УДК 621.357.74

DEPOSITION CONDITIONS AND CRITICAL INFLUENCE OF ORGANIC ADDITIVES ON THE STRUCTURE AND MORPHOLOGY OF BISMUTH COATINGS

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XRD analysis showed that bismuth coatings formed from perchlorate electrolyte have a rhombohedral type of crystal lattice, the most intense reflex of Bi is (012). The number of organic additives adding into the electrolyte leads changing in the texture of the coatings growth, for example, in presence of acridine yellow and safranin violet, the most intense Bi reflex becomes (110). Surface morphology investigation using a scanning electron microscope showed that coatings obtained without organic additives, as well as in the presence of safranin violet, have the lager crystallite sizes (tens of microns) with different growth textures. The crystallite sizes decrease in the presence of resorcinol and synthanol with the same Bi growth texture (012). The most fine-grained, dense and uniform coatings were obtained with simultaneous syntanol and resorcinol adding into the electrolyte.

Key words: electrodeposition; bismuth; perchloric electrolyte; organic additives; coatings.

Acknowledgements. The work was carried out with financial support of Belarusian Republican Foundation for Fundamental Research (grant No. T17M-046).

Образец цитирования:
Тишкевич Д. И., Грабчиков С. С., Цыбульская Л. С., Шендюков В. С., Перевозников С. С., Позняк С. К., Труханов А. В. Влияние органических соединений и режимов осаждения на структуру и морфологию висмутовых покрытий // Журн. Белорус. гос. ун-та. Химия. 2018. № 1. С. 14–21 (на англ.).

For citation:
Tishkevich D. I., Grabchikov S. S., Tsybulskaya L. S., Shendyukov V. S., Perevoznikov S. S., Poznyak S. K., Trukhanov A. V. Deposition conditions and critical influence of organic additives on the structure and morphology of bismuth coatings. *J. Belarus. State Univ. Chem.* 2018. No. 1. P. 14–21.

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ВЛИЯНИЕ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ И РЕЖИМОВ ОСАЖДЕНИЯ НА СТРУКТУРУ И МОРФОЛОГИЮ ВИСМУТОВЫХ ПОКРЫТИЙ

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Методом рентгенофазового анализа показано, что покрытия, полученные из перхлоратного электролита висмутирования, имеют ромбоэдрический тип кристаллической решетки, самым интенсивным рефлексом является Bi(012). Введение в электролит ряда органических соединений приводит к изменению текстуры роста покрытий: например, при добавлении акридинового желтого и сафранинового фиолетового наиболее интенсивным рефлексом становится Bi(110). Исследование морфологии поверхности с помощью сканирующего электронного микроскопа выявило, что покрытия, полученные в отсутствие органических соединений, а также в присутствии сафранинового фиолетового, имеют наиболее крупные размеры кристаллитов (десятки микрон) с разной текстурой роста. В присутствии резорцина и синтанола размеры кристаллитов уменьшаются при одинаковой текстуре их роста Bi(012). Наиболее мелкозернистые, плотные и однородные покрытия получены при одновременном введении в электролит синтанола и резорцина.

Ключевые слова: электрохимическое осаждение; висмут; перхлоратный электролит; органические соединения; покрытия.

Благодарность. Работа выполнена при финансовой поддержке Белорусского республиканского фонда фундаментальных исследований (грант № Т17М-046).

Introduction

Nowadays, the problem of Bi deposition has attracted attention of the scientific community because of bismuth's unique electrical, chemical and physical properties. Bismuth has found application in electroanalytical chemistry as a new promising environmentally safe electrode for the heavy metals analysis in place of a poisonous mercury dropping electrode [1–4]. Bismuth deposited on various metals is used as protective and antifriction coatings due to chemical resistance and mechanical properties [5]. Bismuth sub-monolayers on some noble metal surfaces have shown enhanced catalytic activity, particularly the two-electron reduction of H_2O_2 to H_2O, the reduction of O_2 in aqueous fuel cells [6; 7], as well as the oxidation of formic on Pt [8–12]. The coatings based on bismuth have shown thermoelectric efficiency [13; 14], large magnetoresistance [15–17] and interesting quantum effects [18]. Bismuth is also used like perspective electrochromic material for electronic devices [19; 20], for resistance and rectifying contacts producing on semiconductors [21] and for films with a giant magnetoresistive effect for magnetic field sensors [22]. Uses of bismuth contents composites offer a very attractive alternative to lead protection from gamma irradiation due to the much more environmentally friendly bismuth [23; 24].

