
NEW SUBSTANCES,
MATERIALS AND COATINGS

Plasma-Electrolytic Oxidation of Valve Metals in Zr(IV)-Containing Electrolytes

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Abstract—The studies devoted to the production of Zr-containing coatings on valve metals (Ti, Al, and Mg) using plasma-electrolytic oxidation are reviewed. The coatings are formed from aqueous electrolyte suspensions containing dispersed ZrO_2 particles, as well as Zr(IV) fluorocomplexes, polyphosphate, and tartrate complexes, and from $\text{Zr}(\text{SO}_4)_2$ electrolytes. The layers that contain both zirconium oxide in either monoclinic or tetragonal modification and zirconium pyrophosphate and layers containing simple and complex zirconium phosphates are obtained. The described approaches enable one to produce protective layers and can form the basis of the technique for obtaining surface structures with a complex chemical composition, as well as coatings that contain certain compounds with specific characteristics.

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Zirconium oxides and some phosphates are widely used in practice or are promising in practical application [1, 2]. For example, ceramics based on $\text{ZrO}_2\text{--Al}_2\text{O}_3$ or $\text{ZrO}_2\text{--MgO}$ systems have mechanical wear-resistance, high toughness, and, in a number of cases, high reflectivity, allowing them to be used in various fields [1, 3, 4]. Ceramics based on zirconium and cerium oxides is used in engine exhaust cleaning systems [5]. Photocatalytic properties of $\text{TiO}_2\text{--ZrO}_2$ films [6, 7] and catalytic activity of zirconium and titanium pyrophosphates [8] with respect to the transformations of a number of organic compounds were studied. Zirconium pyrophosphates are used as substrates of catalytically active composites [9]. Some zirconium phosphates attract attention due to low coefficients of thermal expansion or ion-exchange properties [10]. The stabilized cubic modification of zirconium oxide, including thin films and coatings, is used in ionic conductors, which are sensitive elements of gas-analyzing devices [11].

The aforementioned properties may also be inherent in thin films and coatings involving zirconium oxides and phosphates. This is why there is interest in developing approaches of producing films and coatings that involve zirconium oxides and phosphates on diverse substrates and structural materials, as well as in studying the composition, structure, and properties of the films.

On the surface of valve metals (Al, Ti, Mg, Zr, Nb, etc.) and their alloys, complex oxide and oxide–phosphate layers with a thickness of several to hundreds microns can be formed by plasma-electrochemical oxidation (PEO) and oxidation in electrolytes under the effect of arc or spark electric discharges [12–16]. Electric discharges cause a number of processes and interactions

on the surface of a growing anodic oxide film, including thermal transformations of the electrolytic deposit and electrolyte compounds and particles adsorbed on the surface or concentrated near the anode. The products of reactions and interactions caused by discharges and molten or partially fused solid particles from the electrolyte may become involved in the growing oxide film. Therefore, by adding salts, complexes, or colloid and finely dispersed solid particles containing the necessary elements, e.g., zirconium, to the electrolyte, one can expect to observe the formation of compounds of the corresponding elements in the oxide layer formed with the PEO technique.

Based on the compositions of aqueous electrolytes, we can distinguish five main approaches of the formation of zirconium-containing PEO-coatings on valve metals.

The first approach consists of using electrolyte suspensions containing finely dispersed ZrO_2 particles in a certain polymorphic modification [12, 15–26]. Markov et al. [12, 23, 24] were seemingly the first to propose and establish the idea of using electrolyte suspensions in directed formation of coatings using a PEO technique.

The inclusion of colloidal and solid particles from the electrolyte into the coatings is a complex process depending on numerous factors, such as the concentrations, sizes, charge, mobility, and sedimentation rate of the particles, their nature and concentrations, as well as the nature of salts contained in the electrolyte, electric conditions and stages of the anodic process (sparking, micro-arcs, arcs, anodic or mixed anodic–cathodic conditions, current density, and duration of treatment), the nature of the rectifying metal or alloy, etc. [12, 14–22, 25–28]. In this case, the growth of coatings proceeds also

due to the deposition of colloidal or finely dispersed solid particles on the growing coating and the subsequent thermolysis at the breakdown sites or partial melting followed by hardening. In some cases, this peculiarity enables one to rapidly increase the coating thickness at relatively low energetic costs [15, 17, 19, 26, 28] of up to several hundred microns [17].

