary conditions resulted in the formation of Cu-Sn coatings containing up to 10.9 wt% of Sn. The introduction of TiO₂ nanoparticles in the amount of 5 g/dm³ in the composition of the electrolyte led to an increase in the content of tin in the coating to 12.6 wt%, which was due to an increase in cathodic polarisation during the formation of the alloy (Fig. 1, curve 2). The obtained coating contained 0.8 wt% of Ti which was present due to the integration of TiO₂ nanoparticles into the metal Cu-Sn matrix.

The pulsed mode of electrolysis allowed obtaining coatings of the following composition, wt.%: Cu – 87.2; Sn – 12.1; Ti – 0.7. It should be

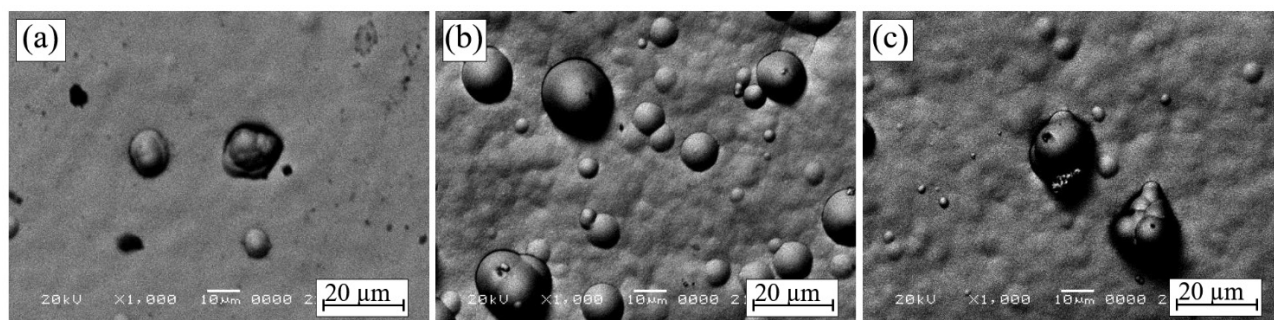


Fig. 3. Micrographs of the surface of Cu-Sn (*a*) and Cu-Sn-TiO₂ (*b*, *c*) coatings. Electrolysis mode: *a*, *b* – stationary; *c* – pulsed

Table. Elemental composition of the surface of Cu-Sn and Cu-Sn-TiO₂ coatings (scanning area of 50×50 μm)

Coating	Current density, A/cm ²	Pulse frequency, Hz	Content in the alloy, wt%		
			Cu	Sn	Ti
Cu-Sn	0.013	–	89.1	10.9	–
Cu-Sn-TiO ₂	0.013	–	86.6	12.6	0.8
Cu-Sn-TiO ₂	0.0225	66.7	87.2	12.1	0.7

noted that the change in the electrolysis mode did not significantly affect the quantitative content of the TiO₂ particles in the alloy.

Fig. 4 shows crosscut SEM images of Cu-Sn (Fig. 4a) and Cu-Sn-TiO₂ coatings (Fig. 4b, c). The obtained coatings had a clear boundary with the substrate metal and were characterised by high adhesive power. The crosscut of the Cu-Sn-TiO₂ coating obtained by stationary electrolysis had defects in the form of globules and microcracks. The crosscuts of CuSn-TiO₂ CECs deposited by means of the pulsed electrolysis had no pronounced defects, which is probably due to the uniform microdistribution of current over the surface of the growing precipitate.

Over the entire thickness of the Cu-Sn-TiO₂ CEC, there were areas (layers) with different image contrasts, which were evenly distributed over the entire thickness of the coatings. The thickness of light sections varied from 3 to 5 μm, while that of dark sections was less than 1 μm. When using the backscattered electrons, this contrast distribution indicated a different elemental composition of these coating regions.

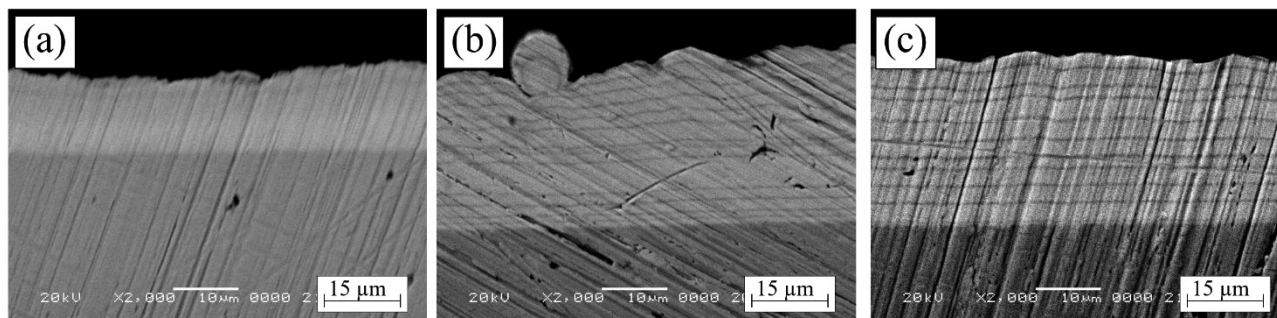
In order to establish the elemental composition and nature of areas of different contrasts, their EDX point analysis was carried out (Fig. 5).