Much attention of the bismuth deposition literature has focused onto noble metals and growth onto non-metallic substrates, such as glassy carbon [25] and semiconductors [26–28]. There is a limited number of authors dealing with continuous bismuth films onto metallic substrates by electrodeposition [29; 30]. The main goal of this paper is to investigate high-speed electrolyte that would obtain thick-layer Bi coatings. Our purpose is the Bi coatings production by the electrochemical deposition method, because this method has significant number of advantages. First of all, it is high growth rate and the possibility of thick coatings producing; for another thing, it is good adhesion to the substrate; thirdly, it is the possibility of a controlled microstructure changing (the grain size, film texture and coating density) due to technological parameters variation; finally it is electrolyte composition changing owing to the adding of various organic additives.

Experimental

Samples of Bi coatings were electrodeposited from an acid perchlorate electrolyte which was prepared from bismuth(III) hydroxide and concentrated perchloric acid solution (concentration – 65 %, density – 1.569 $g \cdot cm^{-3}$) with rapid mixing. Bismuth deposition was produced in galvanostatic regime at the 23–60 °C temperature range onto aluminum substrates 0.4 mm thickness. Bismuth rods were used as anodes. The electrochemical experiments were carried out using a power source B5-78/6 as a stabilized current source. Organic additives of different chemical nature were added into the bismuth electrolyte at a concentration of 1 g/L. Each concentration was 0.5 g/L with simultaneous addition of two additives.

Coatings surface morphology investigation was realized on scanning electronic microscope (SEM) LEO 1455VP with console for measuring the diffraction of reflected electrons. X-ray diffraction (XRD) analysis of bismuth coatings was performed on a PanAnalytical Empyrean diffractometer using monochromatized CuK_α irradiation.

The deposition process polarization voltammetric studies in various electrolytes were conducted using the potentiostat-galvanostats PI 50 Pro2 and Autolab PGSTAT302N. The measurements in a three-electrode two-chamber cell equipped with a platinum auxiliary electrode and a saturated solution of a chloride-silver electrode with a Luggin capillary were performed. The required temperature level was maintained by thermostatic water-jacket connected to an ultratermostat. Polarization measurements in the potentiodynamic regime at a potential sweep rate of 1 mV/s to obtain quasistationary current values were taken. A freshly deposited bismuth coatings with a 5 μm thickness on a copper foil with 1 cm^2 area was used as working electrodes. The non-working electrode surface was isolated with a chemically resistant varnish Lacomit. Electrolyte mixing in electrochemical cell was performed by means of a magnetic stirrer with 600–800 rpm.

Results and discussion

Polarization measurements were realized in a perchlorate electrolyte containing 0.174 mol/L $Bi(ClO_4)_3$ and 3 mol/L $HClO_4$ at 23, 40 and 60 °C temperature with mixing and without for the purpose of bismuth electrodeposition conditions optimizing. It can be seen that the bismuth deposition begins at ~30 mV potential (relative to a saturated chloride-silver reference electrode) from the current-voltage curves presented in fig. 1. These values are close to the bismuth electrode equilibrium potential in a given solution. At the beginning the Bi^{3+} ions discharge occurs in kinetic, then in mixed diffusion-kinetic and, finally, diffusion modes (see fig. 1, curve *1*). The current region occurrence in the potential range from minus 200 mV to minus 500 mV indicates the diffusion character of the process. The current region with the electrolyte mixing drops out (see fig. 1, curve *2*). The cathode current begins to sharply rise at potentials less than minus 500 mV. As a result, an easily removable loose powdery precipitate creation at the electrode is observed. The dendritic formation process arising can be associated with the onset of hydrogen evolution in this potential region.

