ISSN 2070-2051, Protection of Metals and Physical Chemistry of Surfaces, 2015, Vol. 51, No. 6, pp. 968–972. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © V.S. Rudnev, T.P. Yarovaya, M.A. Medkov, P.M. Nedozorov, K.N. Kilin, I.V. Lukiyanchuk, A.Yu. Ustinov, 2015, published in Fizikokhimiya Poverkhnosti i Zashchita Materialov, 2015, Vol. 51, No. 6, pp. 613–617.

Coatings with Calcium and Strontium Phosphates and Tantalum Oxide on Titanium for Biomedical Applications

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Received August 15, 2014

Abstract—Layered coatings of the composition Ca- and Sr-phosphate/Ta_2O_5/TiO_2 have been obtained by sequential application of plasma electrolytic oxidation (PEO) in an electrolyte with fluoride complexes of tantalum (stage I) and in one with tripolyphosphate complexes of Ca(II) and Sr(II) (stage II). Calcium and strontium phosphates are contained in the coating surface part, whereas tantalum oxides are present in the coating bulk. The fabricated coating/titanium composites are of interest for testing as biocompatible and bioinert implants to be used in medical practice.

DOI: 10.1134/S2070205115060192

INTRODUCTON

Titanium and its alloys are used in the manufacture of implants in surgery and stomatology [1, 2]. Medical records of titanium implants application can be enhanced by depositing functional coatings, for instance, those containing calcium phosphates [1–4] or tantalum oxide (Ta_2O_5) [5–8], on their surface.

Coatings with calcium phosphates improve biocompatibility of titanium implants with bone tissue. In the case of biological phosphates, the important role is concerned with their inorganic components, in particular, sodium, strontium, copper, and zinc cations. These elements affect such characteristics of the bone material as crystallinity and mechanical properties and the processes related to its formation in the organism, which is of importance in application of implants [9, 10].

Coatings with tantalum oxide that are bioinert with respect to living tissue increase the chemical resistance of implants and allow, upon relevant treatment, a slowly relaxing electric charge (electret properties of Ta_2O_5) to be imparted to the surface, which positively affects interaction the living tissue cells with the implant.

As we demonstrated earlier, coatings with phosphates of di-, tri, and tetravalent metals could be obtained on valve metals using the method of plasma electrolytic oxidation (PEO) in electrolytes containing polyphosphate complexes of M^{2+}, M^{3+}, and M^{4+} [11–13]. Coatings with transition metal oxides can be obtained in electrolytes containing fluorocomplexes of these metals [13–15]. The above approaches have been applied to form coatings with Ca(II) phosphates [16], Ca(II) and Sr(II) phosphates [17], and tantalum oxide [18,19] on titanium. A combination of PEO and extraction–pyrolysis methods was used to obtain layered coatings on titanium: these coatings contained a layer of tantalum oxide deposited on a layer with calcium phosphates and titanium oxides; i.e., Ta_2O_5/Ca phosphates/TiO_2/Ti composites were formed [20]. Fabricated coatings with calcium phosphates, strontium/calcium phosphates, and tantalum oxide, as well as layered ones with tantalum oxide and calcium phosphates, can be promising in view of their deposition on titanium implants in order to improve the implants' biocompatible and bioinert properties.

Since the goal is to improve biocompatibility with bone tissue and stimulating bone tissue growth relative to Ta_2O_5/Ca phosphates/TiO_2/Ti composites, special interest is focused on composites with an inverse layer order, for example, Ca- and Sr-phosphates/Ta_2O_5/TiO_2/Ti. As is known from the literature, no phosphate-oxide layers on titanium of such structure and composition have been obtained yet.

The objective of the present work was to apply the above-described approaches in formation of Ca- and Sr-phosphates/Ta_2O_5/TiO_2/Ti composites using the PEO method and study their element and phase composition and surface morphology.

EXPERIMENTAL

Coatings were formed on flat samples of technical grade titanium VT1-0 of a size of 10 × 5 mm and a thickness of 0.5 mm. The samples pretreatment included chemical polishing in a mixture of concentrated acids $HNO_3 : HF = 3 : 1$ (by volume) at 70°C.

The polished samples were washed in distilled water and dried at 70°C in air.

The combined coatings were formed by the method of plasma electrolytic oxidation (PEO) in two stages. First of all, coatings were produced in an aqueous solution of $NH_4[TaF_6]$ [18, 19]. Peculiarities of the electrolyte preparation are described in the cited works in detail [18, 19]. Here, oxidation was carried out in the electrolyte placed into a polyethylene vessel of a volume of 100 mL. To cool the solution, the vessel was placed into cold water with ice. Prior to the anodization process start, the electrolyte temperature was ~10°C. A titanium plate with a size of 3 × 13.5 cm and a thickness of 0.5 mm bent according to the cylindrical vessel shape was used as a cathode. The electrolyte was stirred using a magnetic stirrer. Coatings were formed in the potentiostatic mode under a constant voltage of 70 V fed to the electrodes. The PEO process duration was 2 min.

