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NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

# The Effect of Acetonitrile Additives to Tetraborate Electrolyte on the Composition and Morphology of PEO Layers on Titanium

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**Abstract**—The effect of the CH<sub>3</sub>CN acetonitrile additives to a tetraborate electrolyte on the composition and morphology of oxide layers on titanium formed by the method of plasma electrolytic oxidation has been studied. The composition and morphology of the coatings have been investigated by means of scanning electron microscopy and energy-dispersive and X-ray diffraction analysis. The addition of 3 vol % acetonitrile to the tetraborate electrolyte's composition without modifying of electrical parameters of the process has resulted in a decrease of the coatings' porosity and incorporation in them of up to 20 at % of nitrogen. Oxide layers with low manganese content and the absence of nitrogen have been formed upon the acetonitrile addition to a tetraborate electrolyte with manganese acetate. The surface of the Mn-containing oxide layers is heterogeneous. On the surface, there are separate areas that are "leaf-like" structures with a high content of manganese.

*Keywords:* plasma electrolytic oxidation, titanium, acetonitrile, manganese oxide **DOI:** 10.1134/S2070205119030262

#### 1. INTRODUCTION

One advanced method of modifying metal surfaces and alloys is plasma electrolytic oxidation (PEO). At present, this method is used extensively to obtain multicomponent oxide coatings to protect metals from corrosion and mechanical wear [1, 2], promising for use in catalysis [3, 4], photocatalysis [5–7], as sensors in environmental monitoring [8, 9], and magnetoactive materials [4, 10]. The functional properties of oxide coatings applied on metals by the PEO method are determined primarily by their composition and morphology, which can be controlled by varying the process parameters and electrolyte composition. In most cases, aqueous solutions of inorganic compounds are used as electrolytes for PEO [1-12]. The application of anhydrous acetonitrile [13] or aqueous electrolytes with the addition of different organic compounds, including surface-active substances (SASs) [14, 15], ethanol [16], urea [17], methanol [18], glycerin [19], or EDTA [20-22], in the role of an electrolyte for PEO enables one to change considerably the composition and morphology of the surface. For instance, it was shown in [17] that the addition of urea to an electrolyte based on sodium aluminate increases the nitrogen content in the PEO layer, reduces its thickness, increases the porosity, and preventes the formation of  $\alpha$ -aluminum oxide. The authors of [18] demonstrated that the addition of up to 8 vol %  $CH_3OH$  in aqueous electrolytes resultes in the increase of the coatings' thickness and the decrease of the average pore diameter. The consequence of adding certain amounts of glycerol to silicate electrolyte is a reduction in pore size and microcracks, smoothing the relief of coatings obtained on the ZK60 magnesium alloy [19]. Similar results on the formation of a smooth low-porosity PEO coating surfaces on metals were described in [14] with the addition of SASs and in [22] with the addition of EDTA.

One of the most interesting and understudied organic substances that is used for the formation of anodic films is acetonitrile (CH<sub>3</sub>CN) classified as a dipolar-aprotic solvent. High polarity of the acetonitrile's nitrile group predetermines the possibility of its adsorption on metal surfaces with subsequent electrochemical conversion [13, 23]. For instance, in [13], crystalline anodic films comprising titanium oxide in the rutile and anatase modifications along with nitride and carbide titanium were obtained in the potentiodynamic mode at high voltages of up to 3000 V and current densities of up to 10 mA/cm<sup>2</sup> in anhydrous acetonitrile on titanium. The authors of [23] showed that, at low voltages of about 5 V and currents of up to 80 pA, from acetonitrile thin polymer films are deposited on metal surfaces. According to the authors, processes



**Fig. 1.** Voltage *U* dependence on formation time *t* for coatings in electrolytes containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and CH<sub>3</sub>CN vol %: (1) 0, (2) 1, and (3) 3. Formation current density i = 0.1 A/cm<sup>2</sup>.

similar to the breakdown phenomenon occur during the synthesis of these films. In both cases, the electrochemical synthesis of coatings was performed in a single-component anhydrous acetonitrile. However, due to high solubility of acetonitrile in water and its ability to form complex compounds with transition metal salts by the donor–acceptor mechanism [24–26], the acetonitrile addition to aqueous electrolytes with different compositions could impact on the mechanism and properties of coatings formed by the PEO method. At the same time, to our knowledge, this issue was not considered in the scientific literature before.