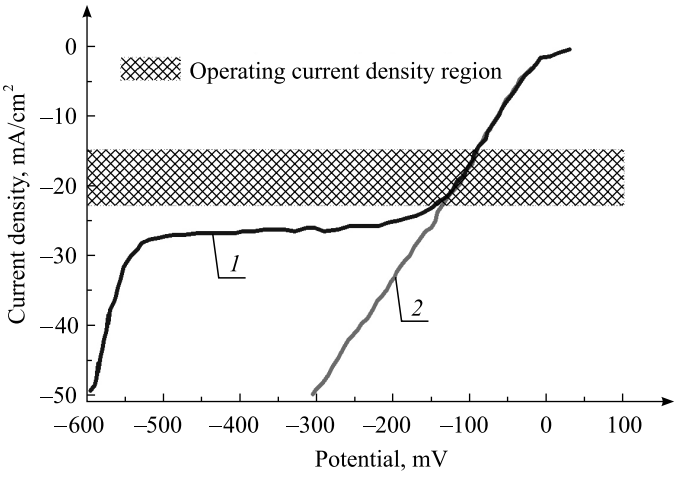

Fig. 1. Bismuth deposition volt-ampere curves
from perchlorate electrolyte (0.174 mol/L $Bi(ClO_4)_3$
and 3 mol/L $HClO_4$, T = 23 °C) without mixing (curve *1*) and with mixing (curve *2*)

The electrolyte temperature influence on the character of the current-voltage curves are illustrated in fig. 2. It can be seen from the figure that the temperature rise results in a noticeable drop in the diffusion current plateau and the increment in the absolute current density values: ~25, ~50 and ~80 mA/cm^2 for 23, 40 and 60 °C temperatures, respectively. This process also leads to potential shift of the dendritic formation beginning to the region of more positive potentials (see fig. 2, curves *1–3*). The bismuth deposition process effectively proceeds in the kinetic regime with mixing. Moreover the current-voltage curve slope ratio is substantially higher at the temperature of 60 °C than when the process is carried out at a temperature of 23 °C (see fig. 1, curve *2* and fig. 2, curve *2*).

A number of organic additives of various chemical nature, capable of effective adsorption on a bismuth surface have been tested to improve the bismuth coatings quality (increasing density, plasticity and flatness). Such additives as benzene derivatives (resorcinol, cresol), oxyethylated alcohol (synthanol), coloring agent (acridine yellow, safranin violet) were chosen. Figure 3 shows the bismuth deposition current-voltage curves

with and without of various organic additives and without electrolyte mixing. The cresol, resorcinol and sintanol adding into the electrolyte leads to an overvoltage growth in the curve kinetic part and an insignificant increas in the limiting diffusion current region. The dendrite formation area transition occurs at potentials more negative than minus 600 mV (see fig. 3, curves *2–4*). Quite another situation takes place when acridine and safranin coloring agents are introduced into electrolyte. In this case, the kinetic region overvoltage sharply decreases, which may indicate a change in the Bi(III) electrode reduction mechanism with these coloring agents. The limiting diffusion current region in the case of the safranin agent visibly increases with dendrite formation area beginning displacement up to minus 700 mV.

This region for the acridine agent remains practically unchanged, with a subsequent decrease in the curve slope in the dendritic area (see fig. 3, curves *5* and *6*).

The most significant effect on the Bi(III) cathodic reduction is achieved by adding syntanol and resorcinol in combination: bismuth electrocrystallization overvoltage is augmented in the kinetic region, diffusion current area becomes less signified, the dendrite formation potential shifts (down to minus 800 mV) to the negative potential region (see fig. 3, curve *7*).

