



Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties



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ABSTRACT

The paper presents some of the directions of developing the plasma electrolytic oxidation (PEO) technique to form the coatings with magnetic, catalytic, biocompatible or biocidal properties on the valve metals and alloys. It reflects the relationships between the structure, composition and functional properties of PEO coatings. The data presented suggest that PEO is an effective method of physicochemical synthesis on metals and alloys of the surface layers with different chemical composition and certain characteristics.

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1. Introduction

In recent years, the plasma electrolytic oxidation (PEO) technique, that is anodization of valve metals and alloys in electrolytes at voltages of spark and microarc electrical discharges in the anode region, is rather actively explored for obtaining 'metal/coating' composites of different composition and purpose. Locally high temperatures and pressures in electric breakdowns zones, evaporation of the solution, partial melting of the oxide and, perhaps, of the metal – all these processes lead to the solid-state and gas-phase reactions [1–7]. From this perspective, PEO is an unconventional method of physicochemical synthesis of the surface layers of a certain chemical composition with various physical and chemical properties [3,5,8–14]. Meanwhile, the possibilities of PEO are underestimated. The works carried out are mainly focused on the application of PEO technique for obtaining protective coatings [13–19]. Only in recent years, some progress has been appeared in the direction associated with the use of PEO for obtaining the coatings of complex chemical composition with various functional properties. In this regard, one can note obtaining 'PEO coating / metal' composites,

whose composition and structure make can them promising candidates for use in medicine as a biocompatible [20–24] or antibacterial materials [25–29], in photocatalysis [30–33], in catalysis of gas phase or liquid phase reactions [34–37], producing PEO coatings having ferromagnetic [38–41] or antiferromagnetic properties [42] and those with certain hydrophilic-hydrophobic balance of the surface, including superhydrophilic [43] or superhydrophobic properties [44]. The studies related to combination of PEO with other surface processing technologies to produce the coatings of certain chemical composition and functional purposes were initiated. Using combination of PEO with impregnating and annealing [37,45,46], extraction pyrolysis [47–49], deposition of corrosion inhibitors [50,51] and compounds imparting hydrophobic properties to the surfaces [44], template sol-gel synthesis [52–54] can be gives as examples.

Conducting the anodizing process under electrical discharges of various types such as spark, microarc, propagating ones (Fig. 1a–c) allows forming the coatings of complex chemical composition [55]. Depending on the electrolyte composition and processing modes, structures of three types can be obtained. The coatings may be built mainly of an oxide of the treated metal (Fig. 1d). In addition to the substrate oxides, the coating composition can involve crystalline inclusions and compounds based on the components of electrolyte or those of electrolyte and substrate (Fig. 1e). Moreover, the coatings may be multilayers

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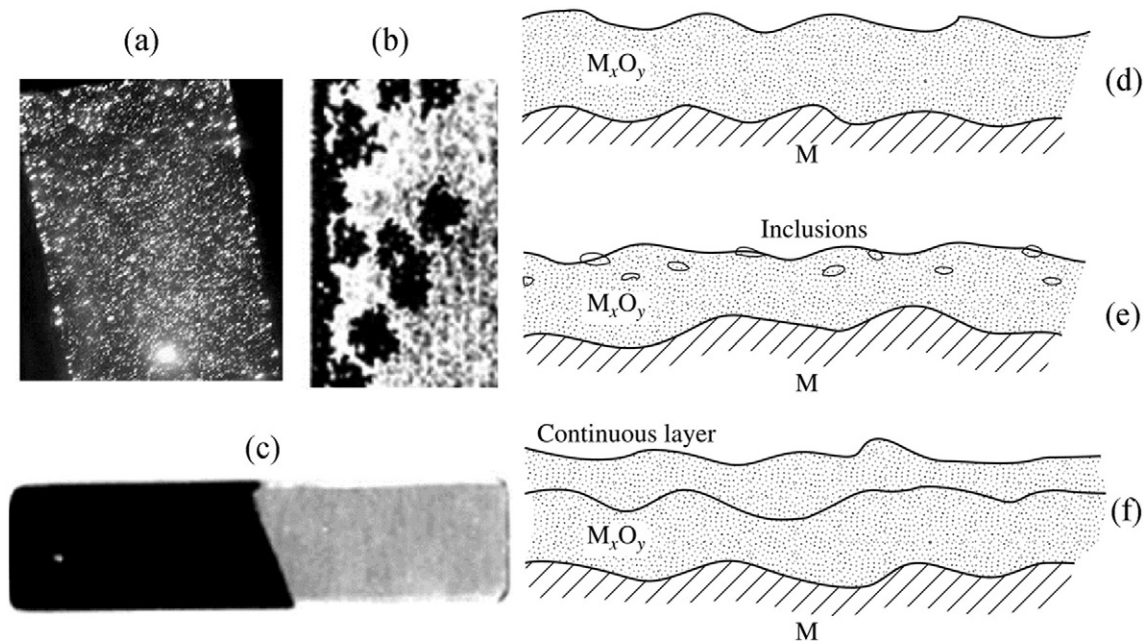


Fig. 1. Main types of electric discharges at anode during PEO treatment [55]: (a) an uniform ensemble of spark discharges transitioning over time into more powerful microarc ones; (b) the occurrence of isolated discharges which are subsequently concentrated along the perimeter of new phase areas (in the figure is painted black) increasing over the primary oxide layer; (c) the occurrence of a single discharge, which as a line or a spot migrates at the surface of the sample leaving behind an oxide film of a definite thickness (shown in black); and (d, e, f) the structures formed by spark and arc discharges.

with the external layer predominantly containing compounds based on the electrolyte components (Fig. 1f).

From a technological point of view, the following features of PEO technique are of interest to produce functional systems [2,4,5,7,11,13,15,16,18,19]. The method allows (1) conducting the synthesis of high-temperature compounds on metal anode surface in an aqueous electrolyte under atmospheric pressure and average temperature not exceeding 100 °C during from a few to tens of minutes; (2) processing the products of complicated geometrical shape, including those with through narrow openings by pumping the electrolyte through them; (3) restoring the properties of the coating by re-treatment of the products; (4) forming the surface layers with high-temperature compounds on low-melting-point metals and alloys, such as aluminum and magnesium. Moreover, PEO technique (5) does not require a vacuum or gas protection and provides (6) good adhesion between the coating and the substrate, relatively low cost of the coating and processing, and (7) environmental acceptability of electrolytes (in most cases, aqueous solutions of inorganic salts).

The mechanisms of PEO coatings' growth and main ways of obtaining the coatings with specific composition, structure and functional properties have been the subject of discussion and analysis in a number of reviews and monographs, including [1–7,11,13,15–19]. However, as noted above, new areas regarding the application of both single-stage PEO technique and its combination with other methods of surface modification were formed in recent years to obtain compositions 'composite oxide coating/metal' with certain functional properties. The review deals with some directions and research results regarding obtaining PEO coatings with specific magnetic, catalytic, or bioactive properties. The authors believe that the review of publications in these areas can be useful for professionals working in these and similar research areas.

2. Coatings with certain magnetic characteristics

Scientific background of new methods for forming 'coating/metal' magnetic materials is very important. Application of PEO for these purposes is unconventional. The research in this area has been recently started [38–42,46,56–61].

The main approaches for fabricating the PEO coatings with certain magnetic characteristics are as follows: (1) using the electrolytes containing dispersed particles of Fe^0 , Co^0 for obtaining ferromagnetic coatings [38,41]; (2) introducing the dispersed particles of iron oxides into electrolytes for producing antiferromagnetic coatings [42]; (3) the use of electrolytes containing metal-complex ions, for example, EDTA-Fe^{3+} [40] or $[\text{FeP}_6\text{O}_{18}]^{3-}$ [57] for ferromagnetic properties; (4) tribological application of nanoscale particles on the preliminarily formed PEO coating for ferromagnetic ones [41]; (5) using slurry electrolytes (suspension-electrolytes, sols) for introducing various metal oxides into PEO coatings for ferro-, ferri- and antiferromagnetic properties [19,39,46,56–64]; (6) applying the impregnation of preformed PEO coatings in aqueous solutions of iron salts followed by annealing, resulting in ferromagnetic properties [46].

In [38], PEO coatings on an aluminum alloy were formed in a $\text{Na}_2\text{WO}_4 + \text{Na}_3\text{PO}_4$ electrolyte containing dispersed iron particles with sizes no larger than 5 μm . Coatings with an iron content of 10.2 at.% were produced. Scattered dispersed particles smaller than 5 μm in size were included in the coating surfaces. The authors believe that these are iron particles. The electromagnetic properties of the coatings were judged from the absorption of microwave radiation. The coatings were characterized by negligibly small dielectric loss tangents. The magnetic permeability of the coatings depended on the frequency of electromagnetic microwave radiation. Noticeable magnetic losses were observed at frequencies of 9.6 and 12.6 GHz. In the authors' opinion, the approach proposed makes it possible to create and synthesize microwave absorbers in an efficient and simple way.

Introducing Fe_2O_3 particles with a mean size of about 0.1 μm (in a range from 0.03 to 0.15 μm) in an alkaline silicate electrolyte enabled one to produce PEO coatings with a thickness up to 6–7 μm containing 16–19.5 at.% iron, which was homogeneously distributed over the cross section of the oxide layer, on a titanium foil [42]. The coatings involved the $\alpha\text{-Fe}_2\text{O}_3$ (hematite) phase. According to the data of Mössbauer spectroscopy, the material of the coating was antiferromagnetic.

