
BRIEF
COMMUNICATIONS

Tantalum Oxide-Modified Calcium Phosphate Coatings on Titanium for Biomedical Applications

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Abstract—A combination of plasma-electrolytic oxidation method with extraction-pyrolytic technique was used for preparation of layered coatings with a developed surface relief. The coating surface is composed of segments enriched in tantalum oxide, alternating with those containing titanium oxides and calcium and phosphorus compounds.

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Titanium and its alloys are widely used for the manufacture of implants in surgery and dentistry [1, 2]. The medical application parameters of titanium implants can be improved by deposition onto their surface of functional coatings, e.g., those containing calcium phosphates [1–4] or tantalum oxide Ta₂O₅ [5–8]. Calcium phosphate-containing coatings are used to improve biocompatibility of titanium implants with bone tissue. Tantalum oxide-containing coatings, bioinert with respect to living tissue, promote chemical stability of implants whose surface, after appropriate treatment, acquires a slowly relaxing electric charge (electret properties of Ta₂O₅), thereby beneficially affecting the interaction between the living tissue cells and the implant.

Coatings containing both calcium phosphates and tantalum oxide combine their intrinsic properties and hold promise for deposition onto different-purpose titanium implants.

Previously [9] we demonstrated the possibility of deposition onto titanium and its alloys of coatings containing calcium phosphates, in particular, hydroxyapatite, by the electrochemical method of plasma-electrolytic oxidation (PEO, oxidation in electrolytes under conditions of spark and microarc discharges) in electrolytes with polyphosphate Ca(II) complexes [9]. Here, we report on

the composition and structure of the coatings formed by the previously described procedure [9] and additionally modified by the extraction-pyrolytic method [10] via deposition onto their surface of a Ta-containing organic extract, followed by an annealing treatment.

EXPERIMENTAL

Combined coatings were formed on 2.2×2.2×0.1-cm flat commercial VT1-0 titanium specimens. The pre-processing of the specimens consisted in chemical polishing in a mixture of concentrated acids HNO₃ : HF = 3 : 1 (vol:vol) at 70°C, after which the specimens were rinsed with distilled water and air-dried at 70°C.

According to the approach described in [9], plasma-electrolytic oxidation of the titanium specimens was carried out in an electrolyte comprised of 0.098 mol l⁻¹ Na₅P₃O₁₀ and 0.1568 mol l⁻¹ Ca(CH₃COO)₂·H₂O at the molar ratio in the electrolyte $n = [P_3O_{10}^{5-}]/[Ca^{2+}] = 0.625$. Each of the components (chemically pure grade) was preliminarily dissolved in distilled water, after which the resulting solutions were mixed in the indicated ratio and kept under stirring for at least 1 h.

The coatings were formed on the titanium specimens by 5-min anodic polarization at the average current

density of 8 A dm^{-2} . The electrochemical cell was a 1-l heat-resistant glass beaker into which a nickel alloy coiled cathode and a thermometer were placed. A TER4-100/460N computer-controlled thyristor operating in the unipolar regime was used as the current source. The electrolyte solution was stirred with a magnetic stirrer. The electrolyte temperature during the PEO process did not exceed 30°C .

The composition of the PEO-coating formed was modified by deposition onto its surface of a Ta-containing paste with organic composition. For preparation of the paste, tantalum oxide was preliminarily fused together with potassium pyrosulfate at 700°C . The resulting fused mass was leached with 0.35 M aqueous solution of ammonium oxalate. This yielded a 0.0027 M aqueous solution of tantalum, from which tantalum was extracted with a 0.04 M solution of trialkyl benzyl ammonium sulfate at the 1:1 phase ratio. After extraction and separation, tantalum virtually completely passed into the organic phase (distribution coefficient $D=70$), which was subsequently evaporated, and the resulting paste was deposited onto the specimens with coatings. After drying, the specimen with the paste was annealed in a muffle furnace at 600°C in air for 1 h.