At the second stage, samples with coatings formed in the electrolyte with tantalum fluoride complexes were repeatedly oxidized in the solution with polyphosphate complexes of Ca^{2+} and Sr^{2+}. An aqueous electrolyte containing (g/L) 36 $Na_5P_3O_{10}$, 8.6 $Ca(CH_3COO)_2 \cdot H_2O$ and 0.1 $Sr(CH_3COO)_2$ was used (see [17]). Commercial chemical reagents of chemically pure grade were used. The second oxidation was carried out whether in the potentiostatic mode at an electrode voltage of 80 V or in the galvanostatic mode at a current density of 0.05 A/cm^2 for 5 min. Here, the PEO treatment was carried out in a glass vessel of a volume of 1 L. A hollow coil made of nickel alloy, through which tap water was fed for cooling, served as a counterelectrode. In both cases, a computer-controlled TER4-100/460-2 thyristor device operating in the unipolar mode served as a current source.

The coatings' element composition and surface images, as well as the elements' distribution maps, were determined on a JXA-8100 X-ray spectral analyzer (JEOL, Japan) equipped with an INCA-sight energy-dispersive accessory (Oxford Instrument, United Kingdom). The phase composition was revealed on a DRON-2.0 diffractometer (Russia) in the CuK_α radiation. X-ray photoelectron spectra were measured on a Specs superhigh-vacuum device (Germany) using a 150-mm electrostatic hemispheric analyzer. MgK_α-radiation was used for ionization. The depth of the analyzed surface layer was 2–3 nm. Prior to measurements, the surface was cleaned by a high-energy argon beam (argon etching at a depth of ~3 nm). Spectra calibration was performed on C1s-lines of hydrocarbons, the energy of which was taken to be equal to 285.0 eV.

Changes in the samples' thickness upon oxidation were measured using a micrometer.

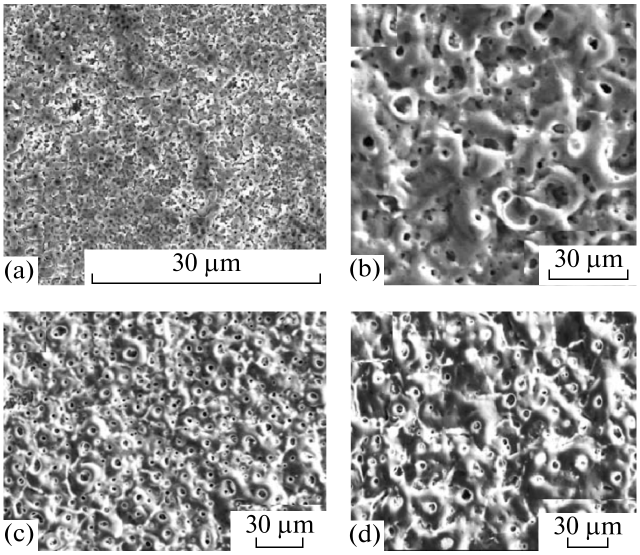

Fig. 1. Morphology of the surface of coatings formed within a single stage: (a) in the $NH_4[TaF_6]$ electrolyte; (b) in the electrolyte with Ca(II) and Sr(II) polyphosphate complexes; in two stages at sequential treatment in both electrolytes, at stage II in (c) the galvanostatic mode and (d) in the potentiostatic mode.

RESULTS AND DISCUSSION

Figure 1 shows SEM images of the surface of coatings formed upon single-stage (Figs. 1a, 1b) and two-stage (Figs. 1c, 1d) treatment. Coatings produced within 2 min in the $NH_4[TaF_6]$ electrolyte in the potentiostatic mode have a rather dense surface covered with numerous small pores (Fig. 1a). Coatings formed in the electrolyte with polyphosphate complexes of Ca(II) and Sr(II) have a surface with alternating elevations and cavities and micron-size pores (Fig. 1b). Upon two-stage treatment (first in the electrolyte with tantalum fluoride complexes, then in that with calcium and strontium tripolyphosphate complexes), the surface morphology is similar to that obtained upon single-stage treatment in the electrolyte with polyphosphate complexes (see Figs. 1c, 1d). The latter indicates deposition of the outer layer characteristic for treatment in electrolytes with metal polyphosphate complexes.

Coatings formed in the electrolyte with tantalum fluoride complexes have a thickness of ~7 μm. Upon secondary treatment in the electrolyte with polyphosphate complexes of Ca(II) and Sr(II), for both galvanostartic and potentiostatic modes, the thickness of the combined coatings is equal to ~32 μm according to micrometer measurements. In other words, the secondary treatment in the electrolyte with polyphosphate complexes results in a significant increase of the coatings' thickness.