The authors of [41] studied magnetic characteristics of cobalt-containing coatings on titanium. Cobalt nanopowder with a mean particle size of ~70 nm was used for formation of the coatings. The powder

was introduced in the coatings in two ways, namely, (I) by means of tribological application on the PEO coating that was preliminarily formed in Na_3PO_4 electrolyte and (II) by adding the nanopowder along with a surfactant to Na_3PO_4 electrolyte and forming PEO coatings directly in this electrolyte. All the specimens obtained were ferromagnetic. Coercive force H_c of kind I specimens was 514 Oe at a temperature of 300 K or 1024 Oe at 2 K. The H_c values of kind II specimens were 38 and 52 Oe at 350 and 2 K, respectively. The authors of [41] related the difference in the ferromagnetic characteristics of the specimens to the difference in the chemical compositions of the coatings formed. In kind II coatings, the total Co content was smaller than in kind I coatings, and Co_2O_3 and CoO oxides were present along with metallic cobalt.

In refs. [40,65] multicomponent oxide coatings including iron oxide on an aluminum alloy surface has been studied. The coatings were formed in aqueous electrolyte containing iron in the form of its complexes with EDTA^{4-} and having a pH value of 9–10. The concentrations of the components in working solutions were the following, (mol/L): $C_{\text{Fe}} = 0.020$, $C_{\text{Na}_2\text{B}_4\text{O}_7} = 0.025$, $C_{\text{Na}_2\text{SiO}_3} = 0.025$, $C_{\text{EDTA}} = 0.022$. The coatings obtained consisted of two layers and contained up to 150 mg/dm^2 of iron. Preliminary evaluations indicated that iron-containing coatings formed exhibit ferromagnetic properties. This was established by using a permanent magnet: the magnet was brought to the aluminum sample with an iron-containing coating hanging on a thread, and the sample was pulled to the magnet. If the sample in form of disk was set on its side surface on the flat surface and the magnet was brought to it, the sample followed (rolled after) the magnet.

In ref. [46] the combination of the methods of PEO and impregnation with subsequent annealing was used to form coatings with ferromagnetic characteristics on titanium. Initial PEO coatings were obtained in base alkaline electrolytes: $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{WO}_4$ (I) and $\text{Na}_5\text{P}_3\text{O}_{10} + \text{Ca}(\text{CH}_3\text{COO})_2$ (II). To modify the samples with PEO-coatings, they were immersed into an aqueous solution of either iron nitrate $\text{Fe}(\text{NO}_3)_3$ (1 mol/L) or iron oxalate $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ (0.04 mol/L) and held there for 1 h. Upon impregnation, the samples were annealed in air at 500°C for 2 h. Iron is concentrated in the composition of dispersed particles of a size of 1–10 μm distributed over the coating surface. The values of the coercive force H_c of ‘coating/titanium’ samples are equal to 20–70 Oe at 300 K.

The idea of using the slurry electrolytes for forming PEO coatings of complex chemical composition [39,46,49,56–64], is as follows. The addition into an basic alkaline electrolyte of water-soluble salts of transition metals, such as oxalates or acetates which are chemically less active to aluminum and titanium leads to releasing the negatively charged colloidal particles of these metals hydroxides in the electrolyte volume as a result of hydrolysis processes. The sols are formed. During PEO, hydroxide particles will migrate towards the anode, where can be built into the growing oxide coating under electrical discharges, undergoing thermal transformations and engaging in high-temperature interaction with the components of the coating. Initially, this approach was proposed for obtaining catalytically active ‘PEO coating/Ti (Al) composites [66].

Advantages of the approach based on using slurry electrolytes are following: (1) the processing is single-stage, embedding the magnetically active components occurs directly during PEO; (2) there is no need in preliminary obtaining the dispersed powders of metal or their oxides by another methods; (3) in basic alkaline electrolytes it is possible to simultaneously obtain hydroxides of various metals in the desired relationship, which allows one to embed various oxygen compounds of metals into the surface layers and, as a result, directly influence the magnetic properties of the coatings.

The slurry electrolyte of composition (mol/L) $0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7 + 0.006 \text{ Na}_2\text{WO}_4$ (basic PBW-electrolyte) + $0.04 \text{ Fe}_2(\text{C}_2\text{O}_4)_3$ (PBWFe-electrolyte) has been used to obtain ferromagnetic coatings on aluminum and titanium (Fig. 2) [39,58]. It is found [46,57–61,63, 64] that the iron determining the magnetic characteristics of the ‘coating/metal’ samples is concentrated, in this case, in the composition of

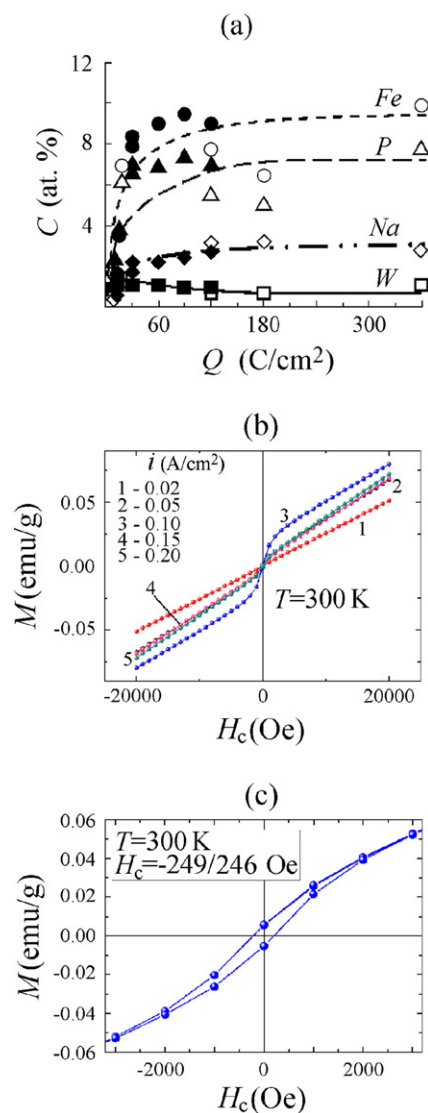


Fig. 2. The effect of the $Q = it$ charge passed through electrodes on the concentration of Fe, P, Na, and W in the coatings on titanium (a), magnetization curves of the samples with PEO coatings obtained during 10 min at different i current densities (b) and shape of the magnetization curve in the magnetic fields H of low intensity (c) [58].

nano- and micro-crystallites in the pores of the coating, Fig. 3. Due to the small oxygen concentration in the crystallites, it is concluded that the nano- and micro-crystallites preferably contain reduced iron and other metals of electrolyte and substrate (Table 1) [58]. The presence of the reduced iron is also confirmed by X-ray diffraction and X-ray photoelectron spectroscopy [58].

Presumably, nano- and micro crystallites are the dispersed metal particles surrounded by oxide-hydroxide shell [62]. The possible reason for reducing the metals from their hydroxides is the presence of reducing atmosphere (carbon, hydrogen) in the electrical breakdown channels. In ref. [67] was shown, that the main component of anodic gases was hydrogen (about 90 vol%), which was released as a result of thermochemical processes occurred in spark discharges. The forming modes (current, time) may affect the size of the pores and, accordingly, the size of crystallites in the pores and value of the coercive force [58].

Because of decreasing the pore sizes and, accordingly, the crystallite sizes the latter can come close to single-domain state that provides the maximum value of the magnetic susceptibility of the samples. By varying the concentration of Fe^{3+} in PBWFe-electrolyte also enables one to change the elemental composition of the crystallites, Fig. 4, and therefore, the magnetic characteristics of samples as a whole, Fig. 5 [60]. As

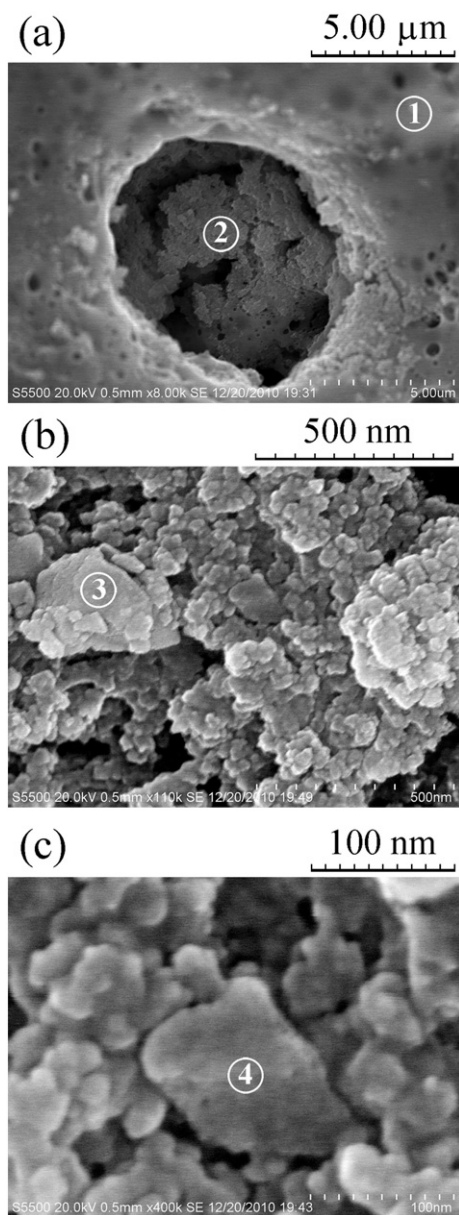


Fig. 3. Scanning electron microscopy (SEM) images of the pore (a) and crystallites in the same pore (b, c) at different magnifications [58].

one can see from Figs. 4 and 5, changing the concentration of Fe^{3+} in an aqueous electrolyte enables one to produce coatings with different magnetic characteristics on aluminum. There is a correlation between the ratio of ferromagnetic metal concentration to summarized concentration of paramagnetic ones $n = \text{Fe} / \Sigma(\text{Al}, \text{W})$ in crystallites in the pores and the magnetic properties of the systems studied. Al-, Fe-, and W-containing oxide layer on aluminum substrate with different magnetic properties can be produced, namely, (i) ferromagnetic materials ($n = 1.9$); (ii) materials that are ferrimagnetic at low external magnetic field intensities and become, first, antiferromagnetic and, then,

Table 1
Examples of the composition of the nanocrystallite in the pore (Fig. 3) and average composition of the coating on titanium [58].