When producing Zr-containing coatings from electrolyte suspensions, aqueous silicate [12, 15, 20–22], or phosphate [17, 21, 22], electrolytes or aqueous KOH solutions containing silicate and phosphate additives [18, 19] are typically used as electrolytes. To stabilize particles in the solution, e.g., $\text{Na}_6\text{P}_6\text{O}_{18}$, sodium hexametaphosphate is sometimes used as a stabilizer in KOH-based electrolyte [19]. Either anodic [15, 17, 21, 22] or mixed anodic–cathodic polarization of the electrodes [18–20] is applied. The duration of the treatment is up to 120 min at current densities of 2–20 A/dm².

In [19] when producing zirconium-containing coatings on aluminum by means of PEO technique, ZrO_2 particles smaller than 50 μm were added to the electrolytes containing KOH + $\text{Na}_6\text{P}_6\text{O}_{18}$ or KOH + $\text{Na}_6\text{P}_6\text{O}_{18}$ + Na_2SiO_3 . Concentration of the powders added to the solution [19] falls generally in a range of 5–100 g/l. It was noticed that, in the case of aluminum alloy, original ZrO_2 particles are concentrated on the coating surface. The wear resistance of the coatings differed slightly from that of the coatings formed in the original electrolytes. At the same time, the growth rate of the coating was two or three times larger than in the case of oxide structures formed in electrolytes with no additive.

In [20–22], zirconium-containing coatings were formed on aluminum (99.99%) [20] or magnesium (99.9%) [21, 22]. The authors added 2–10 g/l zirconium oxide particles (in monoclinic modification) with sizes of 150–300 nm to aqueous electrolytes containing 15 g/l $\text{Na}_6\text{P}_6\text{O}_{18}$ [20] or 5.6 g/l $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ + 2.8 g/l KOH [20–22], as well as 0.025 M $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ + 1.5 M NH_4OH [22]. Either anodic [20, 22] or alternating-current anodic–cathodic polarization [21] was applied.

According to the data of [20–22], zirconium particles are present on the surfaces of coatings, as well as at the hollow or cavity boundaries in the coating. The shape and size of the particles are close to the original ones. In the case of magnesium, the coatings that have a lamellar structure with a relatively compact inner layer and a porous outer layer with hollows and cavities, the particles are also concentrated at the layer interfaces [21, 22]. Zirconium is also present in the coating and its distribution over the surface and in the cross sections of the coatings is heterogeneous. The cross section of the oxide coating has a complex cellular (or mesh) structure [20]. At the cell boundaries, the zirconium content is noticeably higher than inside the structure units. Moreover, there is a difference between the zirconium distributions in the coatings formed in different electrolytes. For example, on the surfaces of coatings on aluminum and magnesium formed in a Na_2SiO_3 + KOH electrolyte, sites enriched in silicon and sites composed of aluminum or magnesium oxides

with sizes of 20–50 and 50–100 μm , respectively, alternate [20, 21]. At the silicon sites, the concentration of ZrO_2 particles is much higher than at the sites where silicon is absent. The authors believe that the codeposition of silicon-containing solution components and ZrO_2 particles from the electrolyte takes place at the discharges.