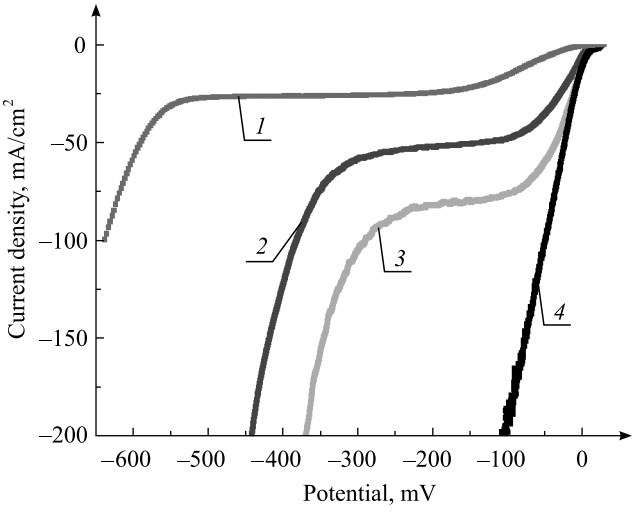

Fig. 2. Bismuth deposition polarization curves
from perchlorate electrolyte (0.174 mol/L $Bi(ClO_4)_3$ in mol/L $HClO_4$)
at 23 °C (curve *1*), 40 °C (curve *2*) and 60 °C (curves *3* and *4*) with mixing (curve *4*)
and without electrolyte mixing (curves *1–3*)

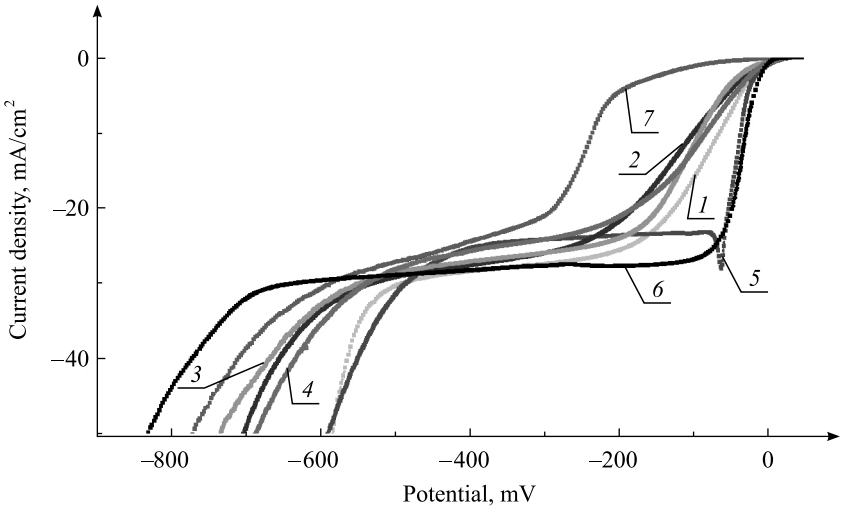

Fig. 3. Bismuth deposition polarization curves
from perchlorate electrolyte (0.174 mol/L $Bi(ClO_4)_3$ in 3 mol/L $HClO_4$, $T = 23$ °C)
without additives (curve *1*) and with additives of different chemical nature (1 g/L):
cresol (curve *2*), resorcinol (curve *3*), synthanol (curve *4*), acridine yellow (curve *5*),
safranin violet (curve *6*), synthanol and resorcinol (curve *7*)

XRD diffraction data (fig. 4) showed that bismuth coatings have a rhombohedral crystal structure (space group $R-3m$). However, the bismuth lattice is commonly described as a hexagonal primitive cell. In this paper we use the three-index Miller system of indices rather than the four-index Miller – Bravais system [31]. All of the diffraction patterns can be indexed to bismuth with lattice parameters $a = 0.455$ nm and $c = 1.186$ nm. It is important to emphasize that coatings with a signified texture (012) are formed in the electrolyte without additives. This texture is retained by adding into the electrolyte the organic additives, which we have studied, such as cresol, resorcinol, synthanol. However, in the presence of coloring agents (acridine yellow and safranin violet), the growth texture changes (see fig. 4, *b*), the most intense reflex becomes (110).