Object	Element composition (at.%)						
	C	O	Na	P	Ti	Fe	W
Crystallite in the pore	–	6.6	–	0.9	8.2	76.8	7.5
Coating	24.7	55.3	3.2	5.1	4.5	6.5	0.7

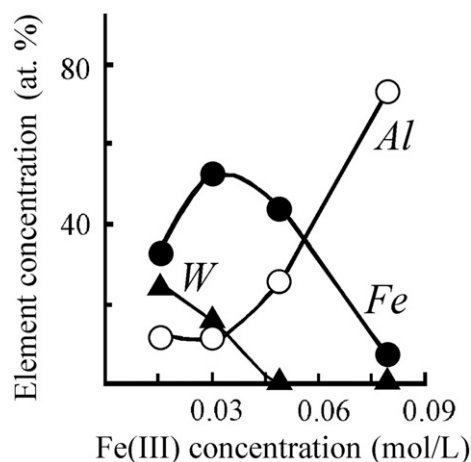


Fig. 4. The effect of Fe(III) concentration in PBWFe-electrolyte on the elemental composition of crystallites in pores for the coatings on aluminum alloy [60]. Oxygen content varies in a range of 10–30 at.%, carbon content is no larger than 5 at.%, and phosphorus content is no larger than parts of at.%.

spontaneously magnetized oppositely to the external field direction with an increase in H ($n = 0.9$ – 1.7); or (iii) materials with a magnetization opposite to the external field at any field intensity and characterized by magnetization hysteresis (reverse ferromagnetic materials, $n = 0.1$) [60].

As experiments show, the composition of the basic alkaline electrolyte used affects the composition of the crystallites in the pores and magnetic properties of 'coating/metal' samples too [61].

Changes in magnetic characteristics (Fig. 5) with a change in the content and ratio of iron, aluminum, and tungsten in the crystallites (see Fig. 4), presumably are related with the presence in the crystallites of two crystalline sublattices with different directions of magnetization, and a predominance of specific direction of magnetization depending on the crystallite composition and the strength of the external magnetic field.

3. Catalytically active coatings

To date, a significant number of publications is known on the synthesis and study of PEO coatings, which can be used in heterogeneous catalysis as photocatalysts [30–33,68–91]. Far less attention is paid to the application of PEO technique for obtaining electrocatalysts [92–95] and catalysts of liquid phase or gas phase reactions [96–123].

The direction associated with obtaining titanium-supported PEO coatings intended for use as photocatalysts in different organic pollutants degradation processes [30–33,68–91] is actively developing. Titanium oxides are well-known semiconductor photocatalysts. In this regard, one of research areas in this field is obtaining and studying the coatings consisting only of anatase (most photoactive titania) [30,31,68–72] and coatings with different anatase/rutile ratios [31,73,74]. However, due to the wide band gap of TiO_2 , titania coatings show photocatalytic properties when irradiated with UV light. To improve the photocatalytic properties of the coatings based on TiO_2 , doping various transition and rare earth metals, such as Fe [75], V [43,76,77], Ag [32,78], Eu [33,79,80], La [81], CeO_2 [82] is used. In addition, PEO coatings containing a mixed metal oxides, for example V_2O_5 - TiO_2 [83,84], SnO_2 - TiO_2 [85], WO_3 - TiO_2 [86–90], ZnWO_4 and NiWO_4 nanostructures [91] are obtained.

In the field of electrocatalysis, the publications related to obtaining ruthenium-modified PEO coatings on titanium and studying their use as anodes in electrochemical processes of chlorine release from aqueous chloride solutions are known [92,93]. There are works showing that titanium-supported PEO coatings of certain composition including

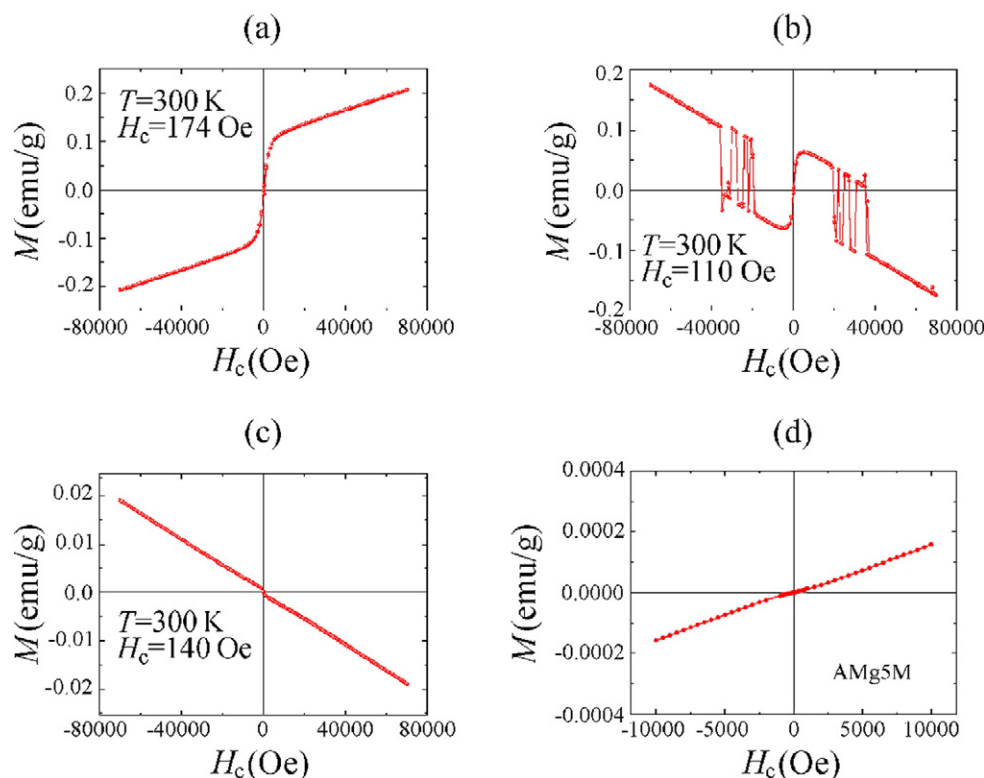


Fig. 5. Magnetization curves at $T = 300$ K of the samples of AMg5 aluminum alloy with PEO coatings formed in an electrolyte with different Fe(III) concentration (mol/L): 0.03: (a), 0.015 (b), 0.079 (c) [60]. Magnetization curve of AMg5 aluminum alloy sample without coating (d). The magnetic moment is normalized to the total weight of the sample: metal + coating. The weight proportion of the coating in the composition is 1–3%.

those modified with noble metals can be used as indicator electrodes in potentiometric titration [94,95].

In this review, we will consider in detail a recently appeared direction associated with the use of PEO technique for obtaining both “oxide coating/metal” carriers designed to deposit and fix the catalytically active compounds and the actual catalysts of liquid phase and gas phase reactions.

3.1. Using PEO for obtaining ‘oxide layer/metal’ carriers

Recently, PEO technique has been began to investigate in terms of obtaining both catalytically active layers on aluminum, titanium, magnesium and their alloys and oxide carriers of catalysts on a metal surfaces [34–37,45,47,48,52,66,96–123]. Table 2 provides the references on the works of various research groups to obtain PEO coatings of complex compositions [2,12,17,42,45,76,84,86–90,97–103,114,124–179]. In particular, the PEO method allows fabricating oxide layers containing γ - and α - Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , CeO_x , VO_x , WO_3 , MoO_3 or their mixtures on valve metals. Such PEO layers may be used as substrates (or secondary carriers) for the deposition of catalytically active substances.

Fig. 6 shows the examples of surface morphologies of PEO coatings on aluminum and titanium substrates. Note, that depending on the nature of the substrate metal, the chemical composition, pH and temperature of the electrolyte, parameters of electrolysis, and the processes occurring in the electrolyte volume (complexation, formation of sols, etc.), the chemical composition of the coating can be quite varied (Table 2). The same applies to the surface morphology, which for example can have a mosaic or coral-like structure, be uneven. The surface of PEO coatings can be penetrated by pores or, vice versa, be substantially non-porous, etc. (Fig. 6). It can have a unique nano-sheet morphology with high hydrophilicity [43], a needle-shape structure with developed surface [161].

Fig. 7 demonstrates the examples of internal structure (cross section) of PEO coatings, element distribution in the depth and on the

surface of the coatings, for example, the distribution of Nb and Al on the surface of the coating formed on an aluminum alloy. A variety of chemical composition and surface morphology, and the ability to control them - all of these factors favor using such metal oxide composites in design of catalysts, including microchannel ones [180–182].

Note that Al_2O_3 and SiO_2 oxides are widely used in the traditional heterogeneous catalysis. The PEO technique is allows technologically forming such oxides on the surface of valve metals and significantly increases the number of oxide systems that can be used as carriers in the

Table 2

PEO coatings containing various oxides or phosphates together with oxide of treated metal. Such PEO coatings of complex composition may itself be of interest as catalytic systems and serve as the basis (the secondary carrier, when a primary carrier is substrate metal) in the manufacture of metal-supported catalysts.