According to the data of X-ray phase analysis, along with monoclinic ZrO_2 (added to the solution), tetragonal ZrO_2 modifications are also present in coatings formed on either aluminum or magnesium [20–22]. The authors suppose that, under the effect of electric discharges, some of the particles are transferred to the melt, then recrystallized in the tetragonal phase. The content of the tetragonal phase increases with an increase in the current density and depends on the polarization conditions (direct or alternating anodic–cathodic current). In addition to ZrO_2 oxide phases, the coatings formed on aluminum involve α -, γ -, and δ - Al_2O_3 phases [20]. It was noticed that the content of α - Al_2O_3 phase in the coatings formed decreases upon the addition of dispersed zirconium oxide particles to the electrolytes [17, 20]. In the coatings produced on magnesium from a silicate electrolyte, MgO , Mg_2SiO_4 and $\text{Mg}_2\text{Zr}_3\text{O}_{12}$ phases are present, along with ZrO_2 [21, 22].

The thicknesses of coatings formed under the same conditions in a $\text{Na}_6\text{P}_6\text{O}_{18}$ electrolyte either containing ZrO_2 particles with a size of 150–300 nm or not are the same [20]. Thus, the earlier discovered phenomenon of the accelerated growth of coatings in electrolyte suspensions [15, 17, 19, 26, 28] only takes place when particles of micron sizes, e.g., < 50 μm are used [19]. Because they are bound to the surface or built in growing coatings, these particles substantially increase the thickness of the oxide layers.

The second approach to producing zirconium-containing coatings with the PEO technique is based on the use of aqueous electrolytes containing Zr(IV) fluoride complexes [16, 29–41]. Aqueous electrolytes based on zirconium, titanium, and hafnium hexafluorides were used, seemingly for the first time, when surface oxide structures were produced on niobium alloys by means of PEO technique in [29, 30]. For example, in electrolytes containing ZrF_6^{2-} and SO_4^{2-} anions, coatings that contain crystalline δ - Nb_2O_5 , ZrO_2 , as well as NaNb_3O_8 and Na_2NbO_3 niobates, were deposited on niobium. Zirconium oxide and niobates were found to be concentrated in the outer coating layer, which is about one-third of the total thickness.

As was shown later, using electrolytes containing water-soluble fluoride complexes of transition metals, particularly Zr(IV), Ti(IV), Hf(IV), and Nb(V), one can produce oxide layers that contain oxides of the aforementioned elements on both niobium and titanium or aluminum using PEO technique [31–33]. The coatings were formed either under the dropping power conditions when U_{in} potential difference was set in the cell or under galvanostatic conditions at the total duration of the pro-

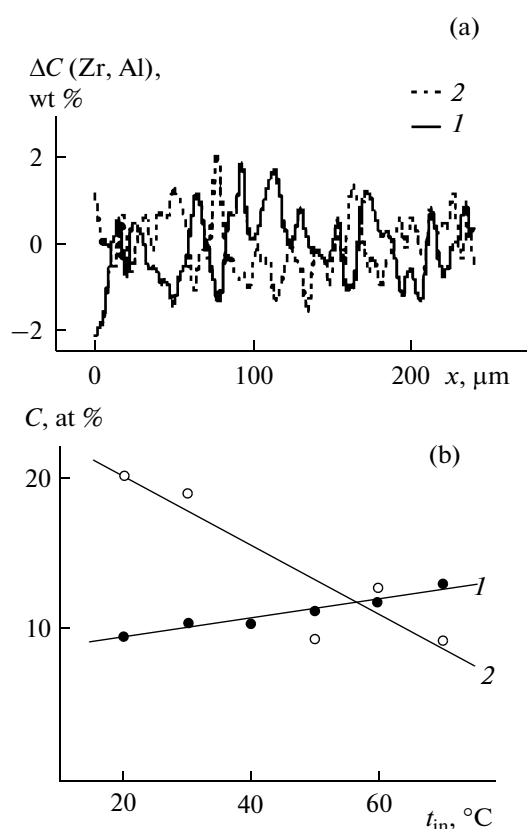


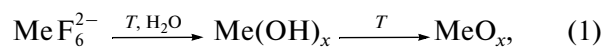
Fig. 1. (a) ΔC content deviation from the mean value of (1) zirconium ($C_m = 42$ wt %) and (2) aluminum ($C_m = 14$ wt %) contents in outer layer of coatings along the x surface coordinate. Conditions of coating production: $t_{in} = 60^\circ\text{C}$ and $U_{in} = 400$ V. (b) Effect of t_{in} initial temperature on content of (1) zirconium and (2) aluminum in outer layer of coatings [36].

cess of five to several dozen minutes. The concentration of fluorozirconate salt in the electrolyte was 6–15 g/l.