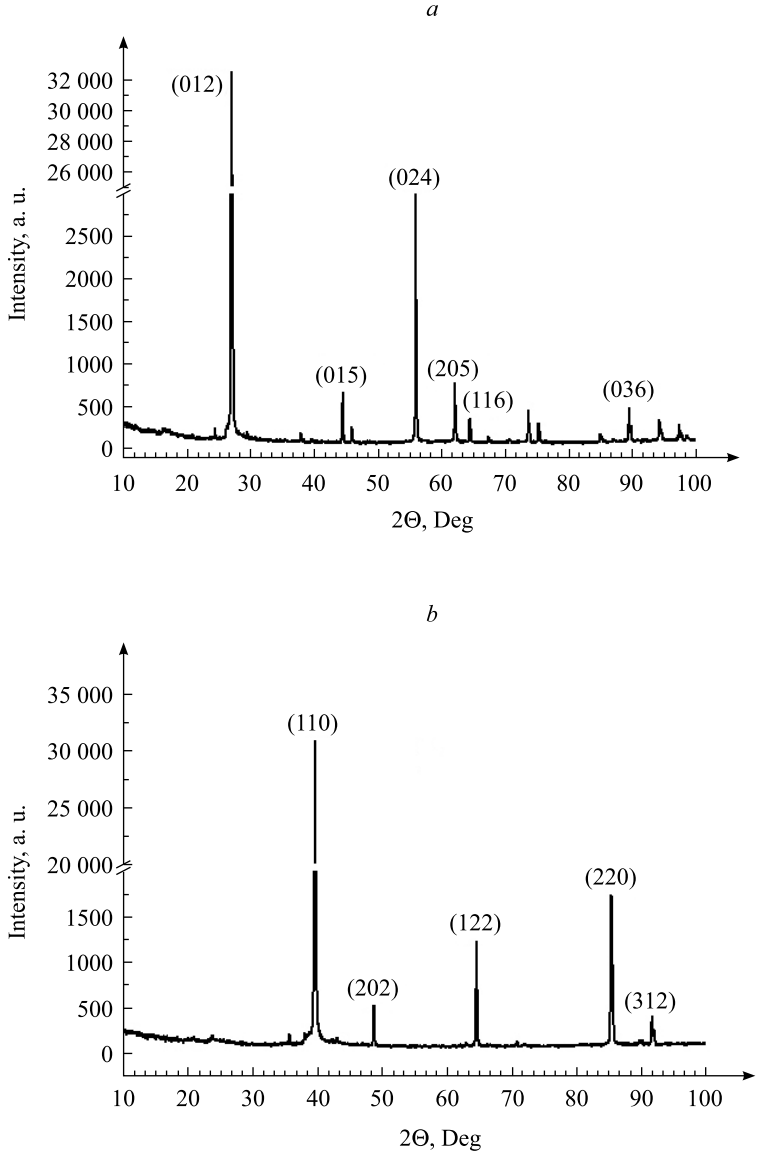

Fig. 4. XRD patterns (CuK_α) of bismuth coatings electrodeposited from perchlorate electrolyte without (*a*) and with safranin coloring agent (*b*). The current density is 23 mA/cm^2, the electrolyte temperature is 23 °C, and the coating thickness is 600 μm

The investigation of same thickness (600 μm) coatings surface morphology using SEM showed that films electrodeposited without additives, as well as with safranin coloring agent, eventually form crystalline coatings with a block size of tens of microns, but with different texture growth (fig. 5, *a*, *b*). Moreover in the presence of additives such as resorcinol, cresol and synthanol, the microcrystalline blocks size decreasing with the same growth texture is observed, but more dense and flat coating is formed. The decrease in the microcrystalline blocks size is particularly significant in cases of simultaneous syntanol and resorcinol adding into the electrolyte (see fig. 5, *f*). In this case, a close grained, flat coating of good quality is formed.