Table 1 shows the results of determination of the element composition of the surface part of the coatings under study by the method of X-ray microprobe analysis. In this case, the analysis depth is, depending

Table 1. Element composition of coatings formed in the $NH_4[TaF_6]$ electrolyte (IA), in the $Na_5P_3O_{10}$ + $Ca(CH_3COO)_2$ + $Sr(CH_3COO)_2$ electrolyte (IB) and in the combined mode: in the $NH_4[TaF_6]$ electrolyte and, thereafter, in the electrolyte with polyphosphate complexes of Ca(II) and Sr(II) (IA + II)

Formation stages	Formation mode at stage II	Element composition, at %							
		Ca	Sr	P	Ta	Ti	O	F	Na
IA	PS, $U_f = 60$ V, $t = 2$ min	–	–	–	12,1	21.7	64.2	2.0	–
IB	GS, $i = 0.05$ A/cm^2, $t = 5$ min	7.0	0.4	14.8	–	9.8	66.0	–	2.0
IA + II	GS, $i = 0.05$ A/cm^2, $t = 5$ min	5.2	0.5	12.4	1.0	11.1	67.7	–	2.1
IA + II	PS, $U_f = 80$ V, $t = 5$ min	5.6	0.5	12.9	0.6	11.4	67.1	–	1.9

GS—galvanostatic mode, i—current density, PS—potentiostatic mode, U_f—formation voltage; t—treatment duration.

Table 2. Element composition of the surface of combined coatings from the data of X-ray photoelectron spectroscopy

Formation stages	Formation mode at stage II	Element composition, at %							
		Ca	Sr	P	Ta	Ti	O	C	Na
IA + II	GS, $i = 0.05$ A/cm^2, $t = 5$ min	10.8	0.1	15.6	–	4.0	43.9	23.9	1.7
IA + II	PS, $U_f = 80$ V, $t = 5$ min	9.8	0.1	14.7	–	3.2	39.2	30.9	2.1

on the composition and structure of the studied material, from 2 to 5 μm. A carbon layer was sputtered on the surface to prevent its charging. Because of that, the carbon content was not determined using this method.

As follows from the data of Table 1, coatings produced in the $NH_4[TaF_6]$ electrolyte contain tantalum, titanium, and oxygen (stage IA). The metal/oxygen ratio approximately corresponds to the presence of TiO_2 and Ta_2O_5 oxides in the coatings. Note that coatings formed on titanium in this electrolyte contain, according to the X-ray diffraction analysis data, crystalline phases of TiO_2 and Ta_2O_5 [18]. Along with the stress increase, the tantalum content in coatings increases and one observes an increase of the intensity of peaks corresponding to the crystalline tantalum oxide and the emergence of peaks assigned to the double oxide $TiO_2 \cdot Ta_2O_5$ [18].

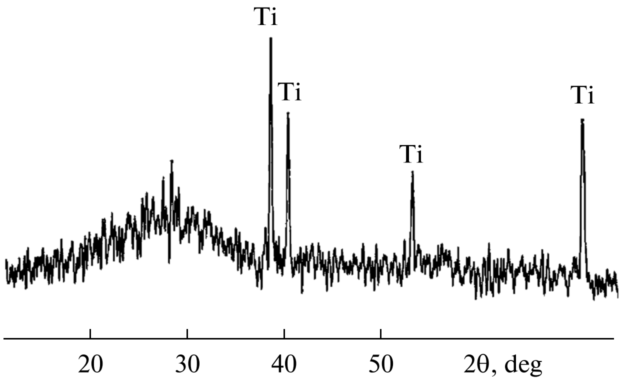

Fig. 2. X-ray diffraction patterns of the combined coating treated at the stage II in the potentiostatic mode (Table 1).

Oxide layers obtained in the electrolyte with polyphosphate complexes of Ca(II) and Sr(II) contain calcium, strontium, phosphorus, titanium, and oxygen (stage IB). According to [17], such coatings contain amorphous high-temperature calcium phosphates (with admixtures of strontium phosphates) and titanium oxide. In this case, the X-ray diffraction patterns contain an amorphous halo and substrate metal peaks. Upon 3-h annealing in air at 600°C, peaks of crystalline phosphates are registered against a background of an amorphous halo.

Upon sequential treatment in the electrolyte with tantalum fluoride complexes and, thereafter, in that with calcium and strontium polyphosphate complexes (stage IA+II), the formed layers are similar to those produced at single-stage treatment in the electrolyte with polyphosphate complexes with respect to the element composition of the analyzed surface part. The difference consists in the presence of about 1 at % of tantalum in the surface part. The appearances of X-ray diffraction patterns of combined coatings (see Fig. 2) are similar to those obtained for coatings formed in the electrolyte with Ca(II) and Sr(II) polyphosphate complexes [17].