The coatings formed on AMts aluminum alloy (~1.6% Mn) under dropping power conditions in an aqueous K_2ZrF_6 solution contained cubic ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$ phases [31]. According to the data of laser mass spectroscopy (evaporation and an analysis of the outer layer with a thickness of up to 10 μm), the coatings had the following composition, wt % [32]: 0.1 C, 27.8 O, 2.3 F, 28.5 Al, and 41.2 Zr. Comparing the data of X-ray spectral microprobe (the penetration depth of the probing beam was 2–5 μm) and mass spectral analyses enabled the authors to conclude that the coatings have a lamellar structure and that electrolyte components are involved in the outer layer, which is about one-third of the total coating thickness [31, 32]. The PEO coatings produced on aluminum alloy under the same conditions from the fluorozirconate electrolytes that contain different cations (Na_2ZrF_6 , K_2ZrF_6 , CsZrF_5 , or $(\text{NH}_4)_3\text{ZrF}_7$) contained different amounts of zirconium [32]. The largest content, which was higher than 50 wt %, was observed in coatings formed from a electrolyte containing

Na_2ZrF_6 . According to the effects produced by alkaline metals involved in zirconium hexafluoride complexes on the zirconium content, the following series was obtained: $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$ [32]. This may be related to the peculiarities of the hydrolysis of the salts involving different cations and the effect of the processes on the mechanism of zirconium inclusion.

The presence of transient metals (M) in oxide films can be a consequence of two processes, namely, the hydrolysis of salts that produce complex anions and subsequent annealing at the breakdown sites as follows [31]:



ZrO_2 layers deposited on aluminum alloy from a electrolyte containing K_2ZrF_6 have a color in imitation white enamel and are decorative, as well as heat and corrosion resistant [31].

Results similar to those of [31–33] were obtained later in [34]. As was shown, foam-white coatings with a thickness of 40–120 μm are formed on aluminum (99.99%) from an aqueous electrolyte containing K_2ZrF_6 in 30–180 min, respectively. Under the same conditions, hard, dark-brown coatings (probably due to alloying with copper compounds) of a similar thickness were produced on a copper-containing alloy (3.8–4.5% Cu and 1.2–1.8% Mg). A change in the electrolyte temperature from 15–70°C did not affect the growth rate of the oxide structures. The coatings contained up to 52 or 54 wt % zirconium, zirconium oxides in tetragonal and monoclinic modifications, and aluminum oxides.

As was mentioned above, the coatings deposited on aluminum from electrolytes containing K_2ZrF_6 are used decoratively in imitation white enamel. In order to estimate the possibility of their use as light-reflecting layers, their reflectivity and the resistance of their coloring against short-wave ultraviolet light were studied [35, 36]. The coatings produced on A7 aluminum alloy (99.7% Al) from a electrolyte containing K_2ZrF_6 under the dropping power conditions had a whiteness $W = 89$ –91% and an integral reflectivity $\rho_s = 81\%$ with respect to MgO reference in a wavelength range of 430–670 nm. Judging from the optical characteristics, the coatings had a satisfactory resistance against ultraviolet radiation (upon irradiation for up to 30 h with an SVD-120 mercury lamp placed at a distance of 13 cm from the specimen, the change in W and ρ_s was 5–6% [35]). According to the data obtained in [36], the upper part of the coatings (analysis of the layer with a thickness of 2–5 μm) consists of two incompletely mixed phases, namely, zirconium and aluminum oxides (Fig. 1a). The total zirconium content, as well as the content of the tetragonal ZrO_2 phase, increased with an increase in the electrolyte temperature (Fig. 1b). The best reflectivity was noticed in the case of the layers formed under the dropping power conditions at a temperature of 30–50°C [36]. This is due to the com-

bined effect of the zirconium content and the roughness of the layers.

