



Fabrication of oxide coatings containing bismuth silicate or bismuth titanate on titanium



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ABSTRACT

Oxide coatings formed on titanium in electrolytes with $\text{Na}_2\text{B}_4\text{O}_7$ or Na_2SiO_3 by the method of plasma electrolytic oxidation and containing TiO_2 or SiO_2 , respectively, were impregnated in an organic solution of bismuth and, thereafter, annealed in air at 700 °C. As a result, layered oxide coatings containing, aside from titanium and silicon oxides, crystalline phases of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) or silicate (Bi_2SiO_5) were obtained. The composition and structure of the coatings surface parts and the distribution of bismuth-containing compounds over the surface have been investigated.

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1. Introduction

Numerous compounds exist in the systems $\text{Bi}_2\text{O}_3\text{--SiO}_2$ and $\text{Bi}_2\text{O}_3\text{--TiO}_2$ [1–4]. Complex oxide compounds of bismuth form different phases, such as Bi_2SiO_5 , $\text{Bi}_4\text{Si}_3\text{O}_{12}$, $\text{Bi}_{12}\text{SiO}_{20}$, $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and $\text{Bi}_{12}\text{TiO}_{20}$. The interest to the above compounds is caused by important optical, electrophysical, thermophysical and catalytical properties of materials, thin films and coatings fabricated on their basis [1–17]. The techniques used for preparing the thin films with bismuth titanate or silicate include chemical solution decomposition [1,7,9], pulsed laser deposition [6,8], sol–gel processing [3,10,13], metalorganic chemical vapor deposition [2,4], etc. The methods for preparing coatings containing both complex oxide bismuth compounds and transition metal oxides are less developed. Such heterostructures and coatings, for example, $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ [16], $\text{Bi}_2\text{O}_3/\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ [17] may have certain dielectric, ferroelectric or catalytic properties.

Photocatalytically active $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ coatings were synthesized via a two-step synthesis [16]. Previously TiO_2 anodic coatings on titanium were electrochemically fabricated in an solution of ethylene glycol additionally containing NH_4F . Then TiO_2/Ti samples

were placed in a solution of $\text{Bi}(\text{NO}_3)_3$ into KOH and the hydrothermal synthesis was conducted at 200 °C for a certain time (12, 18 and 24 h, respectively). That is, the anodic TiO_2 coating was used as a template for the synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ surface heterostructures on titanium.

In our opinion, the use of oxide coatings on titanium obtained by plasma electrolytic oxidation (PEO) is promising as template for the synthesis of titanium-based surface heterostructures containing oxygen bismuth compounds of different composition. PEO consists in formation of anodic coatings on metals under effect of electric spark or arc discharges in the near-anode area [18,19]. Here, the formation and composition of anodic oxide layers are affected by the electrolyte components embedding and high temperatures emerging locally at electric discharges sites. For instance, the PEO method was applied to obtain coatings on titanium, which contained, aside from TiO_2 , the following oxides: SiO_2 , ZrO_2 , WO_3 , Nb_2O_5 , Ta_2O_5 or V_2O_5 [19–24]. Accordingly, the coating with such oxides can obviously be used as precursors for the synthesis of surface heterostructures containing both TiO_2 and complex oxide compounds of bismuth and titanium, silicon, zirconium, tungsten, tantalum, niobium or vanadium. From the practical point, it is important that the PEO method a) is usually implemented at the normal pressure and the average electrolyte temperature not higher than 100 °C; b) ensures the possibility to form oxide layers on articles of complex shapes; c) allows formation of layers with high-temperature compounds on fusible metals and alloys (for

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Table 1
Data on the thickness h , roughness R_a , and phase and element composition of coatings before and after impregnation in the bismuth organic solution followed by pyrolysis.

