Methods for Controlling the Surface Architecture of Coatings Formed by Plasma Electrolytic Oxidation

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Abstract. The paper considers approaches that can lead to the growth of micro- and nanocrystals on the surface of coatings formed on valve metals by plasma electrolytic oxidation (PEO). Among these approaches, there are the use of electrolytes-suspensions, the addition of organic compounds to the electrolytes, the thermal annealing of 'PEO layer/metal' composites, including impregnated ones.

Introduction

Plasma electrolytic oxidation (PEO) technique that is electrochemical formation of coatings on the surface of valve metals under spark and microarc electric discharges originates from traditional anodizing [1, 2]. The advantage of traditional anodizing is the ability to form oxide layers with a regular structure and a controlled length of the pores [3]. In contrast to anodizing, the PEO technique allows one to include electrolyte components into the coatings and form very developed surface structures, which morphology and composition depend on the processing conditions, that is, on the choice of mode and electrolyte formula [4-6].

To give PEO coatings functional properties, two main approaches can be used [6, 7]. The first is the modification of coatings during PEO by introducing the precursors of desirable compounds into the electrolyte in the form of dispersed particles [8-11], complex anions [12, 13], or organic compounds [14-16]. The second is the subsequent processing of PEO coatings, which may be hydrothermal treatment [17], impregnation [18, 19], extraction-pyrolysis [20], or annealing [3, 21]. Using these approaches, oxide layers with catalytic [7, 11, 18-20], photocatalytic [21], magnetic [13], and biocompatible properties [17] were obtained.

Modification changes not only the composition of the coatings, but also the morphology of their surface. A number of studies noted the growth of micro- and nanocrystals on the surface of PEO coatings, enhancing their functional properties due to more developed surface [18, 19, 21].

The paper is devoted to the use of certain approaches, such as using electrolyte-suspensions, adding organic compounds to electrolytes, impregnation of the PEO layer, and their thermal annealing, in order to change the composition and surface morphology of PEO coatings due to the growth of micro- and nanocrystals on their surfaces. We believe that such changes will impart new functional properties to the surface of valve metals.

Experimental

PEO Coating Formation. PEO coatings were formed on flat samples of a size of 20×20×0.5 mm or on wire with a cross section of 2 mm made of VT1-0 titanium (99.9% Ti). Before PEO-treatment, the samples were chemically polished in a mixture of concentrated acids (HF: HNO$_3$=1: 3, volume relation) at 70 °C in order to remove the surface layer of natural oxide film and standardize the surface.

PEO treatment of titanium samples was carried out at effective current density 0.1-0.2 A/cm^2 for 5-10 min in an aqueous electrolytes of different compositions. The electrochemical cell consisted of

a thermal glass of 1 L in volume with a spiral-shaped hollow nickel cathode. The electrolyte was agitated by a magnetic stirrer. The system was cooled by cold water pumped through the cathode to keep the electrolyte temperature below 35 °C. TER4-63/460H (Russia) thyristor unit with unipolar pulse current was used as a power source. After PEO treatment, the samples were rinsed by distilled water and air-dried at room temperature.

Impregnation of PEO-Coated Samples. In some cases, PEO coated samples were immersed in an aqueous solution containing transition metal nitrates. Composition and concentrations will be given later. The samples were kept in an impregnating solution for 1 h and dried over an electric heater.

Air Annealing of the Coated Samples. Impregnated and non-impregnated PEO-coated samples were annealed in a muffle furnace at given temperatures for 1-4 h.

Coating Characterization. The data on morphology and element composition of the surface were obtained using Hitachi S-5500 scanning electron microscope (Japan) quipped with Thermo Scientific accessory for energy dispersive X-ray spectroscopy (EDS) analysis. Previously, gold was sputtered on the coatings to prevent surface charging.