Recently, the compositions, adhesion, and protective characteristics of PEO coatings formed on titanium, aluminum, and magnesium from aqueous K_2ZrF_6 -based electrolytes were estimated [37–41]. The electrolytes additionally contained H_3PO_4 [37, 39], $H_3PO_4 + Na_2SO_4$ [38], phosphate [40], CH_3COONa , or $C_2H_2O_4$ [41]. The coatings were formed under galvanostatic conditions at a pulsating monopolar [38, 39] or bipolar current [40] with a frequency of 60 Hz and effective density of 8 A/dm². Coatings on magnesium were produced under dropping power conditions [41]. The duration of the coating formation was up to 180 min.

The thickness of coatings on a titanium alloy (Ti–6 Al–4 V) and aluminum alloy (LY12) increased in proportion to the treatment duration t [39, 40]. Layers with a mean thickness of 206 μm [38] or 53 μm [39] were formed on titanium alloy in $t = 90$ min; 160- μm layers were formed on aluminum in $t = 180$ min [40]; and layers with a thickness of 39–51 μm were formed on magnesium in $t = 20$ min at $U_{in} = 400$ –550 V [41]. The larger the duration of treatment under galvanostatic conditions and the larger the mean thickness of the coatings, the more heterogeneous they are in depth and the larger the differences between the measured minimal and maximal thicknesses [38, 39].

At a distance more than 10–30 μm from the metal, the elemental composition of the coatings formed on titanium becomes stable [38, 39]. For example, coatings produced on titanium from a $K_2ZrF_6 + H_3PO_4$ electrolyte contain (wt %) ~ 5 Ti, ~ 55 Zr, ~ 30 O, and ~ 10 P [38]. The coatings obtained on magnesium at $U_{in} = 550$ V contain (at %) 11–13 O, 14–26 F, 44–49 Mg, and 14–26 Zr [41]. It is worth noting that the oxygen content is low, while the fluorine content is fairly high in coatings on magnesium. According to the available data, fluorine content in similar coatings formed on aluminum is much lower (3.6 at % [32]).

In all cases, the coatings contain monoclinic and tetragonal ZrO_2 phases [38–41]. The amount and ratio of zirconium oxide phases in the coatings depend on the conditions of their production. Coatings formed on titanium from $K_2ZrF_6 + H_3PO_4 + Na_2SO_4$ and $K_2ZrF_6 + H_3PO_4$ electrolytes contained (along with ZrO_2 phase) $KZr_2(PO_4)_3$ [38] and ZrP_2O_7 phases [39] respectively. According to the data obtained [39], relatively thin coatings formed in short-term experiments contain ZrO_2 and $ZrTiO_4$. With an increase in the duration of formation, zirconium pyrophosphate phase appears in the coatings and becomes prevailing. At the same time, crystalline phosphates were absent in coatings formed on aluminum [40]. Coatings on magnesium contained MgO and MgF_2 phases, along with ZrO_2 [41].

The coatings produced on titanium, aluminum, and magnesium from K_2ZrF_6 -based electrolytes decrease the contact corrosion currents and hamper pitting corrosion; the coatings on magnesium have microhardnesses that are several times larger than that of magnesium itself [39–41].