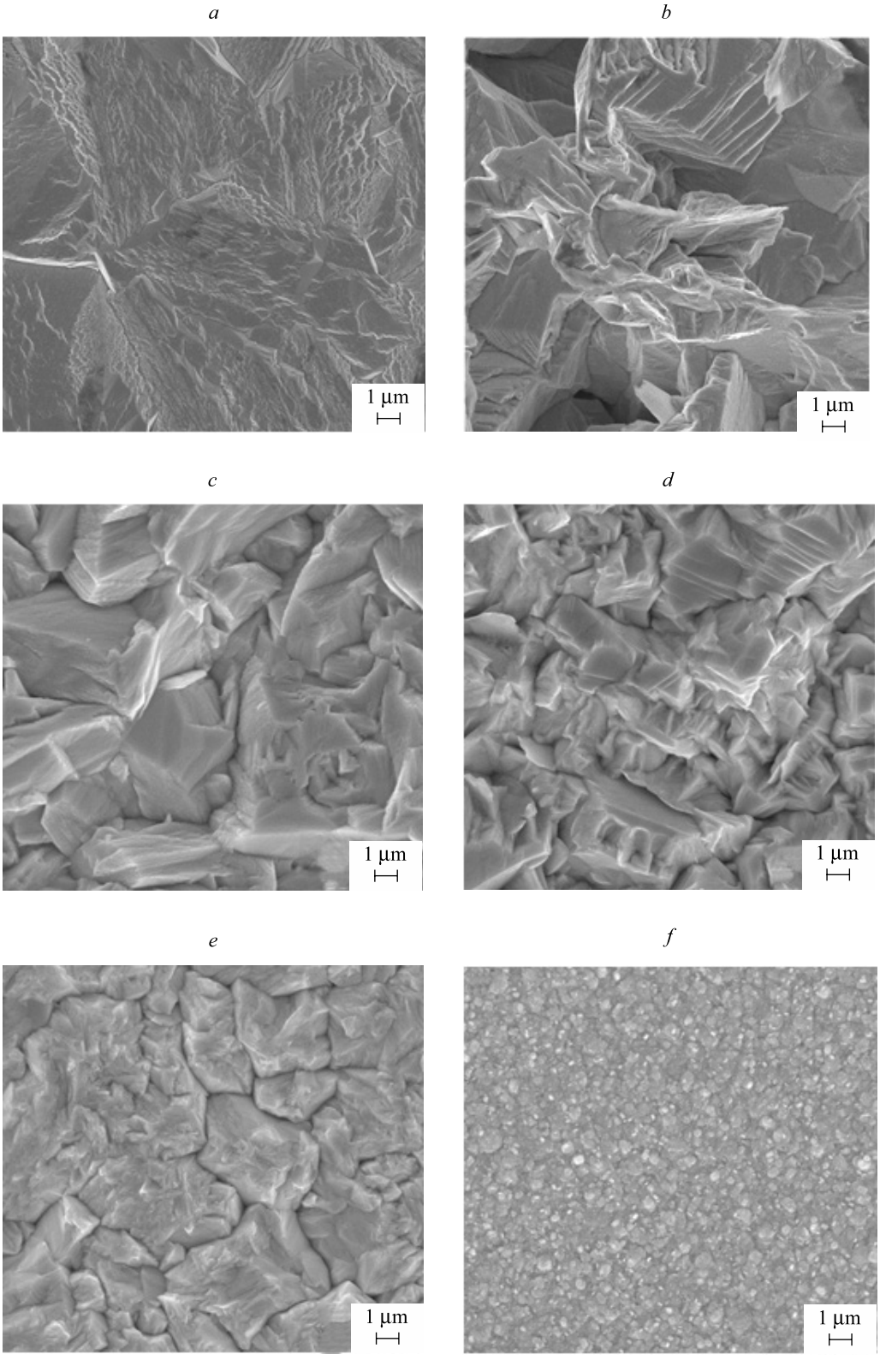

Fig. 5. SEM of the bismuth coatings surface electrodeposited without (*a*) and with organic additives (1 g/L): safranin coloring agent (*b*), cresol (*c*), synthanol (*d*), resorcinol (*e*), sinthanol and resorcinol (*f*). The current density is 23 mA/cm^2; T = 23 °C, coating thickness is 600 μm

Based on polarization measurements results, bismuth deposition regimes were optimized to obtain thick-layer coatings (d = 600 μm). The ranges below the diffusion current mode region were chosen as working cathode current densities. In the absence of mixing, they were: 23 mA/cm^2 at 23 °C; 50 mA/cm^2 at 40 °C; 80 mA/cm^2 at 60 °C. A cathode current density of 100 mA/cm^2 was chosen in the presence of mixing at any deposition temperature. Thus, the deposition time was 8, 4, 3 and 2 h at current density 25, 50, 80 and 100 mA/cm^2, respectively, to bismuth coating obtaining uniform thickness (600 μm) with current output 98–99 %.