This work presents the results of studies of the effect of acetonitrile additives into an aqueous electrolyte on the regularities of plasma electrolytic formation of oxide layers on titanium, their composition, surface morphology, and catalytic activity in CO oxidation.

### 2. EXPERIMENTAL

Electrodes for plasma-electrolytic oxidation were prepared of BT1-0-grade titanium foil in the form of plates of a size of  $2.5 \times 2.5$  cm<sup>2</sup>. The samples were chemically polished in a mixture of concentrated acids HF: HNO<sub>3</sub> = 1 : 3 at 60–80°C for 2–3 s and then washed by distilled water and dried in air.

A vessel of a volume of 1 L made of thermally resistant glass was used as an electrochemical cell for the PEO process. A hollow stainless-steel cathode in the form of a coil that simultaneously served as a cooler was placed inside the vessel. Electrolyte stirring was carried out using a magnetic stirrer. A TER4-63/460H thyristor device with a single polar impulse current waveform was applied as a current source.

The processing was performed in the galvanostatic mode under the effective current density of  $i = 0.1 \text{ A/cm}^2$  for 10 min or of 0.2 A/cm<sup>2</sup> for 5 min. After PEO, the

samples were washed by distilled water and dried in air at room temperature.

The commercial reagents  $Na_2B_4O_7 \cdot 10H_2O$  (chemically pure grade),  $Mn(CH_3COO)_2 \cdot 4H_2O$  (pure grade),  $CH_3CN$  (chemically pure grade), and distilled water were used for the preparation of electrolytes. The oxidation was performed in aqueous electrolytes containing 0.1 M  $Na_2B_4O_7$  or 0.1 M  $Na_2B_4O_7 + 10$  g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, including adding of 1–7 vol % CH<sub>3</sub>CN.

The phase composition was determined by the method of X-ray diffraction analysis (XRD) on a D8 ADVANCE diffractometer (Germany) under  $CuK_a$  radiation. Identification of compounds in the samples under study was performed in the automatic search mode of the EVA software using the PDF-2 database.

Surface morphology was examined using a Hitachi S-5500 scanning electron microscope (SEM) with an Ultra Dry energy-dispersive spectrometer accessory (ThermoScientific, United States).

A BI-CATflow flow-through catalytic device manufactured by the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (Novosibirsk, Russia), was used for the estimation of the catalytic activity of the samples in the oxidation reaction of CO to  $CO_2$ . Titanium plates with a total geometric area of 25 cm<sup>2</sup> deposited with a manganese-containing coating were placed into a quartz reactor of a volume of 3 cm<sup>3</sup>. The initial reaction mixture consisted of 79% Ar, 20% O<sub>2</sub>, and 1% CO. The gas flow rate was 70 mL/min. The measurements were performed at the temperatures from room temperature to 500°C. The rate of temperature change in the reactor was 10°C/min. The composition of the gas mixture was determined 30 min after setting a specified temperature in the reactor. The gaseous components were analyzed using a PEM-2M gas analyzer manufactured by the Institute of Catalysis.

## 3. RESULTS AND DISCUSSION

#### 3.1. The Effect of Acetonitrile Additions to the Tetraborate Electrolyte

Figure 1 presents the curves of the voltage on electrodes (U, V) dependence on oxidation time (t, min) at the formation of oxide layers on titanium in a tetraborate electrolyte with and without the addition of acetonitrile.

In all cases, the intense voltage increasing on the electrodes is observed in the first minutes of the process: the voltage value reaches 200–210 V within ~4–6 min and, further, changes insignificantly during the process for 10 min. In general, the form of U = f(t) curves was the same for all the studied electrolytes and did not depend on the acetonitrile additions.