The third approach is the PEO formation of zirconium-containing oxide–phosphate layers from aqueous electrolytes containing Zr(IV) polyphosphate complexes [42–44]. From aqueous electrolytes containing M^{2+} or M^{3+} polyphosphate complexes, PEO-coatings involving Mg^{2+} , Ni^{2+} , Mn^{2+} , Eu^{3+} , or La^{3+} compounds including phosphates are formed on valve metals [16, 45]. The compositions, thickness, and structure of the coatings, as well as the state of the solution, depend on the $n = [\text{polyphosphate}] / [M \text{ cation}]$ molar ratio of the electrolyte. When polyphosphate is taken in excess, the electrolytes are transparent, the solutions are true, and the coatings are composed chiefly of the treated metal oxide. When n approaches unity, a colloid containing particles of water-bearing M(II) or M(III) polyphosphates is formed, and the content of these metals and phosphorus in the coatings increases. When $n < 1$, solid particles of water-bearing M(II) or M(III) metals are deposited from the solutions, and the thickness of the layers formed sharply increases. The increase in the metal and phosphorus contents and the coating thickness are due to the presence of water-bearing M(II) or M(III) polyphosphate particles adsorbed on the surface or involved in the electrolytic deposit in the vicinity of breakdown sites, their thermolysis produces corresponding phosphates, and the inclusion of the thermolysis products in the coating material. In this respect, this approach is similar to that using electrolyte suspensions. The difference consists of the possibility of controlling the electrolyte state via the n value and, hence, the possibility of controlling the composition, structure, and thickness of coatings in relatively broad ranges [16, 45].

As was shown in [42–44], the approach can be generalized for the PEO production of surface oxide structures involving Zr(IV) compounds (Fig. 2). Coatings on VT1-0 titanium (titanium content is no less than 99.5%) were produced under galvanostatic conditions (at an effective current density $i = 5$ –8 A/dm² and a duration of the process of 2–30 min) from aqueous solutions containing 30 g/l $Na_6P_6O_{18}$ or 36.9 g/l $Na_5P_3O_{10}$ and $Zr(SO_4)_2 \cdot 4H_2O$ by setting the necessary precalculated molar ratio $n = [P_6O_{18}^{6-}] / [Zr^{4+}]$ or $[P_3O_{10}^{5-}] / [Zr^{4+}]$. Either anodic or anodic–cathodic alternating-current conditions were used.

During the formation of coatings when a total charge $Q > 3 \times 10^3$ C/dm² was supplied to the cell, secondary-layer regions are formed on the primary film with a thickness of 15 to 25 μm (Fig. 3) from the electrolytes containing $Na_6P_6O_{18}$ and $Zr(SO_4)_2$ at $n \leq 1$ and from the electrolytes containing $Na_5P_3O_{10}$ and $Zr(SO_4)_2$ at all the studied n values [43, 44]. The thickness of the secondary layer (step) is 30–90 μm . The layers grow under the effect of linearly spreading electric discharges [46]. The secondary-layer regions extend, coalesce, and cover the whole surface over time and multilayer structures appear. The primary layers are either X-ray amorphous or involve ZrO_2 phase. The secondary layer has a developed surface

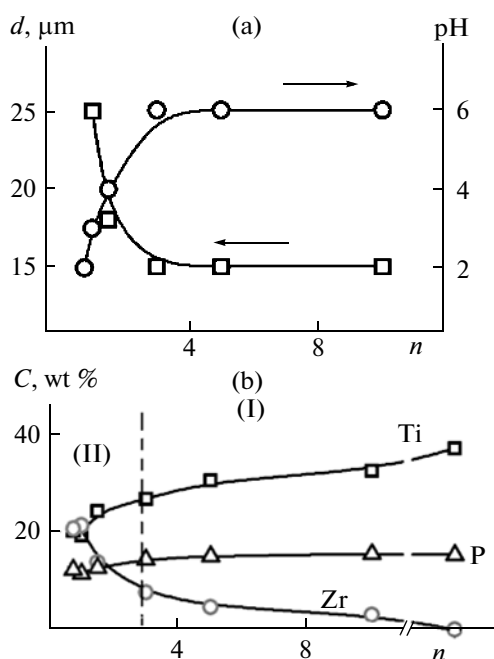


Fig. 2. Effect of $n = [\text{P}_6\text{O}_{18}^{6-}]/[\text{Zr}^{4+}]$ ratio on (a) pH of electrolyte and thickness of layers and (b) elemental composition of layers produced [43].