Sample	h (μm)	R_a (μm)	Phase composition	Element composition (at. %)				
				O	Na	Si	Ti	Bi
1	9 ± 1	1.1	TiO ₂ (r, a)	70.3	–	–	29.7	–
1*	10 ± 1	0.9	TiO ₂ (r, a), Bi ₄ Ti ₃ O ₁₂	62.8	–	–	30.7	6.5
2	26 ± 2	3.7	TiO ₂ (r)	69.2	1.6	25.3	3.9	–
2*	29 ± 2	4.0	TiO ₂ (r, a), SiO ₂ (tridymite), Bi ₂ SiO ₅	67.2	1.4	23.5	3.4	4.5

Note. The data of X-ray electron microprobe analysis, depth of surface analysis up to 5 μm . During the element contents calculations, carbon was excluded, since a thin conducting carbon film was sputtered on the surface in advance to eliminate the effect of surface charging. 1 and 1* – PEO in 0.1 M Na₂B₄O₇; 2 and 2* – PEO in 0.1 M Na₂SiO₃; samples 1, 2 before and samples 1*, 2* – after impregnation with the bismuth organic solution; r – rutile; a – anatase.

example, on aluminum and magnesium). The PEO method comprises an alternative to different sol–gel methods and sputtering and immersion technologies, in particular, at deposition of oxide coatings on complex-profile construction elements and at treatment of large surface areas.

For the sake of formation of complex oxide structures on metallic surfaces, recently, the PEO method has been extensively investigated in combination with others, such as impregnation in salts aqueous solutions with subsequent annealing [25–27] and extraction–pyrolysis consisting in pyrolysis of organic solutions or pastes containing metal compounds deposited on the surface [28,29]. One may expect that deposition of a bismuth organic solution on the surface of an oxide PEO layer containing SiO₂, ZrO₂, WO₃, Nb₂O₅, Ta₂O₅ or V₂O₅ followed by high-temperature annealing would enable one to obtain, as a result of solid-phase reactions, coatings with bismuth titanates, silicates, zirconate, tungstate, tantalate, niobate or vanadates.

The present work was devoted to grounding of the approach to

obtaining bismuth titanates and silicates in the composition of oxide coatings on titanium through combination of the methods of plasma electrolytic oxidation and extraction–pyrolysis.

2. Materials and methods

2.1. Fabrication of oxide layers by plasma electrolytic oxidation

Titanium (grade VT1-0) plates of a size of 5 × 25 × 1 mm were used for plasma electrolytic oxidation. The samples underwent mechanical polishing to remove rough edges and defects formed at metal cutting. Thereafter, the samples were chemically polished in a mixture of acids HF: HNO₃ = 1:3 at 60–80°C for 2–3 s, washed with distilled water, and dried in air.

The PEO cell comprised a vessel made of thermally resistant glass of 1000 mL in volume. Oxide coatings were formed in the galvanostatic mode at a constant effective current density $i = 20 \text{ A} \cdot \text{dm}^{-2}$ for 10 min on anode-polarized titanium immersed