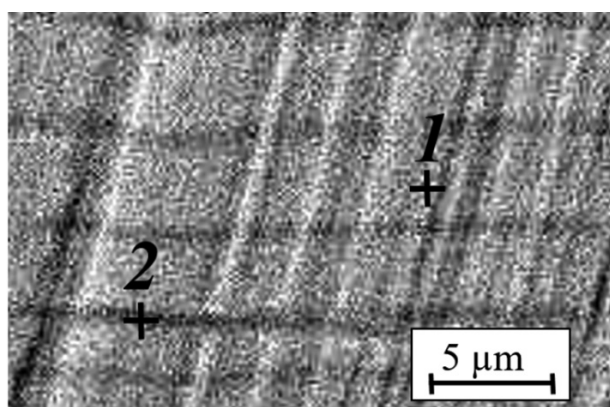
According to the obtained data, dark areas of the coatings were characterised by a lower

content of tin. The ratio of the mass content of tin in the alloy between the light and dark areas was approximately 4 : 1. Stirring of the electrolyte led to depolarisation of the electrode and removal of diffusion limitations for the discharge of copper(II) ions, which made the underpotential deposition of tin impossible to achieve. Thus, when the agitation of the electrolyte was switched on, in order to maintain TiO₂ particles in suspension, ordered alloy layers enriched in copper were formed. Codeposition of copper and tin was observed when agitation was switched off and when the transition time of the discharge of copper(II) ions was reached.

4. Conclusions

In sulphuric acid electrolytes used for the application of the Cu-Sn alloy and the Cu-Sn-TiO₂ composite coatings in the absence of agitation, copper and tin codeposition takes place at potentials corresponding to the process of underpotential deposition of Sn. Introduction of TiO₂ nanoparticles in the amount of 5 g/dm³ into the composition of the electrolyte helps to inhibit the reduction of copper(II) ions and reduces its content in the coating by ≈3 wt%. Application of pulsed electrolysis at a relative current pulse duration of 1.5, a frequency of 66.7 Hz, and cathodic current density of 0.0225 A/cm²

**Fig. 4.** Micrographs of sections of Cu-Sn (a) and Cu-Sn-TiO₂ (b, c) coatings. Electrolysis mode: a, b – stationary; c – pulsed



Point	Chemical Composition, wt. %		
	Cu	Sn	Ti
1	85.9	13.4	0.7
2	96.1	3.5	0.4

Fig. 5. Micrographs of sections and the data of the EDX point analysis for the Cu-Sn-TiO₂ coating section obtained by means of pulsed electrolysis

allows obtaining Cu-Sn-TiO₂ CECs of similar composition (≈ 0.7 – 0.8 wt% of titanium, 12.1 – 12.6 wt% tin) but more homogeneous and uniform than those formed by the stationary mode at a cathodic current density of 0.013 A/cm².

Intermittent agitation of the sulphuric acid electrolytes leads to the formation of ordered multilayer structures consisting of microlayers of the Cu-Sn and copper alloy due to the intermittent elimination of diffusion limitations for the discharge of copper(II) ions when agitation is switched on, which results in suppression of the process of the underpotential deposition of tin. When agitation is switched off, the value of the cathodic potential at which the alloy of copper and tin forms at a cathodic current density of -0.013 A/cm² is reached within 70 s and when using pulsed electrolysis, it is reached within 80 s.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about authors

Aliaksandr A. Kasach, Assistant at the Department of Chemistry, Technology of Electrochemical Production and Electronic Engineering Materials, Belarusian State Technological University (Minsk, Belarus).

<https://orcid.org/0000-0001-5522-2928>
kasach2018@bk.ru

Dzmitry S. Kharytonau, PhD in Chemistry, postdoctoral fellow at Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences (Krakow, Poland).

<https://orcid.org/0000-0003-2071-3975>
dmitry.kharitonov@ikifp.edu.pl

Ivan M. Zharskii, Cand. Sci. (Chem.), Associate Professor at the Department of Chemistry, Technology of Electrochemical Production and Electronic Engineering Materials, Belarusian State Technological University (Minsk, Belarus).

<https://orcid.org/0000-0002-3942-5175>

Irina I. Kurilo, Cand. Sci. (Chem.), Associate Professor at the Department of Physical, Colloid, and Analytical Chemistry, Belarusian State Technological University (Minsk, Belarus).

<https://orcid.org/0000-0002-0016-6719>
september@tut.by

Received 09.12.2021; approved after reviewing 15.02.2022; accepted for publication 15.04.2022; published online 25.06.2022.

Translated by Irina Charychanskaya

Edited and proofread by Simon Cox