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# NEW SUBSTANCES, MATERIALS AND COATINGS

# Plasma-Electrolytic Oxidation of Titanium in Zr(SO<sub>4</sub>)<sub>2</sub>-Containing Electrolyte

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Abstract—It is shown that anodic oxide coatings with a thickness of several to 300  $\mu$ m can be obtained on titanium by varying the charge spent on (Q). The prevailing phase in the coatings is ZrO<sub>2</sub> in monoclinic and tetragonal modifications. The content of zirconium in the layers is up to 20 at %. Distributions of titanium, zirconium, and oxygen in the cross sections of the coatings are obtained, and the effect of Q on the formation and elementary and phase compositions of the coatings is studied. Tentative experiments clarifying the effects of bipolar anodic—cathodic polarization and electrolyte aging on the composition of coatings are carried out. The coatings are shown to be stable at temperature variations in the range of 20–700°C and to decrease the contact corrosion current at the (titanium + coating)—St3 steel interface by a digit of 10–15 in 3% NaCl.

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### INTRODUCTION

The production of zirconium-containing oxide layers on the surfaces of aluminum, titanium, and magnesium in electrolytes under conditions of superficial electric arc and spark discharges (plasma–electrolytic or plasma–electrochemical oxidation referred to as PEO below) attracts noticeable attention [1–19]. It is assumed that coatings containing zirconium oxide, such as Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>, TiO<sub>2</sub>–ZrO<sub>2</sub>, MgO–ZrO<sub>2</sub>, and MgO– ZrO<sub>2</sub>, can have increased protective, mechanical, and light-reflecting properties, are heatresistant and promising as film catalysts and substrates for catalytically active compounds.

In the PEO technique, electric discharges provide conditions for the inclusion of the solution components and electrolytic deposit, including the products of thermolysis and high-temperature interactions, in layers composed chiefly of the oxide of the metal treated. Based on the peculiarities of the method, several ways of producing oxide layers involving zirconium compounds on valve metals were proposed, including the use of electrolyte suspensions containing ZrO<sub>2</sub> particles [1–5], electrolytes containing fluorocomplexes [6–13] or Zr(IV) polyphosphate [14–16] and tartrate complexes [17], and electrolytes containing Zr(SO<sub>4</sub>)<sub>2</sub> [18, 19].

In [19], coatings were formed on specimens of a technical VT1-0 titanium in a electrolyte containing 35 g/l  $Zr(SO_4)_2 \cdot 4H_2O$  at the anodic polarization, an effective current density of 8 A/dm<sup>2</sup>, and a duration of treatment of 10 min. Coatings with a thickness about 6  $\mu$ m were produced. According to the X-ray spectral

microprobe analysis, they contained (at %) 22.1 Zr, 10.3 Ti, and 67.3 O. Judging from the data of X-ray phase analysis, the coating layer was composed of  $ZrO_2$ oxide (prevailing phase) in monoclinic and tetragonal modifications and TiO<sub>2</sub> oxide. The coatings are dense, weakly wettable with water, and seem promising as protective layers. Variations in the pH of solution by adding NaOH were accompanied by the formation of a deposit in the solution; the decrease in zirconium content, and the increase in titanium; and, hence, titanium oxide contents in the coatings. The supposition was made that the change in the composition of the coatings is determined by the change in the pH value, ionic composition, and the state of solution. According to [20], aqueous solutions of normal zirconium salts are acidic, and their hydrolysis results in the appearance of  $H_2[ZrO(SO_4)_2]$  complex compound that involve zirconium in the anionic group. Depositing zirconium from a sulfate solution by alkali produces basic salts of  $Zr(OH)_{3,72}(SO_4)_{0,14}$  composition. In this case, the supply of zirconium, which should be involved in the cationic group, to the anode and its deposition on it during PEO are hampered.

Electrolytes containing zirconium sulfate are ordinary,one-component electrolytes that are ecologically safe. At the same time, both the formation of zirconium-containing coatings on various valve metals and the composition, structure, and properties of the coatings obtained using this approach are still insufficiently studied. In this work, the results of investigating the effects of the total charge and the alternating anodic—cathodic polarization on the formation, structure, and composition of the coatings on titanium formed from a  $Zr(SO_4)_2$ -containing electrolyte are discussed.

## **EXPERIMENTAL**

Similar to [19], an aqueous  $35 \text{ g/l } Zr(SO_4)_2 \cdot 4H_2O$ solution was used as a electrolyte. The electrolyte was prepared from commercial pure salt and distilled water; the pH value of the solution was in the range of 1-2. Surface layers were formed on specimens with a size of  $23 \times 23 \times 0.5$  mm<sup>3</sup> made of technical VT1-0 titanium (with a titanium content more than 99.5%) at the anodic and alternating anodic-cathodic polarization at an effective current density of  $8-20 \text{ A/dm}^2$  and a duration of treatment of 10–120 min. The electrochemical cell, the cooling and agitating systems, and the preliminary treatment of specimens are described in detail in [14–16].