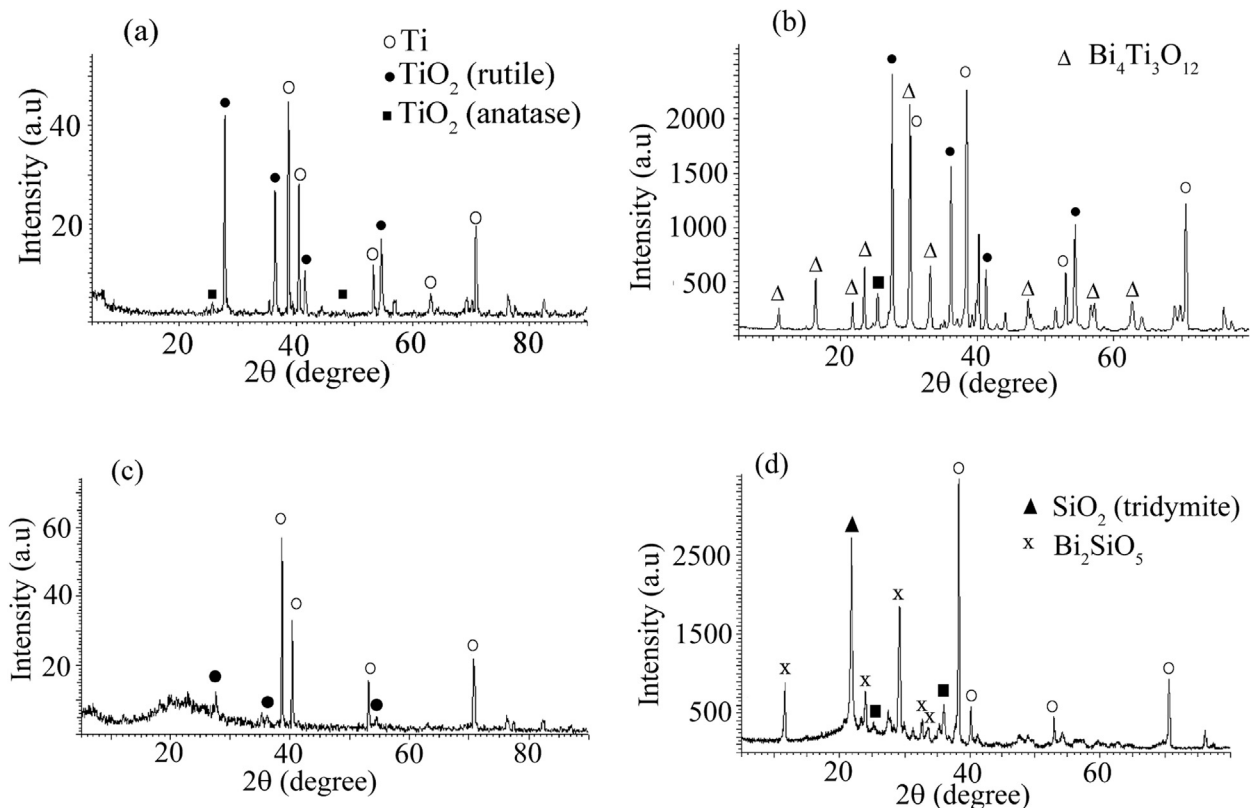


Fig. 1. XRD patterns of the coatings formed by PEO method (a, c) and its combination with impregnation in the organic bismuth solution followed by annealing at 700 °C (b, d). Electrolytes used for PEO: 0.1 M Na₂B₄O₇ (a, b); 0.1 M Na₂SiO₃ (c, d). XRD patterns were recorded on D8-Advance diffractometer (a, c) and STOE STADI P diffractometer (b, d).