PEO coatings on aluminum

$\text{Al}_2\text{O}_3 + \text{ZnO}$ [124]; $\text{Al}_2\text{O}_3 + \text{ZrO}_2$ [125–132]; $\text{Al}_2\text{O}_3 + \text{AlPO}_4 + \text{ZrO}_2$ [133]; HfO_2 [125,126]; TiO_2 [125,126]; Nb_2O_5 [125,126]; V_4O_9 , V_2O_4 [134–139]; V_2O_5 [140]; CoAl_2O_4 [141,142]; Co_2O_3 [141]; WO_3 [12,143–149]; $\text{Al}_2(\text{WO}_4)_3$ [143,146,150]; MoO_3 [151]; SiO_2 [2,152]; $\text{Al}_2\text{O}_3 + \text{Al}_2\text{SiO}_5$ or $\text{Al}_6\text{Si}_2\text{O}_{13}$ [17]; Mn_xO_y [137]; $\text{H}_{0.33}\text{WO}_3$, $\text{Na}_2\text{W}_2\text{O}_7$, $\text{Na}_2\text{W}_4\text{O}_{13}$ [150]; NiAl_2O_4 [153]

$\text{Al}_2\text{O}_3 + \text{phosphates of M (II), M (III), M(IV)}$ [12,154–157]; $\text{Mn}(\text{PO}_3)_2$, MnP_2O_7 [158]; $\text{Mg}_3(\text{PO}_4)_2$ [157,158]; NaZnPO_4 , $\text{NaMn}(\text{PO}_3)_2$ [158]; AlPO_4 [134,153,159]

PEO coatings on titanium

Al_2O_3 [160,161], Al_2TiO_5 [162–164], $\text{TiO}_2 + \text{V}_x\text{O}_y$ [76,84,134,135]; WO_3 [12,86–90,145,151,165]; ZrO_2 [125,126,128–130,166–171]; $\text{ZrO}_2 + \text{Ce}_x\text{O}_y$ [114,172,173]; $\text{ZrTiO}_4 + \text{CuO} + \text{Cu}_3\text{O}_4 + \omega\text{-Zr}$ [174], $\text{Zr}(\text{P}_2\text{O}_7)_2$ [175,176]; Ta_2O_5 [177,178]; HfO_2 , Nb_2O_5 [125,126]; CoAl_2O_4 , Co_2O_3 [97,98]; MoO_3 [151]; SiO_2 [45,99]; $\text{Fe}_2\text{O}_3 + \text{SiO}_2$ [42]; MnO ; Mn_2O_3 , Mn_3O_4 , MnTiO_3 [99–103]

$\text{TiO}_2 + \text{phosphates of M (II), M (III), M(IV)}$ [12,141,142,155,156]; AlPO_4 [134,159]; $\text{Co(II)Co(III)Ti}(\text{PO}_4)_3$ [142,143]; $\text{Mn(II)Mn(III)Ti}(\text{PO}_4)_3$ [156,157,179]; TiP_2O_7 , $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{P}_2\text{O}_7$, $\text{NaZr}_2(\text{PO}_4)_3$, ZrO_2 [176]

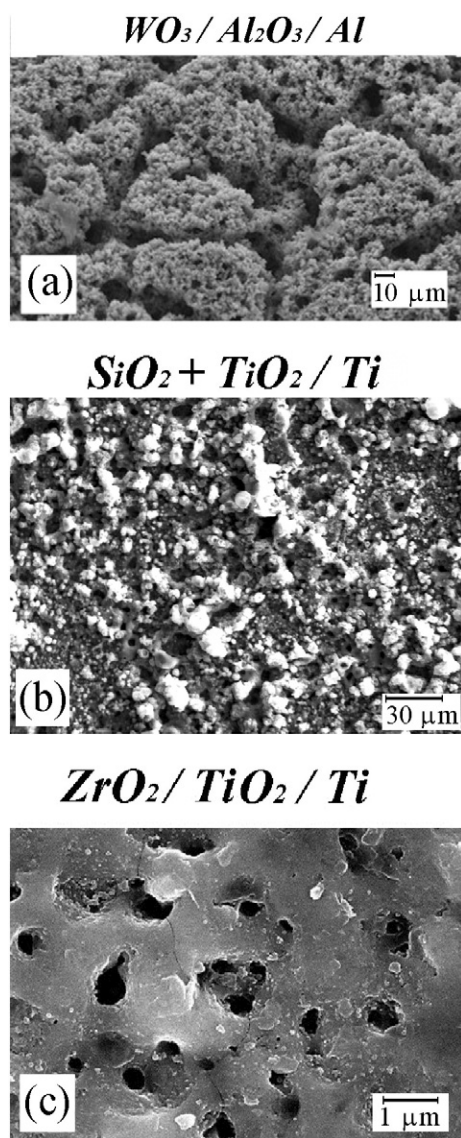


Fig. 6. The examples of surface morphology (SEM images) of PEO coatings of different chemical composition on the surface of aluminum and titanium [117,145,172].

manufacture of catalysts (Table 2). Since the nature of the carrier influences the activity of the catalysts, the PEO opens a simple way of varying the design of oxide carriers on metal substrates.

3.2. Using PEO for obtaining 'catalytically active coatings'

The works [34,35,96] are among the first known publications related to the use of PEO in catalyzing the gas-phase reactions.

In ref. [96] PEO coatings active in the oxidation of methane were obtained on aluminum alloys in electrolytes containing Na_2SiO_3 , alkali metal hydroxide and additives of ultrafine powders of alumina and/or zirconia and transition metal salts selected from the group consisting of Mn, Cr, Cu, Co, Fe or mixtures thereof. Cr-containing coating showed 50% CH_4 conversion with increasing temperature up to 610 °C and the subsequent lowering temperature to 520 °C. The authors suggest that 'PEO coating/M' composites proposed can be used as catalysts for deep oxidation of organic compounds and carbon monoxide in the exhaust gases of chemical and petrochemical industries and internal combustion engines.

In ref. [34], the aluminum foil-based catalysts were fabricated by combination of PEO and impregnation in aqueous solution with various salts of transition and rare earth metals with next annealing. The catalysts were tested in the reactions of CO and CH_x oxidation, NO_x selective reduction by hydrocarbons and demonstrated a high performance and a low pressure drop at high space velocities. City diesel buses field tests of converters equipped with those catalysts demonstrated their high and stable performance in clean-up of exhausts from CO, gaseous hydrocarbons and NO_x .

In ref. [35] metal-supported egg-shell catalysts were obtained by single-stage PEO technique in aqueous solution containing (g/L): 32 KH_2PO_4 , 20 $\text{NH}_4(\text{H}_2\text{PO}_4)$, 18 Na_2CO_3 , 40 NH_4OH (26 wt.%) and 10 citric acid as basic electrolyte as well as different precursors of the catalytically active components ($\text{Ni}(\text{CH}_3\text{COO})_2$, $(\text{NH}_4)_2\text{CrO}_4$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$). In comparison with molybdenum and chromium, the nickel-containing egg-shell catalysts based on Ti, Al or Mg exhibited high efficiency in the catalytic gas-phase oxydehydrogenation of cyclohexane to cyclohexene. The intrinsic activity of the nickel catalysts supported on $\text{Al}_2\text{O}_3/\text{Al}$, MgO/Mg or TiO_2/Ti were found to be within an order of magnitude higher than on a conventional alumina supported nickel oxide catalyst. Additionally, the corresponding cyclohexene selectivity was higher.

To date, a significant amount of information is accumulated on obtaining the layers containing transition metal oxides using PEO and their catalytic activity in CO oxidation. The layers can be formed by a single-stage PEO technique [36,66,97,98,104,106–113] (Fig. 8a), by PEO followed by impregnating and annealing [97–99,101,103,106,114–120] (Fig. 8b–d), by combination of PEO with extraction-pyrolytic method [47].

When using the single-stage PEO technique, the precursors of the catalytically active compounds may be incorporated into the electrolyte in the form of soluble salts of transition metals [105,108,109,111], including the complex compounds [183], as well as dispersed particles of transition metal oxides [112]. Introduction of noble metals precursors into electrolyte enables one to increase significantly the activity of the compositions formed under anodic and bipolar anodic-cathodic polarizations (Fig. 8a) [104]. It should be noted that Pt-containing catalysts formed by PEO and known bulk catalysts exhibit activity in CO oxidation at about the same temperatures [184]. There is evidence that Ce-, Zr-, Cu-containing coatings formed by single-stage PEO technique on titanium indicate 100% conversion of CO at 140 °C [174]. Hence, the PEO technique is promising for obtaining oxide systems active in redox reactions. However, the questions of preparation of such catalysts, the relationship between their composition, structure and catalytic activity in various reactions are still poorly understood.

The combination of PEO with subsequent impregnation can improve the catalytic activity of the compositions formed. For example, Ni-, Cu-containing PEO coatings on aluminum and titanium are active in CO oxidation at temperatures above 350 °C (curves I in Fig. 8b, c). Their additional impregnation of such coatings in aqueous solutions of nickel and copper nitrates produces compositions active in CO oxidation at temperatures above 200 °C (curves II in Fig. 8b, c) [105].

A certain amount of information about of combination of PEO technique and extraction-pyrolytic method is accumulated in order to obtain catalytically active layers on metals [47,48,122]. In ref. [47], the TiO_2/Ti composites previously prepared by PEO were immersed into Pt-containing organic extract for a 1–2 s with next drying over electric stove. The operations of immersing and drying were successively carried out for several times. Then the samples were annealed in air at 700 °C for 0.5 h. The resulting composites converted into CO_2 at temperatures above 220 °C [47].