The X-ray diffraction (XRD) patterns of the coated samples were recorded on a D8 Advance X-ray diffractometer using the Bragg-Bretano method with rotation of the sample in CuK_α-radiation. XRD analysis was carried out using the EVA retrieval program based on the PDF-2 database.

Diffuse reflectance spectra for some coatings were recorded in the range of 200-800 nm using a Cary Varian 5000 spectrophotometer with a spectral resolution of 1 nm. Halogen and deuterium lamps were used as radiation sources. The band gap Eg was determined by the value of the second derivative of the reflection coefficient at a wavelength of zero, similarly [22].

Catalytic Tests. Catalytic tests of the samples in oxidation of CO to CO_2 were carried out using BI-CATflow flow-type catalytic system (Institute of Catalysis of Siberian Branch of RAS, Novosibirsk, Russia). The PEO-coated samples (geometric surface area of the coating was 25 cm^2) were placed into the active zone of a tubular quartz reactor of a volume of 3 cm^3. The measurements were performed at the temperatures from room temperature to 500°C. The gas flow rate was 70 ml/min. The initial reaction mixture consisted of 79% Ar, 20% O_2, and 1% CO. The concentrations of CO and CO_2 were determined using a PEM-2M gas analyzer (Boner LLC, Novosibirsk).

Results and Discussion

Electrolytes with Disperse Particles. The use of electrolyte-suspensions or slurry electrolytes is a fairly common approach for incorporating dispersed particles into PEO coatings [8-10]. The conditions for the formation of dispersed particles can be created during electrolyte preparation [11]. We use such approach to obtain $WO_3 – MWO_4$ oxide structures (M = Fe, Cu, Ni, Mn, Zn) on titanium. It is known that tungsten oxides and transition metal tungstates are of interest as photoluminescent materials, sensors and catalysts [21, 23]. PEO coatings, containing stoichiometric or non-stoichiometric tungsten oxides, tungsten bronzes, can be obtained in aqueous electrolytes based on Na_2WO_4 [21, 24]. In our case, PEO coatings were formed for 10 min at $i = 0.2$ A/cm^2 in electrolytes containing 0.1 mol/L Na_2WO_4 acidified by 0.05 mol/L H_2SO_4 or 0.1 M CH_3COOH (for WO_3+ZnO_x samples) with addition of 0.05 mol/L of $Cu(CH_3COO)_2$, FeC_2O_4, $Ni(CH_3COO)_2$ or $Zn(CH_3COO)_2$.

As to XRD, the most of such coatings include tungsten oxide and transition metal tungstate (Table 1). On the surfaces of a number of the coatings, we found micro- and nanocrystals (Fig. 1). Their elemental composition (Table 1) is consistent with the phase composition of the coatings. Cubic granules of 100 nm in size on the surface of $WO_3 + NiO_x$ correspond to $NiWO_4$. Stars on the surface of $WO_3 + ZnO_x$ samples can be $ZnWO_4$. Granules on $WO_3 + FeO_x$ samples meet $WO_3 + FeO(OH)$ and rectangular plates on the surface of $WO_3 + CuO_x$ correspond to the mixed crystalline phases WO_3 and Cu_2WO_4. The formation of micro- and nanocrystals seems to be associated with the thermolysis of dispersed particles from electrolyte-suspensions that have fallen on the surface area exposed to spark and microarc electric discharges.
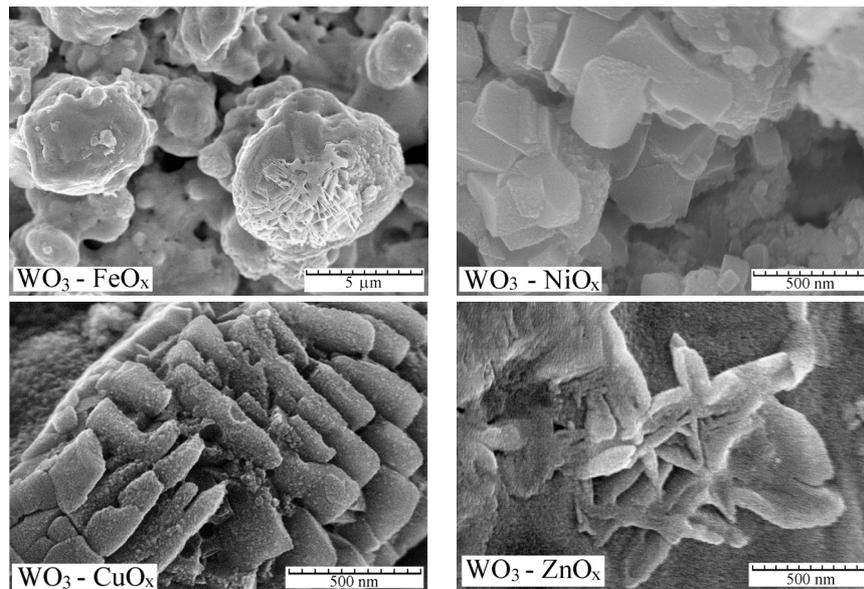
Fig. 1. SEM-images of micro- and nanocrystals on the surface of PEO coatings on titanium.