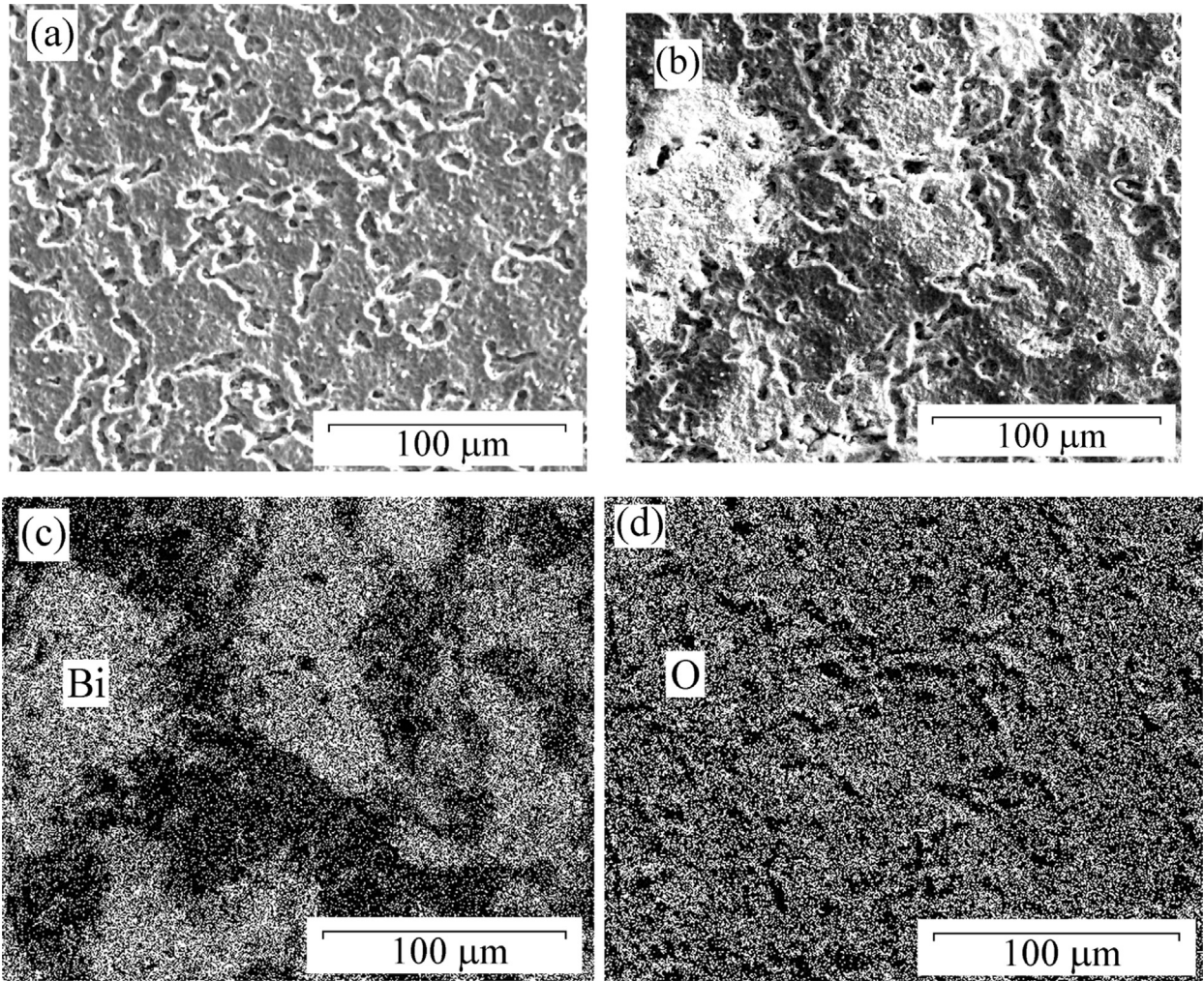


Fig. 2. SEM images (a, b) and maps of element distribution (c, d) for the coatings formed by PEO in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ (a) and its combination with impregnation in the organic bismuth solution followed by annealing (b, c, d).

into the electrolyte. 0.1 M solutions of $\text{Na}_2\text{B}_4\text{O}_7$ and Na_2SiO_3 were utilized as electrolytes: commercially available reagents $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (pure grade) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (chemically pure grade) and distilled water were used for their preparation. A coil

made of a hollow (diameter 0.5 cm) stainless-steel tube was used as a counter electrode (cathode). Cold water was fed through the hollow coil for electrolyte cooling. The electrolyte in the vessel was stirred using a magnetic stirrer. A TER4-63/460N thyristor device

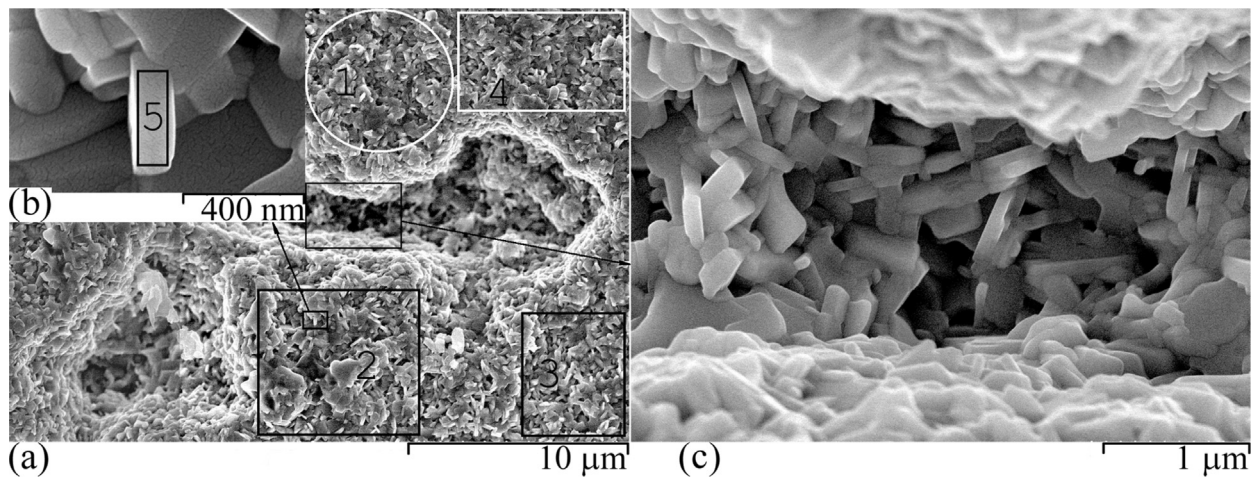


Fig. 3. SEM images of the area of the coating surface enriched with bismuth. The coating was formed on titanium by combination of PEO in 0.1 M solution of $\text{Na}_2\text{B}_4\text{O}_7$ and impregnation in the organic bismuth solution followed by annealing. General overview of the surface (a), fragments of area with larger magnification (b, c). Highlighted areas 1–5: the data on element composition are given in Table 2.