In refs. [48,122], organic pastes containing a desired stoichiometric ratio of molybdenum and copper ions (1:1) were deposited on PEO coatings, like those shown in Fig. 7a, obtained on titanium in the alkaline silicate electrolyte. Then the samples were annealed in air first at 200 °C for 2 h, then – at 550 °C within 2 h. As a result, the layered coatings

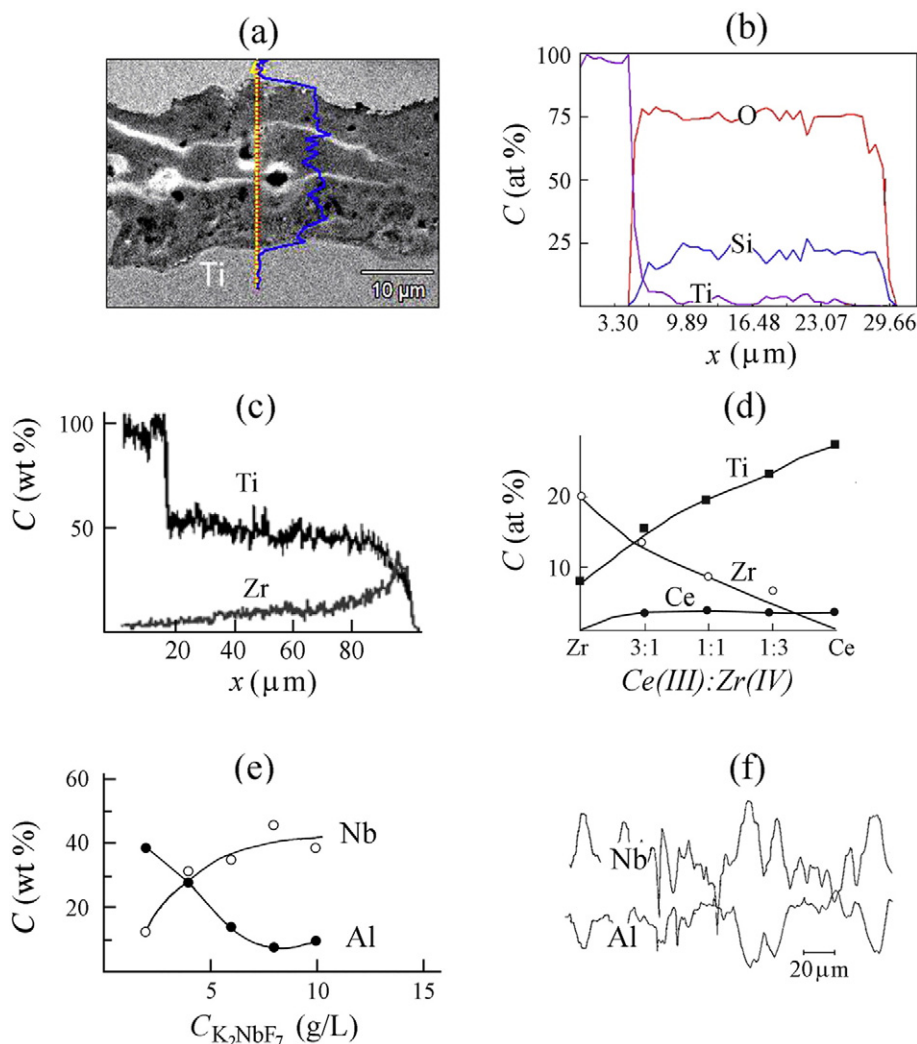


Fig. 7. Structure (a) of the cross section of the coating on titanium formed in silicate electrolyte and the element distribution over the cross section (b) [99]; the distribution of Zr and Ti over the cross section of the coating formed on titanium in $Zr(SO_4)_2$ electrolyte (c) [166]; the effect of replacing $Zr(SO_4)_2$ by $Ce_2(SO_4)_3$ in electrolyte on the content of Ce, Zr and Ti in the surface part of the coating (d) [172]. The effect of electrolyte concentration on the content of aluminum and niobium in the surface part of the coating formed on aluminum in K_2NbF_7 electrolyte (e), and the profile of distribution of these elements on the coating surface (f) [11,12].

comprising nanoparticles of copper molybdate $CuMoO_4$ in outer layer were fabricated (Fig. 9a) [48]. Such coatings activated diesel soot ignition since temperature of 280 °C (Fig. 9b).

Recently the first studies were initiated in respect of the use of the combination of PEO technique and the sol-gel synthesis to produce catalytically active compositions with palladium nanoscale particles, distributed and anchored on the surface (Fig. 10) [52]. PEO-coatings were formed in an aqueous solution of 0.05 mol/L Na_2SiO_3 + 0.05 mol/L NaOH. Pd-containing composites were formed by dipping oxidized titanium samples into sol containing hydrated titanium dioxide with palladium nanoparticles immobilized inside micelles of siloxane-acrylate emulsion followed by drying and annealing. The palladium concentration in such a sol was about 7.5×10^{-3} mol/L. Samples with PEO-coatings were dipped into sol for 1 s with intermediate drying in air at 90 °C. The data of catalytic tests and element analysis on the palladium content in deposited layers show that 10-fold deposition of the applied sol on silicate PEO-coatings on titanium with next air annealing at 500 °C is sufficient to fabricate quality Pd-containing coatings active in oxidation of CO into CO_2 . The compositions with an average palladium concentration on the coating surface not more than 0.2 at.% were obtained. Palladium is concentrated in nanosized structures of a diameter

of 25–60 nm (Fig. 10c). The fabricated composites catalyze the reaction of oxidation of CO into CO_2 at temperatures above 170 °C.

This approach is promising for the obtaining the coatings with nanoparticles of various transition and noble metals. Moreover, such compositions may be active at low concentrations of active components, which saves precious metals.

Thus, to date two main approaches regarding to application of PEO technique to form catalytically active compositions based on valve metals were developed. These approaches were discussed in ref. [123] (Fig. 11). The first one is one-stage PEO technique, in which precursors of catalytically active compounds are directly included in the forming electrolyte. In this case, the method ensures the formation of oxide layers with controlled porosity and their conversion into target catalytically active coatings in a continuous one-pot process by choosing appropriate electrolyte compositions. The second approach is related to modification of PEO coatings (both oxide and phosphate ones) using other methods such as impregnation in precursor solutions, extraction pyrolysis, and template sol-gel synthesis. Additional application of impregnation followed by annealing increases the surface area of 5–10 times and more, for example, due to the growth of whiskers on the modified surface. Of course, the use of other methods and modification

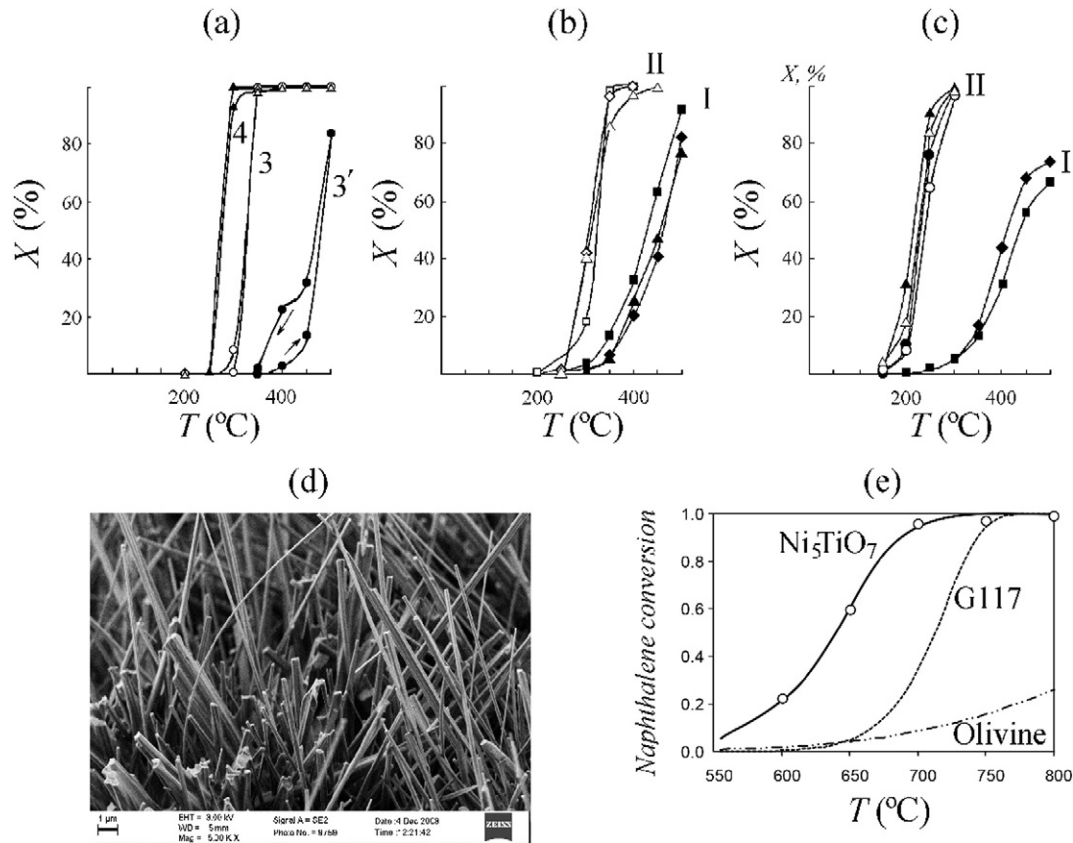


Fig. 8. CO conversion X vs. temperature T : (a) for titanium samples with PEO coatings formed in $Zr(SO_4)_2 + Ce_2(SO_4)_3$ electrolyte (3') and in the same electrolyte with H_2PtCl_6 under anodic (3) and bipolar anodic-cathodic (4) polarizations [104]; (b, c) for aluminum (b) and titanium (c) samples with Ni-, Cu-containing coatings (I) obtaining in Ni-, Cu-containing electrolyte by PEO and (II) additionally impregnated with nitric acid aqueous solutions of nickel salts and copper, followed by annealing in air at 500 °C [105]. The surface morphology (d) of the impregnated titanium samples (2) after annealing in air at 800 °C [37,106] and the temperature dependence of naphthalene conversion (d) over these samples (Ni₅TiO₇) [37].

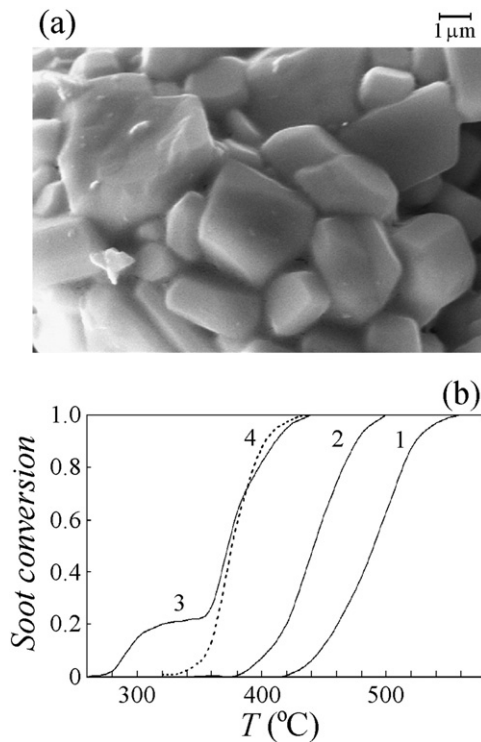


Fig. 9. Nanoparticles of CuMoO₄ on the surface of composite coating (a) and TG curves of diesel soot catalytic combustion in presence of uncovered oxidized titanium (1), single covered by CuMoO₄ (2), two times covered by CuMoO₄, and bulk CuMoO₄ (4) [48,122].

of PEO coatings, for example, gas-thermal or laser treatment is not excluded.

