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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 $Na_2B_4O_7$ 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 ($Bi_4Ti_3O_{12}$) 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.

1. Introduction

Numerous compounds exist in the systems Bi_2O_3–SiO_2 and Bi_2O_3–TiO_2 [1–4]. Complex oxide compounds of bismuth form different phases, such as Bi_2SiO_5, $Bi_4Si_3O_{12}$, $Bi_{12}SiO_{20}$, $Bi_2Ti_2O_7$, $Bi_4Ti_3O_{12}$, and $Bi_{12}TiO_{20}$. 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, Bi_4Ti3O_{12}/TiO_2 [16], $Bi_2O_3/Bi_4Ti_3O_{12}/TiO_2$ [17] may have certain dielectric, ferroelectric or catalytic properties.

Photocatalytically active $Bi_4Ti_3O_{12}/TiO_2$ 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 $Bi(NO_3)_3$ 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 $Bi_4Ti_3O_{12}/TiO_2$ 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), $Bi_4Ti_3O_{12}$	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_2SiO_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 $Na_2B_4O_7$; 2 and 2* – PEO in 0.1 M Na_2SiO_3; 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 SiO_2, ZrO_2, WO_3, Nb_2O_5, Ta_2O_5 or V_2O_5 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: HNO_3 = 1:3 at 60–80C 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 $i = 20\ A \cdot dm^{-2}$ for 10 min on anode-polarized titanium immersed

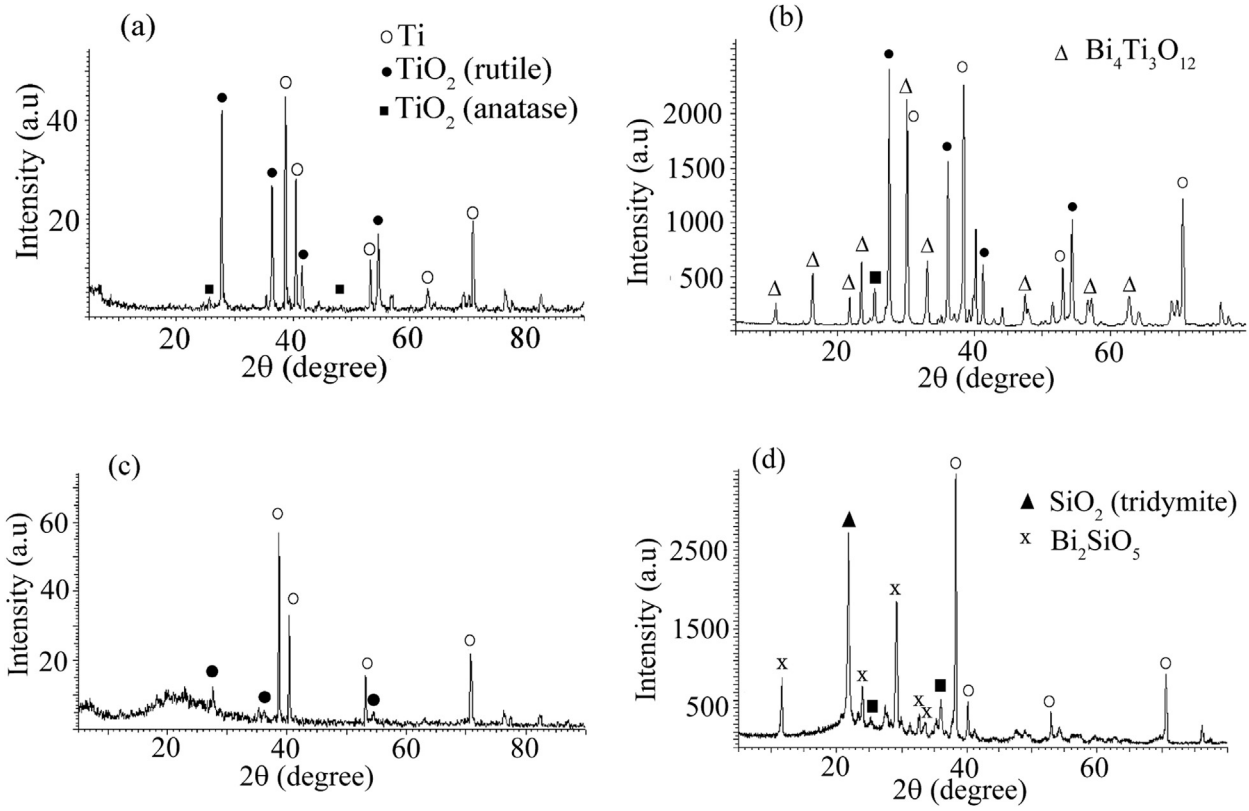

Fig. 1. XRD patterns of the coatings formed by PEO method (a, c) and its combination with impregnation in the organic bismuth solution followed by annealing at 700 °C (b, d). Electrolytes used for PEO: 0.1 M $Na_2B_4O_7$ (a, b); 0.1 M Na_2SiO_3 (c, d). XRD patterns were recorded on D8-Advance diffractometer (a, c) and STOE STADI P diffractometer (b, d).