According to the element analysis data, oxygen and titanium at a ratio of 1.6 were revealed on the coatings' surfaces formed in the tetraborate electrolyte (Table 1),

No.	C(CH <sub>3</sub> CN), vol %	Phase composition	Elemental composition, at %				
			0	Ti	С	Ν	
1	0	TiO <sub>2</sub> (anatase, rutile)	60.9	39.1	_	—	
2	1	TiO <sub>2</sub> (anatase, rutile)	50.0	17.9	6.7	25.4	
3	3	TiO <sub>2</sub> (anatase, rutile)	51.5	19.7	5.6	23.2	

**Table 1.** Element and phase compositions of the coatings formed in 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution with addition of CH<sub>3</sub>CN. Formation current density i = 0.1 A/cm<sup>2</sup>

which indicates the formation of titanium oxide. In the tetraborate electrolyte with acetonitrile, coatings were formed, which additionally contained carbon and significant amounts of nitrogen on the surface. The latter was obviously caused by sorption of acetonitrile molecules on the titanium surface involving the lone electron pair of nitrogen of the nitrile group followed by their thermal transformation during the PEO and migration of carbon and nitrogen atoms into the growing oxide film. The incorporation of a significant amount of nitrogen and carbon into the oxide film was also observed in [13] when conducting the process in pure acetonitrile.

Using electron microscopy It was found that the addition of acetonitrile to a tetraborate electrolyte affects the morphology of the formed coatings (see Fig. 2). The smoother coatings with smaller pore sizes were formed in a tetraborate electrolyte with the addition of 3 vol % acetonitrile. Perhaps acetonitrile behaves like surfactant molecules. According to the authors of [14], the adsorption of surfactant molecules on the anode surface leads to a change in the surface tension at the gas/liquid, liquid/solid interface. As a consequence, it improves of the wetting conditions of the growing oxide surface with an electrolyte solution, reducing the size of gas bubbles detaching from the surface during anodizing and, accordingly, reducing the diameter of the pore mouths on the surface.

Thus, the addition of small amounts of acetonitrile into the tetraborate electrolyte resulted in significant changes in the formes coatings' morphology and composition of elements without affecting the appearance of formation curves.

## 3.2. The Effect of Acetonitrile Additives into Tetraborate Electrolyte with Manganese Acetate

The additional introduction of manganese acetate into the tetraborate electrolyte resulted in the formation of layers containing  $Mn_2O_3$  and  $Mn_3O_4$  manganese oxides along with the rutile on the external part [16]. The amount of manganese in the surface layer depended on the formation conditions and the concentration of manganese acetate in the electrolyte. The obtained manganese-containing structures on titanium exhibited catalytic activity in the oxidation of CO to CO<sub>2</sub> in the temperature range of  $250-350^{\circ}$ C. The catalytic activity is determined by the amount of manganese in the layers, its distribution over the surface, and the surface morphology.

The addition of ethanol to the electrolyte contributes to smoothing of the surface and may have resulted in the formation of oxides with different states of manganese oxidation in the coatings' composition (by creating a more reducing medium at the anode) [16].

This section presents data on the effect of acetonitrile additives into electrolyte with sodium tetraborate and manganese acetate on the formation, composition, and morphology of the formed coatings' surface and their catalytic activity in the oxidation of CO to  $CO_2$ .

Figure 3 presents the U = f(t) dependences for processes of formation of coatings in electrolytes containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, and acetonitrile. The addition of manganese acetate to the initial tetraborate electrolyte resulted in the formation of white amorphous precipitate of manganese hydroxide and more than twofold decrease (from ~200 to 75 V) of the electrode voltage during the coating formation process (compare Figs. 1, 3a, 3b, curves *I*). The latter can be related to changes in the electrolyte's ion com-



**Fig. 2.** The SEM images of the coating surfaces formed in (a, b) 0.1 M solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and (c, d) 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> with addition of 3 vol % CH<sub>3</sub>CN. Formation current density i = 0.1 A/cm<sup>2</sup>.



**Fig. 3.** Voltage *U* dependence on formation time *t* for coatings in electrolytes containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub> and CH<sub>3</sub>CN. (a) i=0.1 A/cm<sup>2</sup>, C (CH<sub>3</sub>CN), vol %: (1) 0, (2) 1, (3) 3, and (4) 5; (b) i=0.2 A/cm<sup>2</sup>, C(CH<sub>3</sub>CN), vol %: (1) 0, (2) 3, (3) 5, and (4) 7.

position. Under these conditions, dark brown coatings are formed with poor adhesion to the titanium base. The addition of 1-7 vol % acetonitrile to the aqueous tetraborate electrolyte with manganese acetate resulted in a gradual increase of the formation voltage up to 130 V. Light brown coatings with good adhesion to the titanium base were formed in aqueous–organic electrolytes. Current density increasing from 0.1 to 0.2 A/cm<sup>2</sup> more enhances the formation voltage and adhesion of the formed manganese-containing coatings to the metal base.