with the unipolar pulse current waveform was used as a current source. Thereafter, PEO samples were rinsed with distilled water and dried in air at room temperature.

2.2. Preparation of bismuth organic solution

Preparation of the bismuth organic solution was carried out in accordance with the technique described in Refs. [30,31]. For this purpose, the basic bismuth nitrate was dissolved in the molten colophony, and the final melt was diluted with turpentine. As a result, the solution containing 0.3 M of bismuth was obtained. The solution was used to impregnate samples treated by the PEO method, which were then annealed in air at 700 °C for 1 h.

2.3. Study of surface morphology and phase and element composition of coatings

The data on morphology and element composition of the surface as well as its individual parts were obtained using a SUPERPROBE JXA-8100 microprobe X-ray spectral analyzer (JEOL, Japan) and an S-5500 scanning electron microscope (Hitachi, Japan) with the system for energy-dispersive X-ray spectral microanalysis. In the case of microprobe analysis, the element composition of the coating surface was determined on 5 randomly selected areas of a size of $300 \times 200 \mu\text{m}^2$, and the obtained data were averaged. The analysis depth was up to 5 μm . The areas, within which the element composition was determined using an energy-dispersive accessory of the scanning electron microscope, are shown on respective surface images in the text. In this case, the analysis depth was $\sim 1 \mu\text{m}$.

The value of the surface roughness R_a was measured using a LEXT OLS3100 confocal laser scanning microscope (Japan). The coatings thicknesses were determined using a VT-201 vortex-current thickness meter (Russia).

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) in the $\text{CuK}\alpha$ radiation using D8-Advance diffractometer (Bruker Inc., Germany) or STOE STADI P diffractometer (STOE & Cie GmbH, Germany). Identification of compounds present in samples under study was performed in an automatic search mode Eva using the PDF-2 database.

3. Results and discussion

3.1. Coatings phase and element composition

The results of X-ray diffraction analysis (XRD) and X-ray-based electron microprobe analysis (EMPA) of coatings before and after extraction-pyrolysis treatment are shown in Table 1. According to the EMPA data, surface layers of PEO coatings obtained in the borate electrolyte contain oxygen and titanium (sample 1). PEO coatings

Table 3

Element composition of the surface of the sample 2* (from the data of energy-dispersive analysis).

Element composition (at. %)										
Element	Coral-like structure							Pore		
	1	2	3	4	5	6	C_{av}	7	8	C_{av}
C	27.4	9.9	—	—	—	—	6.2	—	—	—
Na	—	4.2	3.6	3.4	2.9	4.0	3.0	—	—	—
Si	19.6	18.3	32.0	33.5	40.9	28.6	28.8	37.6	33.2	35.4
O	46.1	63.4	62.5	60.5	50.9	64.7	58.0	37.6	31.6	34.6
Ti	3.2	1.0	0.5	0.0	2.1	0.7	0.9	24.4	34.5	29.5
Bi	3.6	2.7	1.4	2.6	3.0	1.9	2.5	0.3	0.7	0.5

Note. Results of determination of the element composition of areas 1–8, Fig. 5. C_{av} – the average value of the element content. The analysis depth $\sim 1 \mu\text{m}$. For current sink, the surface was sputtered with gold, which allowed determination of the carbon content.

formed in the silicate electrolyte contain oxygen, sodium, silicon, and titanium (sample 2). In the latter case, one observes low titanium content (several-fold lower than for coatings in the borate electrolyte) on the background of high silicon content (~ 25 at %) in the composition of the coatings surface part. As a result of treatment of organic bismuth solution, bismuth becomes embedded in coatings of both types (samples 1*, 2*), the titanium content in coatings does not change, and the oxygen content somewhat decreases. Since the roughness factor and the coating thickness change insignificantly in the course of coating modification (Table 1), one can conclude that bismuth mostly diffuses into the oxide coating bulk, i.e., bismuth compounds do not form an expressed additional outer layer.