Table 1. The composition of PEO coatings, microcrystals on their surfaces and the bandgap values

| PEO coating | Coatings | | Crystallites | | E_g [eV] |
	Phase composition	Element composition [at. %]	Element composition [at. %]	Shape	
WO_3+FeO_x	WO_3 + FeO(OH)	13.7 C; 65.9 O; 4.9 Fe; 15.5 W	4.5 C; 70.0 O; 5.8 Fe; 19.6 W	Granules	2.36 and 2.73
WO_3+NiO_x	WO_3 + $NiWO_4$	71.1 O; 0.8 Na; 4.7 Ti; 7.2 Ni; 16.1 W	18.9 C; 56.0 O; 13.7 Ni; 11.3 W	Cubic granules	2.08, 2.47 and 3.08
WO_3+CuO_x	WO_3 + Cu_2WO_4	2.9 C; 68.2 O; 12.1 Cu; 16.7 W	19.4 C; 57.6 O; 5.6 Cu; 17.4 W	Plates	2.8
WO_3+ZnO_x	TiO_2 (rutile) + WO_3 + $ZnWO_4$	5.0 C; 65.6 O; 6.4 Ti; 5.3 Zn; 17.7 W	15.7 C; 56.5 O; 2.4 Ti; 11.1 Zn; 14.3W	Stars	2.78