Thus, the formation voltage in the acetate-tetraborate electrolyte increases both along with the increase in the current density and as a result of the acetonitrile addition to the electrolyte. At the same time, it allows to form the more homogeneous coatings with high adhesion to the coating base.

As is shown in Tables 2 and 3, the acetonitrile addition to the tetraborate electrolyte with manganese acetate (the solution with the amorphous precipitate of manganese hydroxide) resulted in the formation of coatings with lower manganese content and higher titanium content. In addition, one should mention that coatings containing carbon but not containing nitrogen were formed in the electrolytes containing an amorphous precipitate (dispersed particles of manganese hydroxide) and acetonitrile. This indicates that acetonitrile added to the tetraborate electrolyte with manganese acetate interacts with the dispersed particles of manganese hydroxide, which results in the above-described effects. One can suggest that CH<sub>3</sub>-CN : Mn(OH)<sub>2</sub> nitrile complexes of manganese were formed as a result of the coordination of acetonitrile to the manganese ion by the lone electron pair of the nitrogen atom. Thus, the composition and, therefore, the charge and mobility of disperse particles change. The latter resulted in it being more difficult for dispersed particles to reach the anode surface, which explains the decrease of the manganese content in the PEO layers' composition. In addition, as a result of the binding of acetonitrile into complexes, it cannot interact with the anode surface, which explains the absence of nitrogen in the PEO layers' composition. Thus, changes in the nature and quantity of dispersed particles reaching the anode surface change the electrical parameters of the process and the formed coating's properties.

The SEM images show (Fig. 4) that the addition of manganese acetate to the tetraborate electrolyte resulted in the formation of heterogeneous surfaces, the morphology of which depended on the oxidation conditions. Heterogeneous coatings with alternating smooth areas and areas covered by numerous granules (Fig. 4a) were formed at fabrication of films in the tetraborate–acetate electrolyte for 10 min at i = 0.1 A/cm<sup>2</sup>. At higher magnification two types of nanostructures-the granule-shaped particles associated into larger microstructures (Fig. 4b) and the ordered "leaflike" grid nanostructures (Fig. 4c) were revealed on the surface of these coatings. The heterogeneous coatings covered by numerous granules (Fig. 4d) were formed at fabrication in the tetraborate-acetate electrolyte for 5 min at  $i = 0.2 \text{ A/cm}^2$ . The nanostructured objects similar to coatings formed at the lower current density were not observed (Figs, 4e, 4f).

The introduction of acetonitrile in the tetraborate-acetate electrolyte in all cases resulted in a noticeable change in the formed coatings' morphology. As in the case of a tetraborate electrolyte, the surface becomes smoother (compare the images of Figs. 4s, 5a and 4d, 5d).

The crystal-like nanostructured objects located on surface separated areas were reaveled on the surface of all coatings by more detailed surface study (Figs. 5b, 5c, 5e-51). The objects resemble the drops (or "hedge-

No.	C(CH <sub>3</sub> CN), vol%	Phase composition	Element composition, at %						
			Mn	Ti	Na	0	С		
1	_	MnO <sub>2</sub> (traces)	46.0	0.0	2.2	41.4	10.4		
2	1	TiO <sub>2</sub> (anatase, rutile)	34.7	1.0	1.2	50.1	12.7		
3	3	TiO <sub>2</sub> (anatase, rutile)	4.6	26.9	0.0	64.3	4.2		
4	6	TiO <sub>2</sub> (anatase, rutile)	6.3	19.2	2.0	66.5	5.9		

**Table 2.** Element and phase compositions of coatings on titanium formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, and CH<sub>3</sub>CN. Formation current density i = 0.1 A/cm<sup>2</sup>

**Table 3.** Element and phase compositions of the coatings on titanium formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, and CH<sub>3</sub>CN. Formation current density i = 0.2 A/cm<sup>2</sup>