4. Using PEO for obtaining bioactive coatings

4.1. Biocompatible and bioinert coatings

Titanium and its alloys are widely used as implants in dentistry and surgery owing to their mechanical properties, chemical stability and satisfactory biocompatibility [185]. Biocompatibility of titanium can be improved by deposition on its surface of calcium phosphates, such as tricalcium phosphate $Ca_3(PO_4)_2$, or hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ [186–189]. The latter is the most commonly used for the coating on the surface of titanium implants, because of its chemical composition is similar to that of bone. Various techniques: biomimetic [190], electrochemical [191], sol-gel method [192,193], hydrothermal [194], a combination of hydrothermal and electrochemical methods [195,196], plasma spraying [197,198] are used for calcium-phosphate coating processes on titanium and its alloys.

To date, plasma electrolytic oxidation (PEO) is one of the progressive techniques of calcium-phosphate coating processes on titanium [21–24, 27,198–202]. The ref. [21] is one of the first publications, which describes the fabrication titanium-supported coatings with hydroxyapatite by using PEO technique. The method allows formation on titanium substrate of oxide-phosphate coating with the development of relief and high porosity that promotes adhesion of the implant with surrounding tissues and filling of coatings by drugs and their subsequent release at the surface of implants. Inorganic (chloride, carbonate, phosphate) or organic (acetate, citrate, lactate, propionate) calcium salts are introduced into electrolyte as calcium source; phosphorus sources

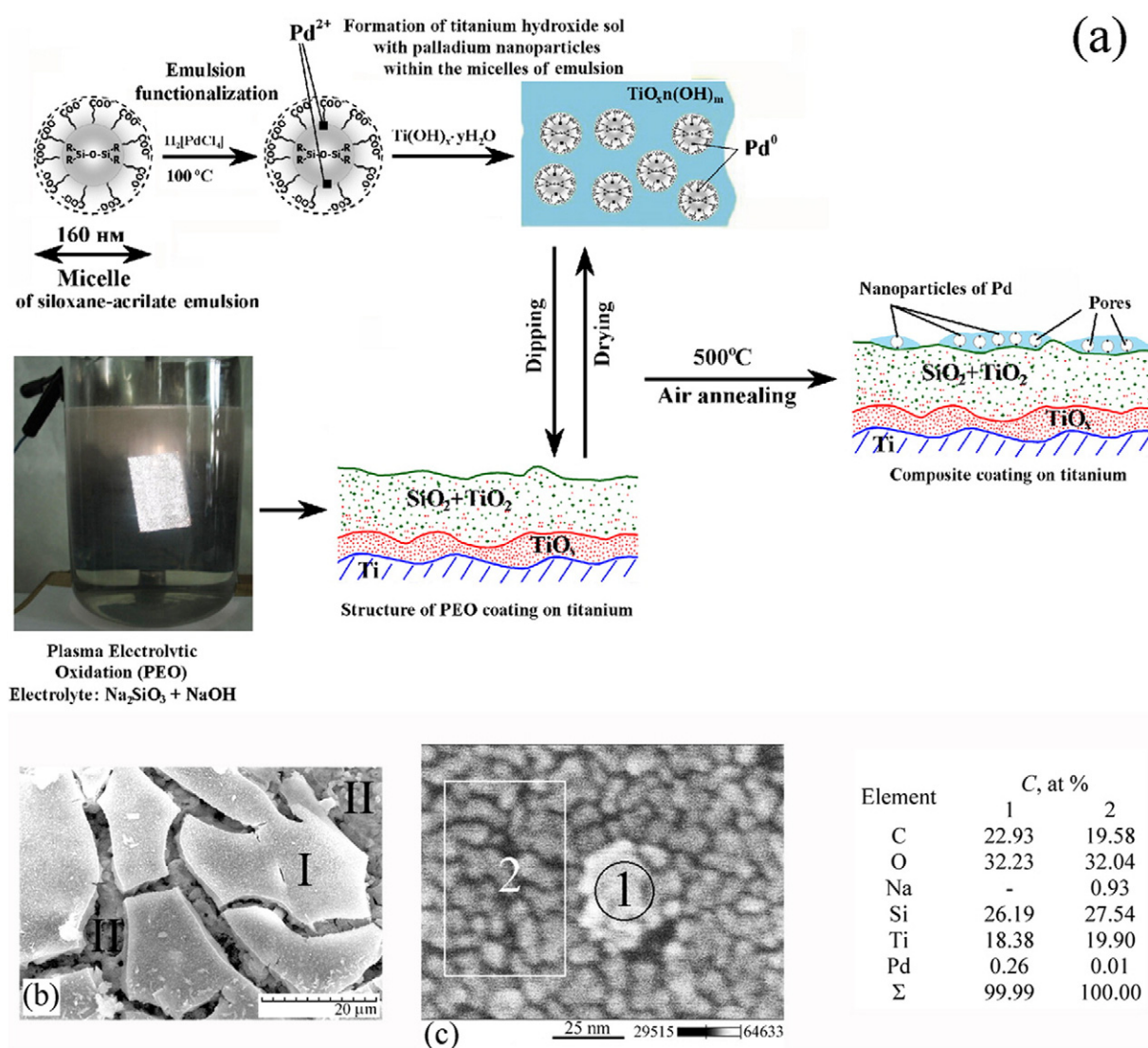


Fig. 10. Scheme of two-layer coatings fabrication by combination of plasma electrolytic oxidation and sol-gel synthesis (a); SEM image of the surface of the layer deposited on the PEO coating by sol-gel method (b); Pd-containing nanoparticle of ~20 nm in diameter and the composition of 1 and 2 analyzed sites (c) [52].

include phosphoric acid, phosphates, hydrogenphosphates, dihydrogenphosphates, and glycerophosphates of sodium, potassium or calcium; the desired calcium phosphates, for example hydroxyapatite in form of dispersed micro- and nanoparticles are added into electrolyte [21–24,27,199–204].

A number of studies carried out by scientific groups from around the world to obtain biocompatible coatings using PEO technique or its combinations with other methods of surface treatment is significant. A noticeable series of reviews, such as [24,188,205–208], is devoted to the analysis of the results, including the issues of laboratory or clinical tests of the biocompatible compositions formed. Therefore, this review will consider only the aspect of using PEO in electrolytes with polyphosphate metal complexes to form bioactive coatings on titanium and its alloys. In our opinion, this pathway is of interest, because it allows one not only to obtain the coatings with various calcium phosphates on titanium and its alloys, but also to introduce phosphates of various metals in the desired ratio into the coatings' composition from a single electrolyte. As it will be demonstrated below, this makes it possible to form not only biocompatible coatings, but also the coatings with strong biocidal properties.

Previously it was shown that by using aqueous electrolytes with polyphosphate complexes of M(II), M(III) and M(IV), the oxide-

phosphate coatings containing high-temperature metal phosphates can be produced on the surface of valve metals by single-stage PEO technique (Table 2) [11,12,141,142,155,156]. Using polyphosphates of different structure, changing the concentration of polyphosphate, the molar ratio $n = [\text{Polyphosphate}] / [\text{Metal}]$, and pH, we can control the amount of phosphorus and metal introduced into the coating, M/P ratio in the coating, and also exert an influence on the formation of any metal phosphates.

The analysis of the data in Table 3 [209] shows that applying aqueous electrolyte containing sodium triphosphate and calcium acetate, at the molar ratio $n = [\text{P}_3\text{O}_{10}]^{5-} / \text{Ca}^{2+} = 0.625$, we can obtain the coatings on titanium, which annealing results in crystallization of hydroxyapatite.

In the case of biological phosphates inorganic components (cations of sodium, strontium and copper and zinc) containing in them play an important role. These elements affect parameters of the bone material: crystallinity and mechanical properties, processes associated with its formation in the body that is important in the application of implants [210,211].

The above approach involving the use of electrolytes with polyphosphate complexes of differently charged metals, in principle, allows one to form the coatings simultaneously containing metal

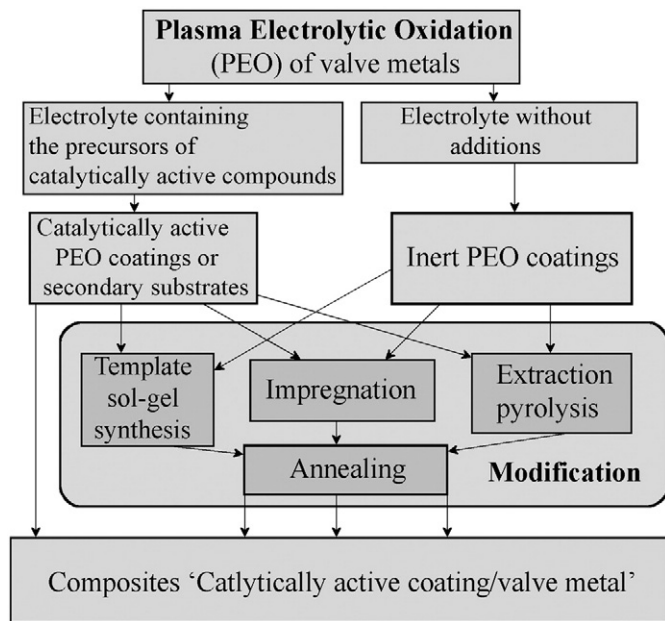


Fig. 11. Diagram of using PEO technique for obtaining catalytically active structures on valve metals [123].

phosphates of different nature. This assumption was confirmed by obtaining the coatings with calcium and strontium phosphates on titanium (Fig. 12) [212].