The X-ray diffraction patterns of oxide layer/titanium samples with coatings formed by different methods are shown in Fig. 1. The X-ray diffraction patterns of samples with oxide coatings formed in sodium tetraborate or silicate solutions (Fig. 1ac) include rather intensive reflections of titanium and titanium dioxide in the rutile modifications and, in the case of the borate electrolyte, small peaks of TiO_2 in the anatase modification. The diffraction patterns of the coating formed in the silicate electrolyte is characterized by a broad band with the maximal intensity at $2\theta = 22^\circ$ and a large shoulder in the direction of big diffraction angles characteristic for amorphous silica as shown in Fig. 1c.

Upon the stage of impregnation in the organic bismuth solution followed by pyrolysis at 700 °C, there occur significant changes in the coatings phase compositions, as seen from the analysis of respective X-ray diffraction patterns as shown in Fig. 1bd. In both cases, one observes the emergence of intensive peaks on the X-ray images indicating to predominantly crystalline structure of coatings. On the X-ray diffraction patterns of the modified coating formed in the borate electrolyte, intensive peaks corresponding to reflections of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the orthorhombic modification are

Table 2

Element composition of the surface of the sample 1* enriched with bismuth (from the data of energy-dispersive analysis).

Element	Area					C_{av}	Crystal
	Element composition (at. %)						
	Surface						
	1	2	3	4		5	
C	12.1	23.0	20.0	21.3	22.8	27.2	
O	53.3	54.1	50.5	55.6	50.3	56.7	
Ti	17.8	12.3	15.2	12.5	14.1	9.0	
Bi	16.8	10.5	14.3	10.6	12.4	7.0	

Note. Results of determination of the element composition of areas 1–5, Fig. 3. C_{av} – the average value of the element content. The analysis depth $\sim 1 \mu\text{m}$. For current sink, the surface was sputtered with gold, which allowed determination of the carbon content.