The thickness of the layers was determined by a VT-201 (Russia) eddy current thickness gauge. The thickness and roughness of the coatings was also measured by an LEXT 3100 (Japan) confocal laser scanning microscope (resolution $0.01 \mu\text{m}$, $\times 120$ – $\times 14400$ magnification). The surface elemental composition and surface images were obtained using an INCA energy dispersive X-ray spectrometer attachment (UK) of a JXA-8100 electron probe microanalyzer (JEOL, Japan). The X-ray diffraction patterns were measured on a D8 ADVANCE X-ray diffractometer (Bruker, Germany) using $\text{CuK}\alpha$ radiation. The Bruker EVA package coupled with PDF-2 database

Average elemental composition of the surface layer of the coating and of the characteristic surface formations according to the point measurement data

Scanning	c, at %				
	O	Ti	Ta	Ca	P
Across the area	65.6	14.9	13.4	2.6	2.8
On elevations	67.9	2.8	27.9		
In depressions	47.0	16.4	30.1	2.3	1.0

served for phase identification.

The PEO coatings formed on titanium within 5 min had a thickness of $15 \pm 2 \mu\text{m}$ and contained, at.%, 65.7 O, 5 P, 2.5 Ca, 17.6 Ti. The X-ray phase analysis showed that the coatings comprised TiO_2 crystalline phases in rutile and anatase modifications. These data are close to those reported previously [9] for coatings formed under identical conditions. Figure 1a demonstrates the relief features of the PEO-coatings, specifically, prominent elevations with a pore at the top and depressions (“valleys”), also perforated with pores, the pore diameter being $\leq 5 \mu\text{m}$. As shown by our previous studies [11, 12], the characteristic surface formations (elevations, pores, pore openings, valleys) on the PEO-coatings can differ in composition.

Upon deposition of the Ta-containing paste and annealing, an additional layer, a “crust”, was formed on the surface (Fig. 1b). The crust is not uniformly continuous; rather, it consists of individual continuous segments separated by depressions. Rounded pores appear on the

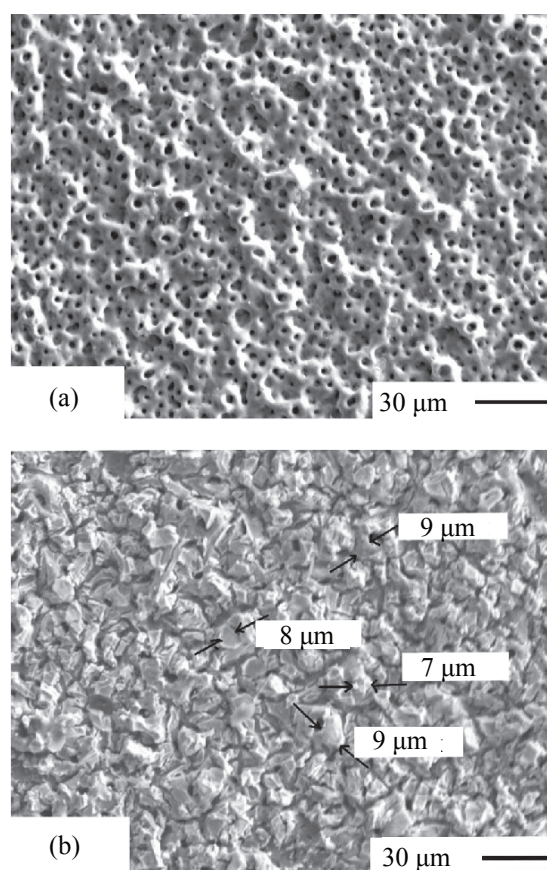


Fig. 1. Image of the surface of the Ca, P-containing PEO-coatings (a) before and (b) after modification with tantalum oxides.