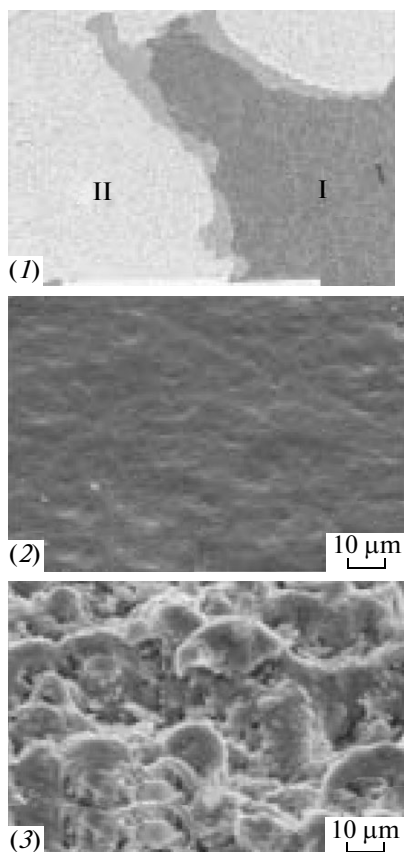


Fig. 3. (1) Lamellar coatings: (I) primary and (II) secondary layers. Surface structure of (2) primary and (3) secondary layer.

with hollows and crests with typical sizes of about 10 μm . The secondary layer contains a ZrP_2O_7 phase and traces of $\text{Na}_2\text{Zr}_2(\text{PO}_4)_3$. Taking into account the data of [39], it is quite possible that zirconium polyphosphates are formed not only as a result of the thermolysis of $\text{Zr}(\text{IV})$ polyphosphate complexes, but also due to the high-temperature interaction between ZrO_2 and phosphates in the breakdown domains.

Introducing $\text{Ba}(\text{CH}_3\text{COO})_2$ salt in the $\text{Na}_6\text{P}_6\text{O}_{18} + \text{Zr}(\text{SO}_4)_2$ electrolyte, e.g., at a $\text{Zr} : \text{Ba}$ ratio of 3 : 1, affects the morphology of the coatings and causes additional inclusion of barium in the film and the formation of ZrP_2O_7 , $\text{NaTi}_2(\text{PO}_4)_3$, $\text{BaTi}_2(\text{P}_2\text{O}_7)_2$, and $\text{Zr}_{0.2}\text{Ti}_{0.8}\text{P}_2\text{O}_7$ crystalline phases in the films [44]. Oxide–phosphate layers involving simple and binary zirconium, barium, sodium, and titanium phosphates are formed. Annealing specimens covered with multilayer coatings in air at 800°C causes the additional crystallization of the already present and novel compounds [43, 44]. For example, the coatings that are formed from an $\text{Na}_6\text{P}_6\text{O}_{18}$ electrolyte in the absence of zirconium salts, then annealed involved the TiP_2O_7 phase. The annealed coatings produced from $\text{Na}_6\text{P}_6\text{O}_{18} + \text{Zr}(\text{SO}_4)_2$ electrolyte at $3 \leq n \leq 10$ contained ZrP_2O_7 and $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{P}_2\text{O}_7$ phases. In the layers formed at $n \leq 1$, the $\text{NaZr}_2(\text{PO}_4)_3$ compound was present. There are grounds to expect that the described approach enables one to produce coatings that involve binary zirconium and titanium phosphates with different bi- and trivalent metals.

The fourth approach is the PEO formation of coatings from aqueous electrolytes containing $\text{Zr}(\text{SO}_4)_2$, which was founded in [47, 48]. Coatings were produced on VT1-0 specimens (with a titanium content higher than 99.5%) at the anodic polarization, effective current density $i = 8 \text{ A/dm}^2$, and a duration of treatment of 10 min in a electrolyte containing 35 g/l $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [48]. Coatings containing (at %) 22.1 Zr, 10.3 Ti, and 67.3 O were produced with the prevailing ZrO_2 phase (monoclinic and tetragonal modifications) and TiO_2 . The coatings are compact, poorly wetted by water, and are promising as protective coatings.