Figure 6 shows bismuth coatings photographs synthesized with optimal deposition regimes in the absence and presence of mixing. It can be seen from the figure that cathode current density grows with a simultaneous temperature raise and in absence of mixing, the coatings quality deteriorates: the graininess and surface roughness increases, the evenness decreases, and coating thickening is visible on the substrate edge (see fig. 6, *a*–*c*). These disadvantages are almost completely eliminated with the electrolyte mixing at a speed of 600–800 rpm, only a slight substrate edge thickening is observed (see fig. 6, *d*). The most qualitative, dense, homogeneous and flat coatings were electrodeposited with the simultaneous syntanol and resorcinol adding in the electrolyte (see fig. 6, *d*). High quality coatings with the thickness of 600 μm were obtained at room temperature with cathode current density of 100 mA/cm^2 and electrolysis duration of 2 h.

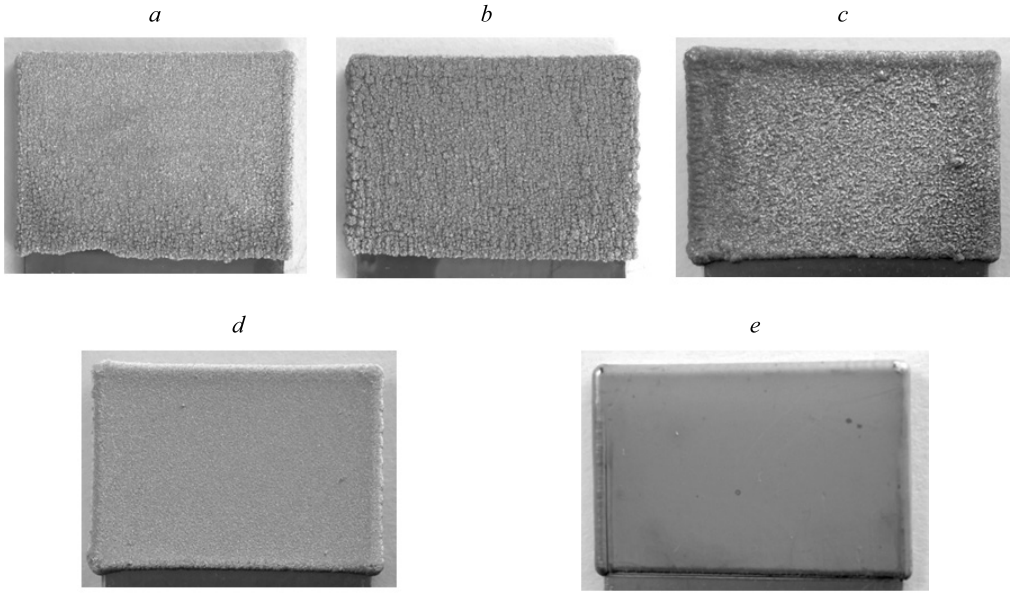

Fig. 6. Photos of bismuth coatings electrodeposited under the following conditions:
T = 23 °C, Dc = 25 mA/cm^2 (*a*); T = 40 °C, Dc = 50 mA/cm^2 (*b*); T = 60 °C, Dc = 80 mA/cm^2 (*c*);
T = 23 °C, Dc = 100 mA/cm^2 (*d*); T = 23 °C, Dc = 100 mA/cm^2 (*e*) in the presence of synthanol and resorcinol

Conclusion

The influence of various factors on the process of bismuth electrodeposition was examined. It was established that electrolyte mixing, deposition temperature, organic additives adding exert a noticeable influence on the electrode process of the discharge of Bi^{3+} ions in acid perchlorate electrolyte. The temperature rise from 23 to 60 °C makes it possible to expand the range of the cathode current density from 23 to 80 mA/cm^2, the intensive mixing (600–800 rpm) – up to 100 mA/cm^2. Bismuth coatings have a rhombohedral crystal structure (space group $R-3m$). Coatings with a signified texture (012) are formed in electrolyte without additives. This texture is retained by adding into the electrolyte the organic additives such as cresol, resorcinol, synthanol. However, in the presence of coloring agents (acridine yellow and safranin violet), the growth texture changes, the most intense reflex becomes (110). The additional presence of such organic additives as synthanol and resorcinol in the electrolyte guarantees flat, dense, close grained and uniform coatings with a thickness of 600 μm at room temperature and the highest cathode current density.

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Received by editorial board 16.11.2017.