No.	C(CH <sub>3</sub> CN), vol %	Phase composition	Elemental composition, at %						
			Mn	Ti	Na	0	С	Ν	
1	-	Mn <sub>2</sub> O <sub>3</sub>	30.3	3.4	0.6	42.9	22.5	_	
2	3	TiO <sub>2</sub> (anatase, rutile)	5.5	20.4	0.4	60.2	13.5	_	
3	5	TiO <sub>2</sub> (anatase, rutile)	9.7	19.4	0.8	63.2	6.9	_	
4	6	TiO <sub>2</sub> (anatase, rutile)	7.3	27.1	0.6	53.1	11.9	_	
5	7	TiO <sub>2</sub> (anatase, rutile)	5.5	20.2	0.8	65.5	4.8	3.1	

hogs") with the developed structure in the shape of "leaflike" formations. One should mention that "leaflike" formations were observed on the surface of coatings obtained in the electrolyte without acetonitrile as well (Fig. 4c). These facts allow to suggest that the formation of crystal-like objects locally arranged on the surface is associated with the getting into these areas of dispersed particles of manganese hydroxide not connected with acenonitrile. According to the element analysis data, sites containing nanostructures (site 1, Fig. 6) included (at %) 11.2 Mn, 18.5 Ti, 56.2 O, and 14.1 C, while adjacent sites (site 2, Fig. 6) were manganese-depleted and contained (at %) 6.3 Mn, 26.3 Ti, 58.6 O, 7.8 C, and 1.1 Na.



**Fig. 4.** SEM images of the coating surfaces formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>. Formation current density:  $i = (a-c) 0.1 \text{ A/cm}^2$ , t = 10 min, and  $(d-f) \text{ and } 0.2 \text{ A/cm}^2$ , t = 5 min.

PROTECTION OF METALS AND PHYSICAL CHEMISTRY OF SURFACES Vol. 55 No. 3 2019



**Fig. 5.** SEM photographs of the surface of coatings formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub> and CH<sub>3</sub>CN, vol %: (a–f) 3, (g–i) 5, and (j–l) 7. Formation current density: i = (a-c) 0.1 and (d-l) 0.2 A/cm<sup>2</sup>.

The results of a study of the formed manganesecontaining oxide layers' catalytic activity in the oxidation of CO to CO<sub>2</sub> are shown in Fig. 7. The degree of conversion of CO to CO<sub>2</sub> at 400°C in the presence of samples formed in the tetraborate electrolyte with the amorphous precipitate of manganese hydroxide at the current density of 0.1 A/cm<sup>2</sup> was 98.8% (Fig. 7, curve *I*), whereas the coatings formed in the electrolyte with the addition of acetonitrile were not active for the studied reaction (Fig. 7, curve *2*). Thus, the addition of acetonitrile to tetraborate electrolyte with manganese acetate results in a change in the surface morphology of the coatings, a significant decrease in the content of manganese in them and, as a result, the samples almost completely lose their activity in the oxidation of CO to  $CO_2$ .

# CONCLUSIONS

To sum up, the acetonitrile addition to the electrolyte with sodium tetraborate or with tetraborate and manganese acetate has resulted in smoothing of the surface of the formed PEO coatings and the increase of adhesion to the metal basis. The addition of 3 vol % acetonitrile to the tetraborate electrolyte's composition without changing the electric parameters of the process is accompanied by the incorporation of up to 20 at % of nitrogen into the coatings. In the electrolyte with tetraborate and manganese ace-



**Fig. 6.** SEM photograph of the coating surface formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, and 5 vol % CH<sub>3</sub>CN. Formation current density: i = 0.2 A/cm<sup>2</sup>.



Fig. 7. The dependence of the CO conversion degree on the reaction temperature for the samples formed in the electrolyte containing 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g/L Mn(CH<sub>3</sub>COO)<sub>2</sub>, and CH<sub>3</sub>CN, vol %: (1) 0, (2) 3. Formation of coatings' current density i = 0.1 A/cm<sup>2</sup>.

tate, acetonitrile changes the mechanism of incorporation of manganese into coatings as a result of interaction with dispersed particles of manganese hydroxide through changing their charge and mobility. Apparently, the addition of acetonitrile to electrolytes-suspensions can reduce the precipitation of various transition metals in PEO-coatings of hydroxides. The surface of the Mn-containing oxide layers is heterogeneous. On the surface, there are separate areas that are "leaf-like" structures with a high content of manganese.

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