Figure 3 shows the general appearance of the surface in phase representation and element distribution maps for the coatings formed within two stages. At the second stage, the coatings were formed in the potentiostatic mode (Table 1). The elements' contents and distribution are shown by light areas (points). One can see that the analyzed surface layer of a thickness of 2–5 μm contains predominantly calcium, phosphorus, and oxygen, whereas their concentration distributions are the same. For instance, pore outlets contain significantly smaller quantities of these elements than the remaining surface. Strontium and tantalum are present in trace quantities in the surface layer. Similar distribution and concentration of elements in the sur-

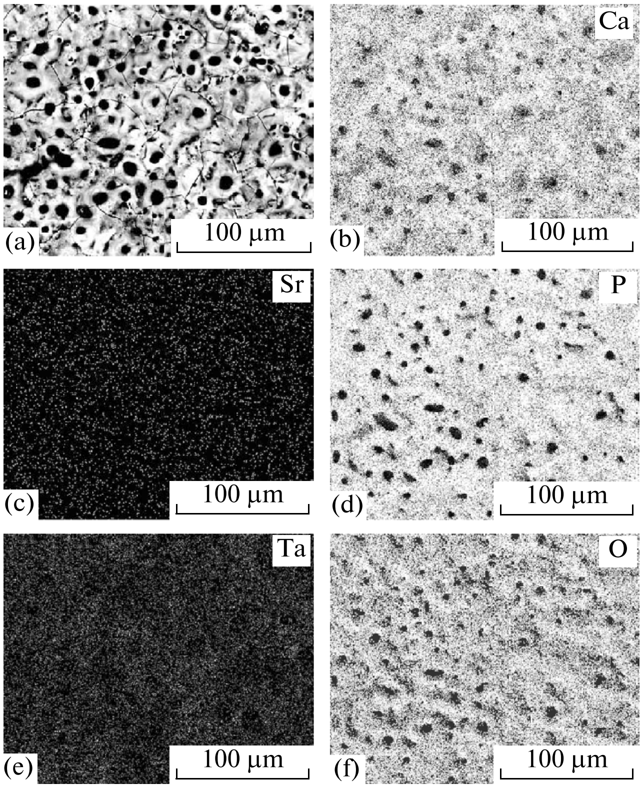

Fig. 3. Maps of elements' distribution in the surface part of the coating formed within two stages in the potentiostatic mode: (b) Ca, (c) Sr, (d) P, (c) Ta, and (f) O. The general appearance of the analyzed surface (phase representation) is given in (a).

face layer is also characteristic of the combined coatings that were treated at the second stage in the electrolyte with polyphosphate complexes in the galvanostatic mode (Table 1).

According to the data of X-ray photoelectron spectroscopy (Table 2), the coatings' surfaces contain oxygen, titanium, calcium, strontium, carbon, sodium, and phosphorus. Since tantalum was not found on the surface, it follows from comparison of the data from Tables 1 (microprobe, analysis depth of 2–5 μm) and 2 (XPS, analysis of a layer of a thickness of ~3 nm), tantalum and its compounds are present in the coating bulk; i.e., coatings have a layered structure. According to the XPS data, carbon is present on the surfaces in quantities comparable to those of oxygen. The presence of carbon can be related as to surface contamination with this element during manipulations with samples as to its embedding to the coating composition from the electrolyte during plasma electrolytic oxidation. Possible reasons for carbon embedding and forms of its presence in PEO coatings are discussed in [21, 22].

CONCLUSIONS

To sum up, the obtained data on morphology, element composition of the surface layer and the surface at large, maps of distribution of elements in the surface layers, and phase composition have corroborated that the sequential oxidation in the electrolyte containing tantalum fluoride complexes (stage I) and in the electrolyte containing Ca(II) and Sr(II) tripolyphosphate complexes (stage II) yielded the formation of combined layered coatings of the composition Ca- and Sr-phosphates/ Ta_2O_5/TiO_2 on titanium. Here, calcium and strontium are present in the coatings' surface parts, while tantalum oxides are contained in the coating bulk. Note that, according to [16], the increase of pH of the electrolyte with tripolyphosphate complexes of Ca(II) enables one to obtain calcium hydroxyapatite in the composition of coatings on titanium. Similar changes in the composition must be observed at an increase of pH of the electrolyte simultaneously containing tripolyphosphate complexes of Ca(II) and Sr(II).

The established regularities can serve as a basis for studies devoted to formation of layered coatings with metal phosphates, including hydroxyapatite, in their outer part and tantalum oxides in the inner part. The fabricated Ca- and Sr-phosphates/ $Ta_2O_5/TiO_2/Ti$ composites are of interest for tests as biocompatible and bioinert implants in the medical practice.

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Translated by D. Marinin