As a current source, a computer-controlled reversing thyristor operated in either unidirectional or bidirectional anodic-cathodic mode was used. The current source and its characteristics are given in [21]. In the bidirectional mode, the durations of anodic and cathodic current intervals were  $\tau_a = \tau_c = 0.04$  s. Under these conditions, the effective  $i_c/i_a$  current ratio of the cathodic to anodic intervals was set. In this case, the effective current density during the anodic period was constant and equal to  $8 \text{ A/dm}^2$ .

A hollow condenser made of a stainless steel, through which cold trap water was run for cooling the solution, was taken as a counterelectrode. The electrolyte temperature did not exceed 30°C. Specimens covered with coatings were washed in distilled water and dried at a temperature of 60-80°C in air.

The thickness of films was measured with a VT-201 calibrator. Phase compositions were determined with a D8 ADVANCE X-ray diffractometer (Germany) according to the Bragg-Brentano method of rotating a specimen in  $CuK_{\alpha}$  radiation. X-ray patterns were analyzed with the EVA search program with the PDF-2 database. Elementary composition was determined and images of the surface coating layers were obtained with a JXA-8100 X-ray spectral electron probe microanalyzer (Japan). When treating the specimens before determining their elementary composition, either graphite or gold film was sputtered on them. Analysis was carried out on a surface area of  $300 \times 200$ or  $10 \times 12.5 \,\mu\text{m}^2$ . When studying the distribution of elements in the depth of coatings, the probing beam was focused on a spot with a diameter of about  $1.5 \,\mu m$ .

Cross sections of a specimen were prepared by fastening the specimen with Epoxy resin and polishing it with a special set of polishing agents. When measuring contact corrosion currents of the St3 steel-titanium (individual or covered with a coating) couples on specimens, surface areas about 1 cm<sup>2</sup> were delimited with insulating varnish. Specimens immersed in a 3% NaCl solution were arranged in parallel to each other at a



Fig. 1. Effect of total charge spent (Q) on (a) thickness and (b) contents of titanium and zirconium in the coatings formed at anodic polarization.

distance of 1 cm. The specimens were connected via a resistance of 100  $\Omega$  where a voltage drop was measured with a millivoltmeter, from which the current in the circuit was calculated.

## **RESULTS AND DISCUSSION**

Figure 1 shows the thickness and elementary composition of the coatings formed at the anodic polarization depending on the total charge spent per a unit anode surface area  $(Q = i(A/cm^2) \times t(s))$ . In the experiments, either the duration of treatment was varied from 10 min to 2 h at a constant effective current density  $i = 20 \text{ A/dm}^2$  or the effective current density was varied in a range of  $1-20 \text{ A/dm}^2$  at a constant duration t = 10 min.

With an increase in Q, the thickness of coatings gradually increases and reaches nearly 200 µm under particular experimental conditions (Fig. 1a). With an increase in Q, the content of titanium decreases to 6-10 at %, while that of zirconium increases to 17-21 at %. In the whole studied range of Q values, the concentration of oxygen in the coatings falls in the range of 66– 70 at %. Note that the data obtained upon sputtering graphite for charge draining from the specimen during measurements (carbon was not determined) and are averaged over the areas of  $300 \times 200 \ \mu\text{m}^2$  at a depth of the layer analyzed of  $2-5 \,\mu\text{m}$ .



**Fig. 2.** Effect of total charge spent (Q) on phase composition of coatings formed at anodic polarization: (I) at constant duration of process of 10 min and current density, A/dm<sup>2</sup>: (a) 20, (b) 10, and (c) 5; (II) at constant current density of 20 A/dm<sup>2</sup> and duration of process, min: (a) 120, (b) 60, and (c) 30.

The elementary composition of the coatings formed corresponds to the presence of  $ZrO_2$  and  $TiO_2$ oxides with a small excess in oxygen. The conclusion is supported by the data of X-ray phase analysis (Fig. 2). In the X-ray patterns, reflexes assigned to  $ZrO_2$  prevail. Upon the 10-min formation at a small current density  $(2-5 \text{ A/dm}^2, \text{ Fig. 2}, \text{ curve Ic})$ , reflexes corresponding to ZrO<sub>2</sub> in monoclinic and tetragonal modifications are present. Judging from the intensities of the peaks, tetragonal ZrO<sub>2</sub> prevails. When the current density is increased to 20 A/dm<sup>2</sup> at a constant duration of the formation of 10 min, the total thickness of the coating increases and the intensity of signals corresponding to tetragonal and monoclinic ZrO<sub>2</sub> modifications increases, the former modification prevailing. At the same time, an increase in Q value provided by an increase in the duration of the process at a constant effective current density of 20 A/dm<sup>2</sup> results in the gradual increase in the intensity of the peaks corresponding to monoclinic modification, which becomes predominant in the thicker coatings (Fig. 2, curve IIb).