The band gap E_g values given in Table 1 indicate that the absorption of photons by the structures contained transition metal oxides or tungstates is possible in UV and visible radiation range. A number of E_g values are close to the E_g for WO_3 (2.87 eV) [25], indicating that crystalline WO_3 makes the main contribution to the optical properties of most samples. Several values of E_g suggest that several channels of interband transitions (direct and indirect ones) can be realized in WO_3-FeO_x and WO_3-NiO_x samples.
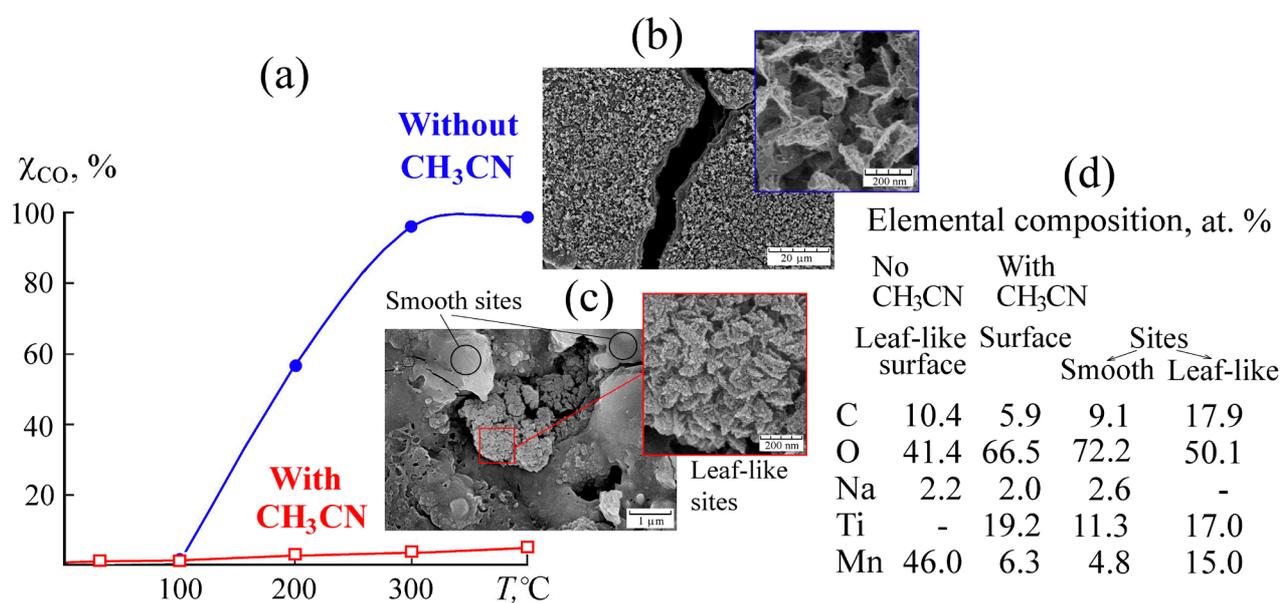
Thus, titanium-supported oxide coatings with WO_3 and/or MWO_4 micro and nanocrystals can be fabricated by the one-step PEO technique in aqueous electrolytes, in which there are conditions for the formation of dispersed particles of transition metal tungstates. In this case, the nature of the dispersed particles in the electrolytes will determine the composition of the crystals on the surfaces and photocatalytic properties of the coatings. The resulting composites are potential candidates for use as photocatalysts operating in the visible light range.

Electrolytes with Additives of Organic Compounds. Aqueous solutions of inorganic compounds are usually served as electrolytes for PEO. The use of aqueous electrolytes with additives of various organic compounds such as surfactants [14], alcohols [15], urea [16] or EDTA [12, 13] allows changing the composition and surface morphology of PEO coatings. The reason may be a change in the solubility conditions of inorganic compounds in the electrolyte due to the salting out

effect (with the addition of alcohols), complexation (when using EDTA), or stabilization of slurry electrolytes (with introducing surfactants).

We studied the effect of organic compound additives on the formation of PEO coating by the example of PEO treatment of titanium in an aqueous electrolyte containing sodium tetraborate, manganese acetate, and acetonitrile (CH_3CN) [26]. Acetonitrile is a dipolar-aprotic solvent. The high polarity of the nitrile group of CH_3CN facilitates its adsorption on metal surfaces with subsequent electrochemical conversion. Due to the good solubility of acetonitrile in water and its complexation ability, its addition to aqueous electrolytes can affect the mechanism and properties of the coatings formed by the PEO.

In the absence of acetonitrile, catalytically active leaf-like structures with high concentration of Mn (46.0 at. %) grow on the surface of PEO-coatings (Fig. 2a, b, d). The addition of acetonitrile to this electrolyte leads to a smoothing of the surface, to a decrease in the number of rough leaf-like sites (~15 at. % Mn), and, as a result, to a decrease in catalytic activity (Fig. 2a, c, d). The conversions of CO to CO_2 at 400°C are equal 98.8 and 4.8 % over the PEO-coated samples formed in the electrolyte without and with CH_3CN.