The composite coatings containing calcium phosphate together with such chemically inert oxides as tantalum or zirconium oxides can be of interest for biomedical applications [204,213,214]. 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 Ta_2O_5), thereby beneficially affecting the interaction between the living tissue cells and the implant. The coatings with transition metal oxides including tantalum oxide are formed on valve metals in the electrolytes containing fluoride complexes of these metals [11,12,177,178]. The coatings with a thickness of from 2 to 18 μm containing up to 20 at.% tantalum were produced within 2 min under potentiostatic conditions in an aqueous electrolyte $NH_4[TaF_6]$ [177,178,215]. Crystalline tantalum oxide was detected in their composition (Fig. 13, Fig. 14) [216]. The coating surface is penetrated by pores of size from 0.5 to 2 μm .

Sequential applying the combination of the above-described approaches, including extraction-pyrolytic method, the systems "Ca + Sr-phosphates/ $Ta_2O_5/TiO_2/Ti$ " and " Ta_2O_5 /Ca-phosphate/ TiO_2/Ti " were formed on titanium [217–219]. Similar techniques have been used to form the coatings with tantalum oxide on stainless steel surface [217–219]. Note that such layered coatings are of interest for biomedical testing.

Table 3

The phase composition, thickness h , atomic ratio Ca/P in the coatings formed in the electrolyte of molar ratio $n = [P_2O_{10}]^{5-}/Ca^2 = 0.625$ [209].

Formation conditions			Coating characteristic			
pH	i (A/dm^2)	t (min)	h (μm)	Phase composition		Ca/P
				Initial coating	After annealing (600 °C)	
7.5	8	5	9.25 ± 1	$TiO_2(a)$	$TiO_2(a + p)$	0.57
7.5	12	5	15 ± 1	–	$TiO_2(p + a)$	–
7.5	8	10	20 ± 1	$TiO_2(p + a)$	–//–	0.61
9	8	20	$\frac{29 \pm 4}{189 \pm 16}$	–//–	$TiO_2(p + a) + CaO + NaTi_2(PO_4) + CaCO_3$	$\frac{0.70}{0.69}$
10.2	8	30	$\frac{34 \pm 3}{191 \pm 6}$	$TiO_2(a) + a.\phi.$	$TiO_2(p + a) + TiPO_4 + CaCO_3 + Ca_{10}(OH)_2(PO_4)_6$	$\frac{0.66}{0.58}$

(–) The phase composition was not detected.

4.2. Biocide coatings on aluminum and titanium

Application of the coatings containing high-temperature of the phosphates of di-, three-, four-, and polyvalent metals are extremely diverse. This may be catalyst supports and catalysts in organic chemistry and exhaust gas afterburning, adsorbents, antimicrobial and antibacterial agents, luminophores, etc. Especially widely, they are used for corrosion protection of metals, as primers for paints, varnishes and other materials, decorative and facing materials.

The antibacterial properties of PEO coatings on aluminum and titanium containing phosphates of a series of metals including Zn (II), Pb (II), Cu (II) and Cd (II) were investigated [25,26].

PEO layers were formed at a constant current density of 5 A/dm^2 during 10 min on electrodes made of aluminum alloy and during 6 min on titanium ones. The electrolytes were prepared from commercial reagents: sodium hexaphosphate ($Na_6P_6O_{18}$) and acetates of different metals.

The bactericidal properties of coatings were estimated by a modified procedure described in Ref. [220]. The data are given in Fig. 15a and Table 4. Petri dishes were filled with a fish peptone agar (FPA) medium A suspension of bacteria, singled out from sea water (the Sea of Japan, Rynda Bay), was sown on the obtained agarized plates. Specimens in the form of rings about 1 cm high and 1 cm in diameter were then placed on the prepared surface. The Petri dishes were put into a thermostat for making bacteria germinate for 2 days at a temperature of 28 °C. The toxicity of coatings was judged from the size of zones uninhibited with bacteria on the external side of the samples.

Additionally, the toxic properties of some coatings were confirmed by field tests. The coated plates with the surface area of 120 cm^2 were exposed at the sea corrosion stand in the Rynda Bay at a depth of 2 m for two summer months. Each week, macrosettlements (encrustations) and periphiton formations on the specimens were visually inspected.

The coatings formed in a simple sodium hexaphosphate electrolyte (in the absence of the metal salts, $n = \infty$) reveal some bactericidal properties (Tables 4 and 5). The uninhabited zone in the vicinity of samples with such coatings reaches 1 mm, and is kept for up to three days. The presence of Cu, Sr, Zn, Cd or Pb (Tables 4 and 5, Fig. 15) noticeably enhances the toxic properties of the coatings, whereas the coatings containing P with Mg, Ba, or Y display no such properties at all. For the coatings with Zn(II), Cd(II), Pb(II), Sr(II), one can trace a correlation between the metal ion concentration and the maximum dimensions of the ungrown zones (Fig. 15b).

5. Conclusion

Thus, the presented data show that the plasma electrolytic oxidation is an effective method of physical-chemical synthesis on metals and alloys of the surface layers of different chemical composition with certain physical and chemical characteristics. These capabilities of the method allow substantiating new areas, in which the coatings formed on metals by PEO and its combination with other methods of surface modification can find an application.

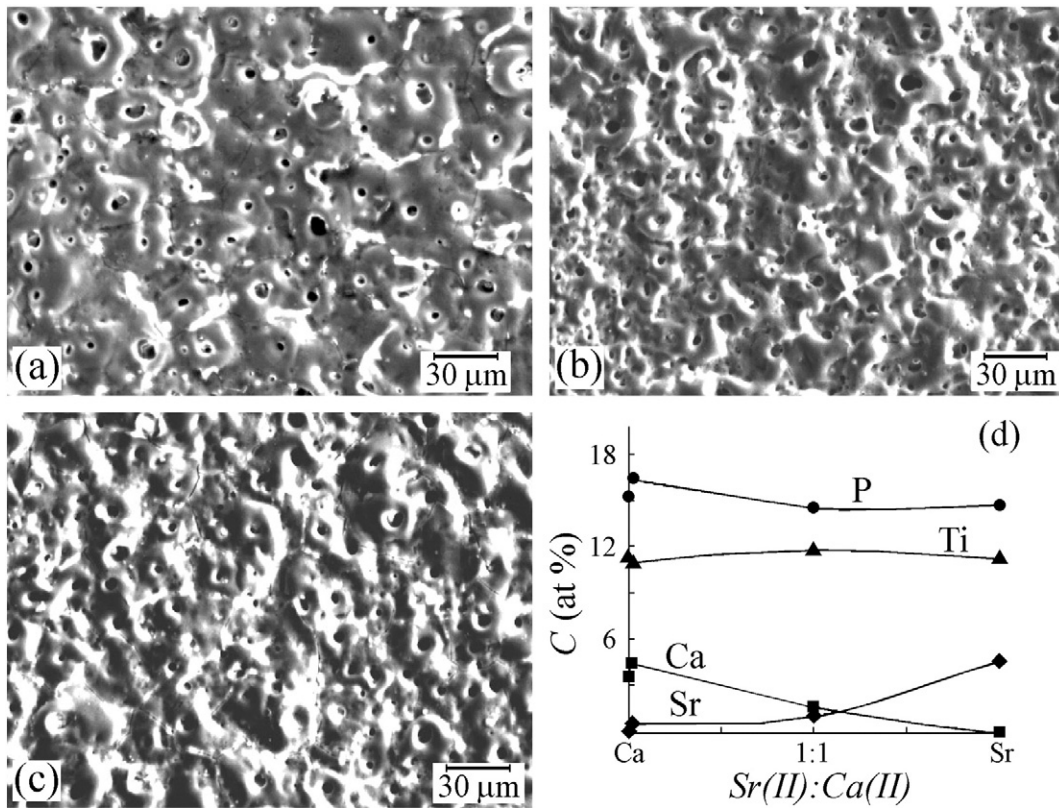


Fig. 12. SEM images of the coatings on titanium containing phosphates of Ca(II) (a), phosphates of Ca(II) and Sr(II) (b), phosphates of Sr(II) (c), and effect of molar ratio of Ca(II):Sr(II) in the electrolyte with sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ on the elemental composition of the surface part (~5 μm) of the coatings [212]. The data on oxygen content (~60 at.%) are not given. The coatings were formed within 10 min in an aqueous electrolytes containing: $\text{Na}_5\text{P}_3\text{O}_{10} + \text{Ca}(\text{CH}_3\text{COO})_2$ (a), $\text{Na}_5\text{P}_3\text{O}_{10} + \text{Ca}(\text{CH}_3\text{COO})_2 + \text{Sr}(\text{CH}_3\text{COO})_2$ (b), $\text{Na}_5\text{P}_3\text{O}_{10} + \text{Sr}(\text{CH}_3\text{COO})_2$ (c).

Recently, such unconventional PEO coatings applications as magnetic materials, carriers of catalytically active substances and particles, systems catalytically active in catalysis of liquid-phase and gas-phase reactions, and materials with antimicrobial or biocidal properties were grounded.

For single-stage forming PEO coatings of complicated composition with specific functional properties, the application of electrolytes with oxide-forming components, such as: (1) electrolytes with complex ions, for example “EDTA-M”, “polyphosphate-M”, isopoly and heteropoly anions, fluoride complexes of transition metals; (2) the sol electrolytes spontaneously precipitating transition metal hydroxides;

(3) suspension-electrolytes with nano- or micro-sized particles of desired compounds, is promising.