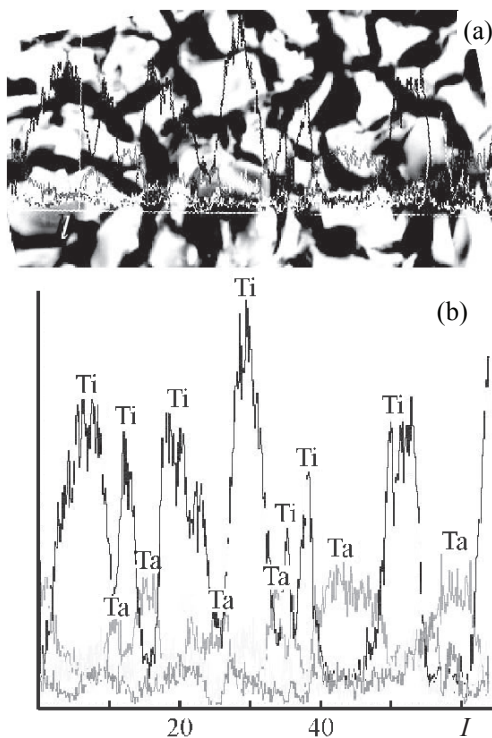


Fig. 2. Distribution of Ta and Ti over the surface of the modified coatings. (a) Surface relief image produced by primary electrons (phase representation) and (b) distribution profiles of elements along line *I* chosen for analyzing the concentrations of elements.

surface. The typical size of the continuous segments and depressions is $\sim 10 \mu\text{m}$, and that of pores, $\leq 10 \mu\text{m}$ (Figs. 1b and 2a). These structural features of the modified surface are evidently due to a better wetting ability exhibited by the organic solvent-based Ta-containing paste with respect to individual surface regions of the primary Ca-containing coating and its aggregation into droplets in these regions during annealing.

The thickness of the modified coating as measured by the eddy-current thickness gauge is $28 \pm 2 \mu\text{m}$, and the thickness determined with the confocal microscope for the coating chip formed in mechanical cutting of the specimen, $32 \pm 4 \mu\text{m}$ (Fig. 3), i.e., the results of independent measurements are fairly close. Thus, considering the fact that the initial PEO-coating was $15\text{-}\mu\text{m}$ -thick, the thickness of the additional layer formed under the experimental conditions upon annealing of the Ta-containing paste can be estimated as $13\text{--}17 \mu\text{m}$. Clearly, the additional layer thickness can be controlled by repeating the paste deposition-annealing cycles or by varying the thickness of the paste layer deposited.

Figure 4 shows the results of X-ray phase analysis

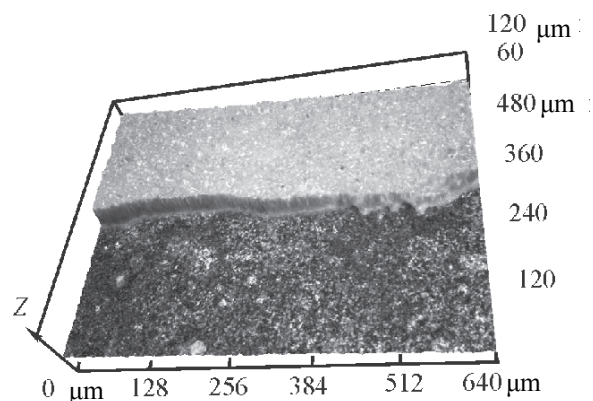


Fig. 3. Modified coating chip formed in cutting of the specimen.

of the modified coatings. Along with anatase and rutile modifications of TiO_2 crystalline phases contained in the primary PEO-coating, the modified coating contains a tantalum oxide Ta_2O_5 phase.

The table presents the X-ray microprobe elemental analysis data for the surface of the tantalum-modified coatings, determined by averaging the scanned data for five $300 \times 200\text{-}\mu\text{m}$ areas and for “points” (with the probe beam focused on a $\sim 1\text{-}\mu\text{m}$ -diameter spot) for the elevations and depressions. The results of the analysis at points are the averages of the measured data for five different surface sites.

The tabulated data show that, with the beam scanned across the area, the titanium concentration (average value) is close to that determined for the depressions and exceeds more than 5 times that on the elevations. By contrast, the surface average concentration of tantalum is more than 2 times lower than those for the depressions and elevations. The data acquired by beam scanning across the area suggest that the depressions significantly contribute to the titanium concentration. The lower tantalum content data acquired by beam sweeping over the surface are due to oxygen redistribution. In the depressions, the oxygen content is by $\sim 20\%$ lower than that in the surface layer. This may be due to a lower oxidation state of tantalum and, possibly, of titanium, deep inside the depressions, probably because of hindered oxygen penetration into depressions during annealing. The surface average concentrations of calcium and phosphorus are close to those in the depressions. At the same time, these elements are lacking on the elevations. Hence, titanium, calcium, and phosphorus are predominantly concentrated in the depressions. Apparently, there are portions of the