Elemental composition, at. %			
	No CH_3CN	With CH_3CN	
	Leaf-like surface	Surface	Sites
		Smooth	Leaf-like
C	10.4	5.9	9.1	17.9
O	41.4	66.5	72.2	50.1
Na	2.2	2.0	2.6	-
Ti	-	19.2	11.3	17.0
Mn	46.0	6.3	4.8	15.0

Fig. 2. The temperature dependences of CO conversion (a) and SEM images for the samples with PEO coatings formed for 10 min at $i = 0.1$ A/cm^2 in the electrolyte containing 0.1 mol/L $Na_2B_4O_7$ and 0.04 mol/L g/L $Mn(CH_3COO)_2$ without (a) and with 6 vol. % CH_3CN (b), as well as element composition of the surfaces and their different sites (d).

During the preparation of $Na_2B_4O_7$ + $Mn(CH_3COO)_2$ electrolyte, amorphous precipitate of manganese hydroxide is formed. When colloid particles of manganese hydroxide fall into the range of spark and microarc discharges, they thermolize with the formation of manganese oxides in the coating composition. According to XRD, traces of manganese dioxide were found in the coatings.

Adding acetonitrile to the solution with an amorphous precipitate of manganese hydroxide leads to the formation of PEO coatings with a lower manganese content and a higher titanium content (Fig. 2d). This means that acetonitrile interacts with dispersed particles of manganese hydroxide, changing the conditions for incorporating manganese into the coatings. One can assume that the nitrile complexes of manganese CH_3-CN·$Mn(OH)_2$ can be formed because of the coordination of acetonitrile with manganese ion by the lone electron pair of the nitrogen atom. This leads to a change in the composition, charge and mobility of the dispersed particles, weakening their movement to the anode. At the same time, the concentration of free acetonitrile in the solution decreases. This explains the decrease in manganese concentration and the absence of nitrogen in the coatings.

The above example shows that organic additives to the electrolytes with transition metal compounds affect the number and composition of micro and crystals growing on the surface of PEO coatings. This fact should be considered when forming functional coatings.

Post-Treatment of PEO Coatings. As to Refs. [6, 18, 19, 21], using impregnation and/or annealing one also can affect the formation and growth of crystallites on PEO coating surface. Annealing of W-containing PEO coatings on titanium at a temperature of 700°C and above leads to regular WO_3 microcrystals on their surface [27]. The results of work [28] have shown that, depending on the air-annealing temperature, crystals of various shapes and compositions grow on the surface of Mn-, W-containing PEO coatings on titanium: tetrahedral prisms of $MnWO_4$ and hexagonal prisms of $Na_2Mn_2Ti_6O_{16}$ are formed at 700 and 850°C, respectively.

The composition of crystals growing on the surface of $NiO+CuO/TiO_2/Ti$ composites formed by a combination of PEO and impregnation strongly depends on the annealing temperature [29]: CuO crystals are formed after annealing at 500–700°C, $NiWO_4$ crystals - at 750–850°C, and $Ni_{2.62}Ti_{0.69}O_4$ whiskers - at ≥900°C. The data obtained indicate that the electrolyte residues and the impregnating solution accumulated on the surface and in the pores of the coatings, as well as the diffusion of titanium from the depth of the coating to the surface play an important role in the formation of micro- and nanocrystals.