The change in electrolyte pH by adding NaOH was accompanied by a decrease in zirconium content; an increase in titanium; and, hence, the proportion of titanium oxide [48]. It was assumed that the change in the composition is determined by the change in the ionic composition and the state of the solution with an increase in pH. According to [49], aqueous solutions of normal zirconium salts are always acidic and seemingly contain the $\text{H}_2[\text{ZrO}(\text{SO}_4)_2]$ complex compound. When zirconium is deposited by alkali (NaOH) from the sulfate solution, basic salts that contain the anion of $\text{Zr}(\text{OH})_{3.72}(\text{SO}_4)_{0.14}$ kind are formed. Electrolytes containing zirconium sulfate are better from the ecological point of view compared to those containing zirconium fluorocomplexes. Therefore, the approach is promising in view of the sanitary and ecological requirements. At the same time, this approach is most poorly studied concerning the deposition of coatings on various valve metals

and the structure, composition, and properties of the coatings produced.

The fifth approach consists of the formation of coatings involving ZrO_2 from aqueous electrolytes containing Zr(IV) tartrate complexes [50]. In the experiments, a electrolyte of the following composition (g/l) was taken: $0.5 \text{ Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + 10 \text{ K}_2\text{C}_4\text{H}_4\text{O}_6 + 1.0 \text{ NaOH}$, pH 4.2 to 5.0. PEO-coatings containing TiO_2 rutile, as well as monoclinic and cubic ZrO_2 modifications, were produced on titanium. The microhardness of the coatings was 4000 MPa. According to [50], adding $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ to the electrolyte provides the formation of $[\text{ZrO}(\text{C}_4\text{H}_4\text{O}_6)]^{2-}$ anionic complexes in acidic solutions; the discharge of the complexes on the anode results in the formation of zirconium dioxide involved in the coatings. It was noticed that cubic modification prevails (over the monoclinic modification) at a formation voltage of the coatings of 350–450 V and that the electrolyte is highly stable (no dimness of the solution caused by the deposition of ZrO_2 particles due to the hydrolysis of $\text{Zr}(\text{SO}_4)_2$ salt was observed). The approach is also still poorly studied with regard to the processes that lead to the formation of zirconium-containing coatings and the characteristics and properties of the coatings produced.

Thus, the PEO technique enables one to produce zirconium-containing coatings on valve metals from aqueous electrolyte suspensions containing dispersed ZrO_2 particles, Zr(IV) fluorocomplexes, polyphosphate, and tartrate complexes, as well as $\text{Zr}(\text{SO}_4)_2$ solutions. Layers containing both zirconium oxide in monoclinic and tetragonal modifications and zirconium pyrophosphate, as well as layers containing simple and complex zirconium phosphates were obtained. By varying the conditions, as well as the composition and pH of the electrolyte, one can produce surface structures of different elemental and phase compositions, as well as different thicknesses, morphologies, and structures. Some of the coatings are decorative and reveal protective and light reflecting properties. The coatings involving zirconium compounds are promising as heat resistant and chemically inert protective structures and as layers with particular electric properties. Compositions of a zirconium-containing coating and a certain metal can be applied in catalysis, e.g., as substrates of catalytically active compounds with a high heat and electric conductivity of the base. The described approaches can form the basis of producing surface structures with a complex chemical composition involving certain compounds and having certain characteristics. The approaches considered can be applied when producing coatings that involve not only compounds of group-IV elements, such as Ti(IV) and Hf(IV), but seemingly also a number of other metals of the Periodic table.

In our opinion, the results already obtained and further investigations devoted to the PEO production of coatings of complex chemical compositions, particularly those involving Zr(IV) compounds, are important in both producing knowledge about the method and underlying processes and regularities, as well as in developing practically important technological solutions.

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