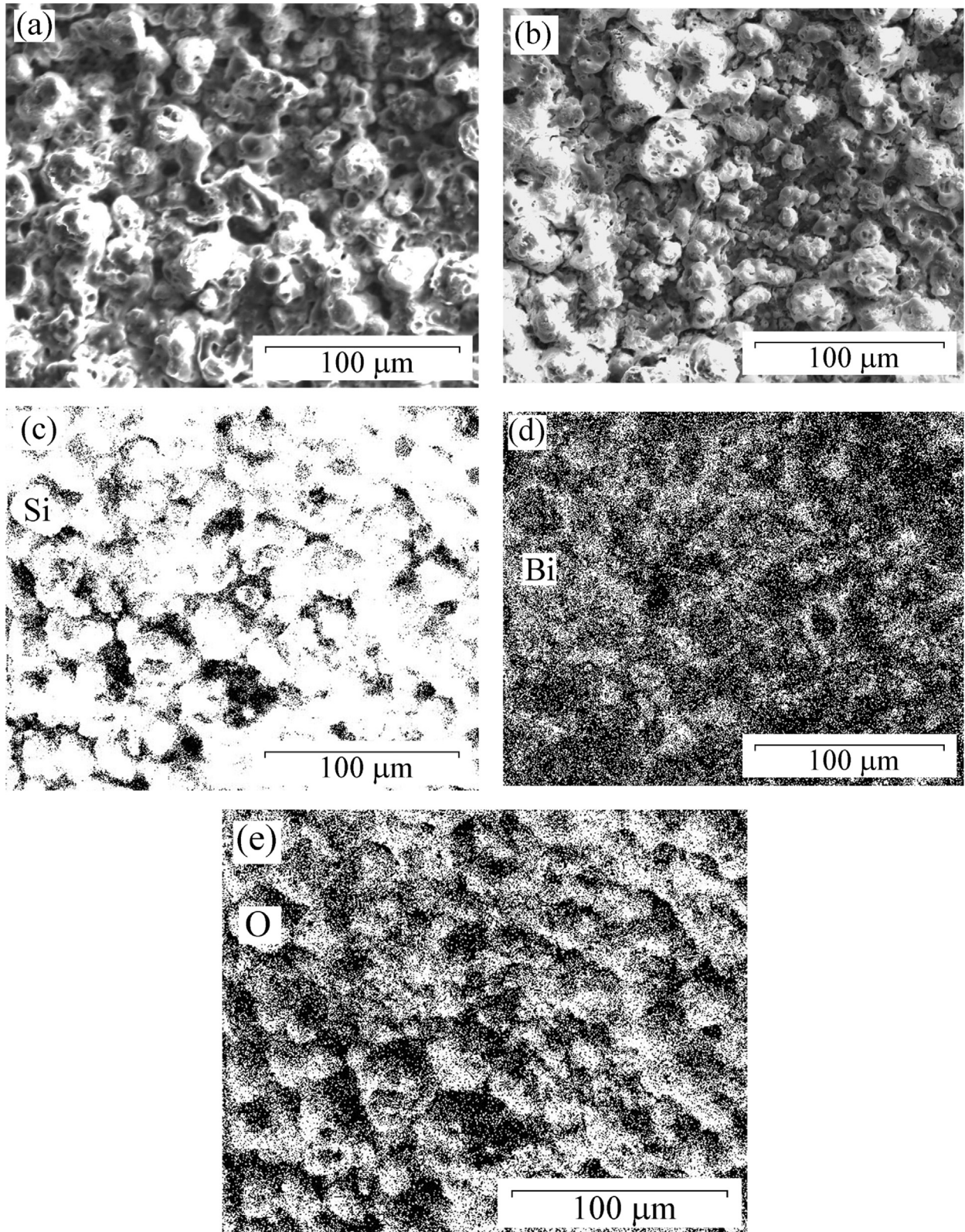


Fig. 4. SEM images of coatings (a, b) and maps of element distribution (c–e) for coatings formed by PEO in 0.1 M Na_2SiO_3 (a) and its combination with impregnation in the organic bismuth solution followed by annealing (b–e).

present. At $2\theta = 22^\circ$, the X-ray diffraction patterns of the modified coating formed in the silicate electrolyte contains, instead of a broad band, an intensive peak corresponding to the SiO_2 phase (tridymite), which indicates to crystallization of amorphous silica

under effect of high temperatures. Besides, on the X-ray diffraction patterns, one observes peaks corresponding to the structure of Bi_2SiO_5 in the orthorhombic syngony as shown in Fig. 1d.

3.2. Surface morphology and element distribution in the surface layer

Figs. 2 and 3 show SEM images and maps of element distribution over the surface of unmodified and modified PEO coatings formed in the borate electrolyte (samples 1 and 1*, Table 1). On the surface of unmodified coatings (sample 1), one observes numerous cavities with pores on their bottoms, which must have been formed under effect of microarc discharges during the PEO process (Fig. 2a).

Upon treatment by bismuth organic solution followed by pyrolysis (sample 1*), the coating surface becomes more heterogeneous with emergence of light and dark parts (Fig. 2b). According to the maps of element distribution, oxygen is distributed homogeneously over the surface (Fig. 2d), whereas light parts in Fig. 2c are enriched with bismuth. The latter indicates to the fact that the bismuth organic solution wets selectively some surface parts during modification (it is accumulated into drops on some surface parts at annealing).

More detailed study of the structure and element composition of surface parts of the sample 1* enriched with bismuth using high-resolution scanning electron microscope with an energy-dispersive accessory for element composition determination (Fig. 3, Table 2) showed that these parts consisted of nanosized crystals. The data on element composition of highlighted areas 1–5 in Fig. 3 containing substantial amounts of nanocrystals are shown in Table 2. The atomic ratios Bi:Ti:O in the analyzed areas correspond to the phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and, therefore, are in agreement with the XRD data (Fig. 1b). In other words, parts of the sample 1* enriched with bismuth are covered with nanosized crystals, whose composition corresponds to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

In the coating of the sample 1* (just like in that of the sample 2*, Table 3), rather high carbon content (up to 23 at %) was determined, see Table 2. One of possible reasons of the presence of carbon consists in interaction of the organic bismuth solution with the oxide coating resulting in formation of high-strength carbon-containing compounds that are stable upon annealing at 700 °C – the temperature of pyrolysis of the organic bismuth solution.