Fig. 3 shows the formations on the surface of air-annealed Ni-, W-containing coatings on titanium produced by one-step PEO technique (a) and by combining PEO and impregnation (b, c). Despite the identical phase composition (TiO_2 (rutile) + WO_3 + $NiWO_4$), the surface morphologies of the resulting coatings noticeably differ. Annealing of Ni-, W-containing coatings obtained by one-step PEO technique in the Na_2WO_4 + CH_3COOH + $Ni(CH_3COO)_2$ electrolyte leads to the formation of WO_3 microcrystals on their surface. The microcrystals are localized in and around the pores of the PEO coating. Upon the annealing of the PEO coatings formed in the Na_2WO_4 + CH_3COOH electrolyte and impregnated in $Ni(NO_3)_2$ solution, $NiWO_4$ microspheres grow in the coatings pores. The combination of PEO in Na_2WO_4 + CH_3COOH + $Ni(CH_3COO)_2$ electrolyte and impregnation in $Ni(NO_3)_2$ solution following by air annealing leads to the formation of $NiWO_4$ microspheres in the pores and WO_3 crystals in the vicinity of them. We believe that electrolyte components accumulated in the pores of PEO coatings play a significant role in the formation of WO_3 crystals, while the products of $Ni(NO_3)_2$ thermal decomposition and their interaction with WO_3 in the pores of impregnated coatings also participate in microsphere appearance.
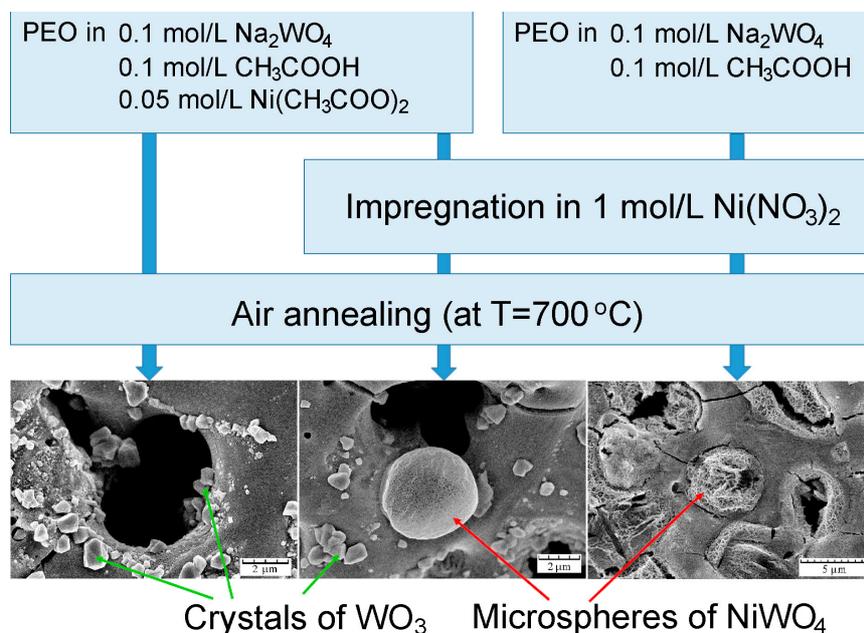
Fig. 3. The growth of crystals of WO_3 and microspheres of $NiWO_4$ on the surfaces of PEO coatings air-annealed at 700°C for 1h, depending of the producing method.

Summary

The analysis of our and literary data shows that micro- and nanocrystals on the surface of the PEO coatings can be formed during one-step PEO treatment as a result of thermolysis of dispersed particles from electrolyte-suspensions under spark or arc electric discharges, and during post-treatment of PEO-coated samples, for example, as a result of their impregnation and/or annealing. Creating conditions for the formation of dispersed particles of transition metal tungstates in the electrolyte-suspension allows one to change the composition and shape of the crystals on the surface of PEO coatings, and thus control their optical and photocatalytic properties. The introduction of organic additive such as acetonitrile into $Na_2B_4O_7 + Mn(CH_3COO)_2$ electrolyte leads to surface smoothing of Mn-containing PEO coatings on titanium, decreasing the number of leaf-like sites, and, as a result, to drop in their catalytic activity in CO oxidation. Annealing of Ni-, W-containing coatings on titanium, obtained by a combination of plasma electrolytic oxidation and impregnation, leads to the formation of WO_3 crystals around the pores and $NiWO_4$ microspheres in the pores of PEO coatings. The formation and localization of the crystals depends on whether nickel was introduced into the coating composition from electrolyte for PEO or from impregnating solution.

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