For obtaining PEO coatings with certain magnetic or catalytic properties, the use of sol-electrolytes is promising. In this case, the colloidal and dispersed particles of transition metal hydroxides are the precursors of nano- and micro-sized particles forming in coatings' composition and containing both oxidized and reduced metals from electrolyte. The available experimental data allow us to conclude that just such particles provide certain magnetic properties to the coatings. The catalytic properties of coatings are probably related to their presence too. In this case, the composition of the particles, apparently, can be changed in a desired

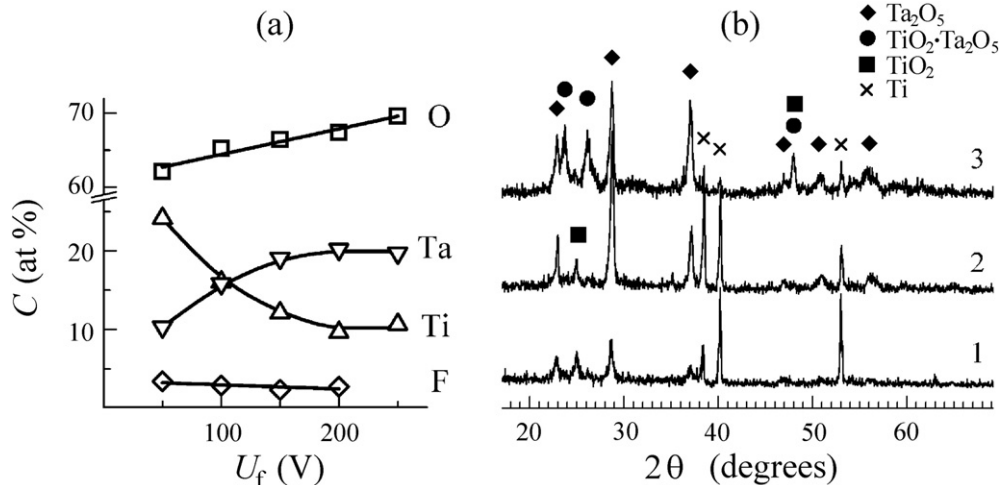


Fig. 13. Effect of the formation voltage U_f on the elemental (a) and phase (b) composition of PEO coatings formed on titanium in $\text{NH}_4[\text{TaF}_6]$ electrolyte. U_f , V: 1–50, 2–150, 3–250. [216].

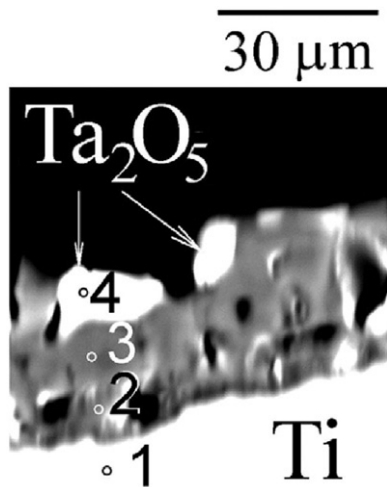


Fig. 14. Cross-section of layered PEO coatings on titanium: tantalum oxide microcrystals are located on the layer containing calcium phosphates and titanium oxides [216].

direction by adding the necessary transition metal salts to the electrolyte thereby affecting the coatings' magnetic and catalytic properties. It is also important that during the use of such electrolytes is no need to introduce the finished nano and microsized particles of desired metal oxides into the electrolyte.

The design of metal-supported catalysts requires a transition layer between the metal and the deposited catalytically active substances, which ensures its fixation on the surface and affects the activity of the catalyst as a whole. For example, it is important in manufacturing metallic microreactors for coupled reactions. PEO offers the interesting opportunities in terms of not only the technology of creation this sub-layer with a well-developed, often nanostructured and defective surface,

Table 4
The composition and antibacterial action of the coatings formed on AMtsM aluminum alloy in the electrolytes with sodium hexaphosphate [25].

N	Electrolyte		Coating composition (wt%)				Antibacterial action	
	M	n	M	P	Al	Na	r (mm)	t (days)
1	–	∞	–	2.4	46.5	0.1	1.0	3
2	Mg	0.5	18.5	15.4	0.9	0.6	0	0
3	Mn	0.5	56.2	17.5	1.2	0.7	1.0	9
4	Ni	0.5	24.8	14.2	0.5	0.8	1.0	9
5	Cu	0.5	5.8	9.6	14.0	0.7	3.0	6
6	Sr	0.5	13.8	3.6	27.6	0.2	2.5	16
7	Y	1.0	29.7	10.1	15.4	0.5	0	0
8	Ba	0.5	39.5	10.7	3.1	0.2	0	0

Note: *r* is the maximum dimension of the zone uninhabited with bacteria; *t* is the duration of the antibacterial action; *n* is the molar ratio $[P_6O_{18}]/[M]$ in the electrolyte.

but also obtaining enough undercoat with various chemical composition. The latter is difficult to achieve in conventional techniques of catalyst preparation. Meanwhile, the chemical nature of the sublayer can noticeably affect the catalyst activity.

The combination of PEO method with other known methods of surface processing and modification opens promising perspectives. In particular, it is shown that the methods of impregnation following by annealing, extraction pyrolysis, and sol-gel synthesis are easily combined with PEO. For example, this combination allows one to modify the surface by nanoparticles of noble metals or desired chemical compounds and to obtain multilayer coatings with layers of different chemical compositions, which may be of practical importance.

PEO technique enables producing the coatings with a strong antibacterial and biocidal activity. For example, such properties can be provided by both silver dispersed particles introduced into the coatings during PEO and zinc phosphates synthesized in the coating

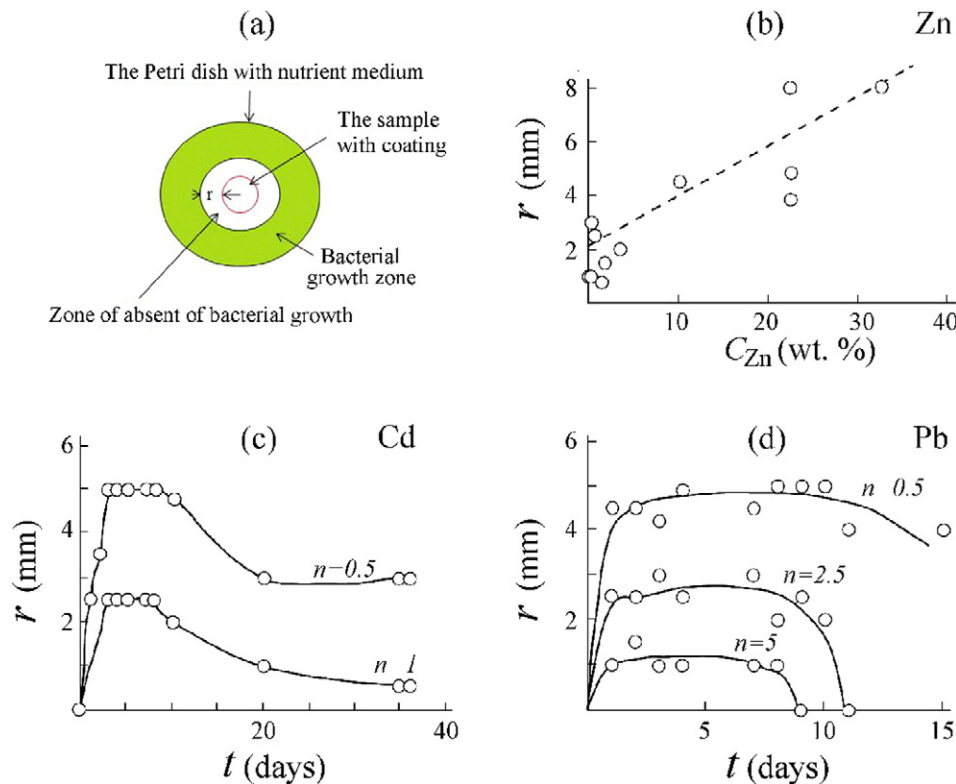


Fig. 15. Biocide coatings on aluminum and titanium: (a) the scheme of laboratory experiment with bacterial inoculation on a nutrient medium and measuring zone of bacterial growth inhibition around the circular sample with the coating; (b) the dependence of the dimensions *r* of zones uninhabited with bacteria on Zn concentration in PEO coatings; (c, d) time variation of *r* in the vicinity of the coatings formed in the following electrolytes: (c) 30 g/L $Na_6P_6O_{18}$ and $Cd(CH_3COO)_2$, $n = 1$ and 0.5 , (c) 30 g/L $Na_6P_6O_{18}$ and $Pb(CH_3COO)_2$, $n = 0.5$, 36.1 g/L $Na_5P_5O_{10}$ and $Pb(CH_3COO)_2$, $n = 5.0$ and 2.5 [25,26].

Table 5

The results of field tests in sea water (the Sea of Japan, Rynda Bay) for the AMtsM aluminum alloy samples with PEO coatings [25].

Electrolyte	$n = [\text{Na}_6\text{P}_6\text{O}_{18}]/[\text{Me}]$	Time of exposition (days)				
		7	14	22	30	60
-(Al)	–	o	o	o	o	o
$\text{Na}_6\text{P}_6\text{O}_{18}$	–	no	o	o	o	o
$\text{Na}_6\text{P}_6\text{O}_{18} + \text{Zn}(\text{CH}_3\text{COO})_2$	3	no	no	no	no	o
	1	no	no	no	no	o
	0.5	no	no	no	no	o
$\text{Na}_6\text{P}_6\text{O}_{18} + \text{Pb}(\text{CH}_3\text{COO})_2$	3	no	o	o	o	o
	1	no	o	o	o	o
	0.5	no	no	no	no	o

Note: o - overgrowth of colonies of the bacterial film, barnacles (*Balanus*), shells, algal, etc.; no - no overgrowth.

composition. Such coatings are of interest for biomedical applications, for applying layers with antibacterial effect on domestic instruments and devices, for use in the protection systems on metallic products.

Analysis of the literature shows that research in applying PEO technique for the synthesis of the coatings of complex chemical composition are actively developing. We can confidently expect that the new ideas will soon be offered to obtain PEO coatings with non-traditional composition, structure, properties and application areas.

Acknowledgments

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