Fig. 4 shows SEM images and maps of element distribution over the surface of unmodified and modified PEO coatings formed in the silicate electrolyte – the samples 2 and 2* in Table 1.

The coating formed in the silicate electrolyte (sample 2) is heterogeneous (Fig. 4a). The surface consists of fused coral-like structures of different shapes and sizes. According to the data of Table 1 showing the excess of silicon relatively to titanium in the surface part of the coating 2 at a depth of up to 5 μm and the data of Figs. 1c and 4, the coral-like structures consist of amorphous silica, whereas titanium and titanium oxide are present in the coating pores. Upon treatment of the sample 2 by the organic bismuth solution followed by pyrolysis, no significant changes in the coating morphology were observed (sample 2*, Fig. 4b). According to the maps of element distribution (Fig. 4cde), the bismuth distribution over the surface (Fig. 4d) is here more homogeneous than for the sample 1* (Fig. 2c). In other words, the organic bismuth solution wets the silicon-containing coatings 2 more homogeneously than the coatings 1 formed in the borate electrolyte. This can be related as to higher hydrophobicity of the coating with high silicon content as to higher roughness and porosity of such a coating.

As seen from the data of Fig. 4ce, bismuth and oxygen are concentrated in jutting silicon-containing coral-like structures and the parts around them. This conclusion is corroborated by detailed studies of the element composition of individual parts using high-resolution electron microscopy with an energy-dispersive accessory (Fig. 5). The obtained results confirm bismuth concentrating in coral-like structures, whereas only trace quantities of it were found in pores (Table 3). In opposite, titanium concentrates in pores.

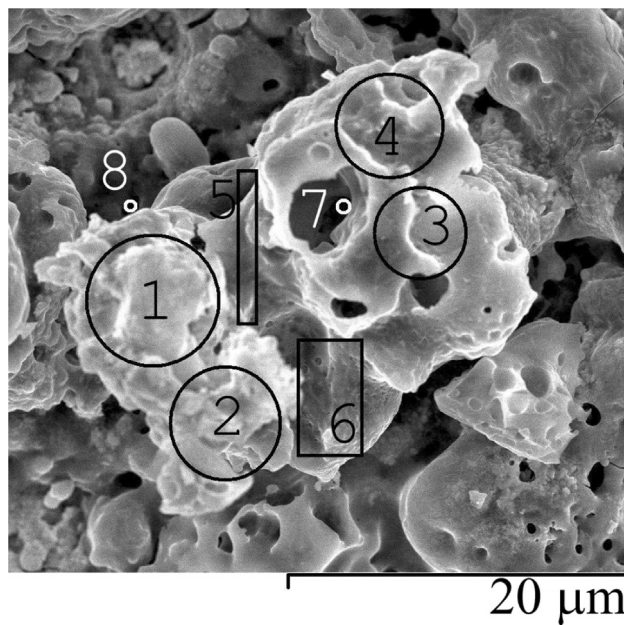


Fig. 5. SEM images of the jutting formation on the surface of the coating formed on titanium by combination of PEO in 0.1 M Na_2SiO_3 with impregnation in the organic bismuth solution followed by annealing. Highlighted areas 1–8: the data on element composition are shown in Table 3.

Heterogeneous coating and structure and element distribution over the surface must cause heterogeneity of distribution of respective phases over the surface. Note that no crystalline formations were found on the surface of the sample 2*.

4. Conclusions

Oxide layers containing crystalline phases of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ or Bi_2SiO_5 have been fabricated using coatings on titanium containing silicon or titanium oxides, which were obtained as precursors by the PEO method, through additional impregnation in the bismuth salt organic solution with subsequent annealing. The coating phase and element compositions, thickness, morphology, roughness, and element distribution over the surface depend on the composition of the electrolyte used in PEO. Bismuth titanate is present in the coating surface layer in the form of nanocrystals. It is evident that the suggested method of combination of plasma electrolytic oxidation and impregnation in the organic bismuth solution followed by pyrolysis can be extended to fabrication of other complex oxide compounds of bismuth in the composition of oxide coatings on titanium, for example, bismuth zirconate-titanates, tungstate, tantalate, niobate or vanadates.

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