**Fig. 3.** (a, b) Appearance of secondary sites on coatings at Q > 60-80 C/cm<sup>2</sup> secondary layer; (c) the secondary layer–primary coating profile; and (d) the surface of the coating obtained upon 576 C/cm<sup>2</sup> spent on.

Concurrently with the changes in the elementary and phase compositions of the coatings, the mechanism of their growth also changes. At a total charge of  $60-80 \text{ C/cm}^2$ , on the primary film with a thickness of  $10-15 \text{ }\mu\text{m}$ , there appear secondary-layer protuberances, which gradually broaden and grow in height (Figs. 3a-3d) and finally cover the whole surface at large Q (Fig. 3d). Figure 3c shows an image (obtained with a laser optical microscope) of the surface covered with a secondary layer, as well as the measured profile between the secondary layer and the primary coating. According to the data obtained, the secondary layer has a complex surface structure and rises above the surrounding primary film by  $6-12 \text{ }\mu\text{m}$ .

In order to compare the composition of the secondary and primary layers, the composition of separate surface areas with a size of  $10 \times 12.5 \ \mu\text{m}^2$ , which formed at the total charge spent of 60, 90, or  $360 \text{ C/cm}^2$ , was determined (table). As follows from the data shown, compositions of the primary and secondary layers are identical in the films of different thickness. This means that the solution components are built in both structures concurrently in the same proportions and, probably, according to the same mechanism. In the thickened layers, titanium is seemingly built from the electrolyte upon its dissolution under the effect of electric breakdowns. The reasons for the appearance and growth of the secondary layers, which do not differ in their composition from the primary ones, are still unclear. This may probably be caused by the etching effect of the acidic (pH 1-2) electrolyte and the appearance of short spreading discharges, behind which a thickened layer is formed [22].

In order to clarify the distribution of zirconium in the cross sections of the layers, the sections of coatings with a thickness of several tens microns were prepared and studied (Fig. 4). Gold was sputtered on the sections, which enabled us to determine carbon with the use of micro probe analysis. As can be seen, the films are sufficiently dense and compact, with no visible large inner pores and voids. The contents of oxygen, titanium, zirconium, and carbon were determined by focusing the probing beam on a spot with a diameter of about  $1.5 \,\mu$ m in either continuous or site-by-site scanning mode.

General trends in the distribution of the elements are as follows. Except for the surface layer of the coatings, which is about 6-9% of the total film thickness, the contents of oxygen and carbon are nearly constant in the depth. On different sections, the following ranges of the oxygen and carbon contents were obtained: 32.5-50.5 wt % (at a mean value of 45.5 wt %) and 4.2–13 wt % (at a mean of 7.8 wt %), respectively. The presence of carbon can be caused by rubbing a polymer on the section during polishing. In connection with this, it is worth noting that the determined average concentration of carbon on titanium is 1.7 wt %, which is much smaller compared to the coating section. The content of titanium in different sections varies from 33 to 53 wt % and decreases from the titanium-coating interface toward to the coating-polymer interface (Fig. 4). The concentration of zirconium monotonically increases from the coating-titanium interface toward the coating-polymer interface. In the layer adjacent to titanium, zirconium content is 1-3 wt %. Closer to the oxide surface, the zirconium content gradually increases. The surface layer, which is in contact with the polymer and has a thickness of 6-9% of the total coating thickness, is noticeably enriched in zirconium (to 40 wt % or above). This is clearly illustrated by the distribution maps of titanium and zirconium in the coating sections (secondary-electron images, Figs. 4c and 4d). Here, the concentrations of titanium and zirconium both in the cross sections of the coatings and within the subsurface layer change in such a way that their sum remains nearly constant. This means that either ZrO<sub>2</sub> and TiO<sub>2</sub> phases are mixed in the coating or zirconium and titanium replace each other in the oxide lattice.

Previously, the accumulation of zirconium in the surface layers of PEO coatings formed on aluminum, titanium, and magnesium was noticed in aqueous  $K_2ZrF_6$  electrolyte electrolytes [6] and in aqueous electrolyte suspensions containing dispersed  $ZrO_2$  particles [2–5].