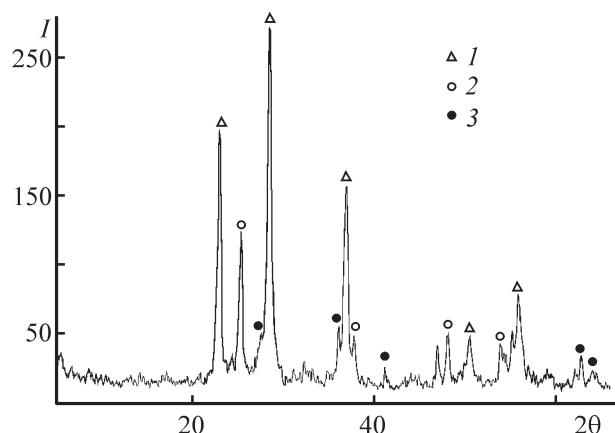


Fig. 4. X-ray diffraction pattern of the calcium phosphate-containing PEO-coating modified with tantalum oxides. (*I*) Intensity, and (2θ) Bragg's angle, deg. (1) Ta_2O_5 , (2) TiO_2 anatase, and (3) TiO_2 rutile.

primary Ca,P-containing PEO-coating at the bottom of the “valleys”. It should be noted that calcium and phosphorus are contained in different depressions in different amounts. The scatter of the data varies within 1.2–4.4 for calcium, 0.7–2.2 for phosphorus, 11.9–45 for tantalum, and 4–22.5 at.% for titanium.

Figure 2 demonstrates the distribution profiles of the elements in the surface layer of the coating, derived from analysis with electron beam swept along a straight line (line *l*). The concentration of tantalum varies in counter-phase with those of titanium, calcium, and phosphorus. These data confirm the finding that the elevations (light areas in the image) are dominated by tantalum compounds, while titanium, calcium, and phosphorus compounds are contained primarily in the depressions.

After a chip of the modified coating came off as a result of mechanical cutting of the specimen (Fig. 3) we estimated the elemental composition, at.%, of the base material from which the coating was detached: 31.5 O, 0.4 Al, 68.1 Ti. The base material does not contain calcium and phosphorus, i.e., the coating chipped off virtually across the metal surface, probably, along the metal/PEO-coating interface, as suggested by the occurrence of oxygen and, possibly, lower titanium oxide TiO. As to trace amounts of aluminum, the reason is the specific composition of VT1-0 commercial titanium. The electron microprobe analysis showed that the alloy used in our experiments contained, at.%, 99.12 Ti and 0.88 Al. According to GOST (State Standard) 19807–91, VT1-0 commercial titanium may contain up to 0.7 wt% Al.

Hence, the modified Ta-, Ca-, P-containing coating chips off at the metal/coating interface, which fact supports strong binding between the Ta-containing layer being deposited and the primary Ca,P-containing PEO-coating.

The structure of the Ta-, Ca-, P-containing coatings on titanium that we synthesized can be represented as follows. The coating has a developed surface relief, and its surface consists of alternating elevations and depressions with nearly identical geometric sizes. The elevations are dominated by tantalum oxides, and depressions, by titanium oxides and calcium and phosphorus compounds (calcium phosphates, according to [9]). The cross-sectional structure of the coatings is represented by several layers. The top layer consisting of tantalum oxide islands separated by depressions is followed by a layer dominated by titanium oxides and calcium and phosphorus compounds. Next goes a transitional layer, apparently containing lower titanium oxides, in particular, TiO.

CONCLUSIONS

(1) A combination of plasma-electrolytic oxidation method with extraction-pyrolytic technique was used for preparation of layered coatings with developed surface relief on titanium. On the coating surface, segments enriched in tantalum oxide alternate with those containing titanium oxides and calcium and phosphorus compounds.

(2) Such coatings may possess properties intrinsic to both tantalum oxides and calcium phosphates and may be promising for biomedical applications.

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