In the experiments described, a question about the presence of carbon in the films is still open. It is not clear whether it is built in the films during the PEO

Elementary composition of separate surface sites with a size of  $10 \times 12.5 \ \mu\text{m}^2$  on the coatings produced at the different total charge spent: (I) primary and (II) secondary coatings

<i>Q</i> , C/cm <sup>2</sup>	Coating	Elementary composition, at %		
		0	Ti	Zr
60	I	69.2	7.1	22.7
	II	73.0	5.4	20.7
90	I	74.0	6.0	19.1
	II	71.7	7.2	20.2
360	I	72.3	11.5	15.0
	II	70.1	9.6	18.5

treatment or it appeared on the surface as a result of manipulations with the specimens (from hands, from polymer rubbed during polishing, etc.). At the same time, carbon was found in many PEO structures [23], including microgranules formed on the surfaces [24]. We believe that the question about the carbon origin in the anodic PEO structures, the mechanisms of its possible building in, and the contribution to the structure and properties of PEO coatings requires special investigation and discussion.

When PEO layers are produced on aluminum from e.g. silicate electrolytes, the bidirectional anodic– cathodic polarization is known to affect the phase composition of the coatings and promote the formation of continuous interlayers of high-temperature  $\alpha$ and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> aluminum oxide phases [25, 26]. We estimated the effect of bidirectional polarization on the composition of coatings formed on titanium from an aqueous Zr(SO<sub>4</sub>)<sub>2</sub> electrolyte.



**Fig. 4.** (a) Cross section of coating with thickness of 60  $\mu$ m; (b) distributions of titanium and zirconium in depth; and (c, d) distribution maps of (c) titanium and (d) zirconium in coatings with thickness of 150  $\mu$ m. Content of element is reflected by light spots.



**Fig. 5.** Effect of effective cathodic-to-anodic current ratio on thickness and elementary composition of coatings formed at bidirectional polarization.



**Fig. 6.** Effect of effective cathodic-to-anodic current ratio on phase composition of coatings formed at bidirectional polarization. X-ray patterns of coatings formed at  $i_c/i_a$ : (*a*) 0, (*f*) 1.5, and residual  $i_c/i_a$  intermediate values. Phase notations are same as in Fig. (b) 2. *S* is relative change in contents of tetragonal (T) and monoclinic (M) phases calculated from comparison of amplitudes of the most typical reflexes.

In the experiment, the  $i_c/i_a$  effective current ratio of the cathodic to anodic intervals was set. The effective current density during the anodic period was constant and equal to 8 A/dm<sup>2</sup>. The durations of the anodic and cathodic current pulses were  $t_a = t_c = 0.04$  s, and the formation of oxide layers took 10 min.

As follows from Figs. 5 and 6, when  $i_c/i_a \le 0.2$ , the cathodic component insubstantially affects the thickness and the content of titanium and zirconium in the analyzed surface part of the coatings. At the same time, the content of high-temperature tetragonal phase increases in the coatings. Further increase in the  $i_c/i_a$  ratio results in the sharp decrease in the thickness of coatings and the substitution of zirconium in the layers with titanium, though tetragonal zirconium oxide phase still prevails over the monoclinic modification. At  $i_c/i_a > 1.5$ , coatings do not form.

The data obtained enable us to suppose that an increase in the duration of the process at  $i_c/i_a < 0.5$  may result in the production of films, whose elementary composition is close to that obtained under anodic



**Fig. 7.** X-ray patterns of coatings formed in (a) fresh and (b) aged (by boiling) electrolytes. Phase notations are same as in Fig. 2.

conditions, but the high-temperature tetragonal phase prevails.

As is shown by the observations and experiments, the state of the  $Zr(SO_4)_2$ -containing electrolyte changes with time, upon treating a set of specimens. under anodic-cathodic especially conditions (exhausted electrolyte), or upon boiling the solution (artificial aging). A noticeable deposit consisting of solid particles appears in the electrolyte, while the coatings formed in an exhausted or aged electrolyte are composed chiefly of tetragonal phase (Fig. 7). As tentative estimates have shown, the aging or exhaustion of the electrolyte results in the production of layers that contain a high-temperature tetragonal phase and do not differ in their thickness and composition from those obtained from a fresh electrolyte. This aspect requires additional investigations.

As regards the protective properties of the layers, the first tentative estimates were obtained. The layers with a thickness of  $15-200 \mu m$  were found to be sufficiently stable at temperature drops in a range of  $20-700^{\circ}$ C. The specimens were heated in a muffle furnace, then taken away and immersed in water at a temperature of  $20^{\circ}$ C. The specimens withstood ten heating—cooling cycles with no visible changes. Similar specimens were used in laboratory experiments as substrates of catalytically active compounds. When carrying out catalytic measurements, the specimens stood repeated cycles of heating to  $500^{\circ}$ C followed by cooling to room temperature.

Measuring the contact corrosion currents of St3– titanium and St3–15–20- $\mu$ m coating–titanium couples showed that the coating decreases the galvanic corrosion currents in the couples by a digit of 10–15 (one-month-long observation). As was found previously [19], these coatings are weakly wettable with water. All of the above peculiarities show that these coatings are promising as protective films, especially at heightened temperatures.

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