
NEW SUBSTANCES, MATERIALS AND COATINGS

Photocatalytic Properties of Zn- and Cd-Containing Oxide Layers on Titanium Formed by Plasma Electrolytic Oxidation

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Received February 17, 2016

Abstract—Element and phase compositions, surface morphology, and photocatalytic activity of oxide coatings on titanium formed by the method of plasma electrolytic oxidation in sulfate and phosphate electrolytes with and without addition of cadmium and zinc salts have been investigated. The coatings were studied by means of the X-ray spectral method, X-ray diffraction analysis, and electron microscopy. The photocatalytic activity of oxide layers depends on their element and phase composition and surface morphology. The highest photocatalytic activity in the reaction of degradation of Methylene Blue is demonstrated by titanium oxide coatings doped with cadmium.

Keywords: plasma electrolytic oxidation, titanium oxide, doping, photocatalytic activity

DOI: 10.1134/S2070205117040232

INTRODUCTION

At present, titanium dioxide is the most thoroughly studied and efficient photocatalyst for destruction of a broad range of toxic chemicals [1, 2]. As a rule, titanium dioxide-based photocatalysts are fabricated in the form of powders, which complicates their extensive practical application in different technologies, first of all, due to the problems related to powder separation from the suspension in the case of catalysis in a liquid medium and catalyst illumination for catalysis in the gas phase. To solve these problems, one can use photocatalysts immobilized on various substrates (glass, ceramics, metal oxides, textiles, etc.).

In view of this, there is substantial interest connected with the method of plasma electrolytic oxidation (PEO), which allows fabricating oxide layers of various chemical compositions, morphology, porosity, etc. on the surfaces of valve metals [3–5]. That this method is promising has been affirmed in numerous recent publications devoted to application of coatings obtained by the PEO method on titanium as photocatalysts in the processes of degradation of various organic contaminants [6–22].

It is worth mentioning that one of the main problems of using TiO₂ as a catalyst consists in low photoquantum efficiency appearing because of fast recombination of photogenerated electrons and holes. Moreover, TiO₂ is inactive in visible light due to its wide forbidden band (3.03 eV for rutile and 3.18 for anatase).

To increase the photocatalytic activity of titanium dioxide-based photocatalysts, modification or doping with transition metals—in particular, cadmium [23, 24] and zinc [25, 26]—is used.

The objective of the present work was to form Zn- or Cd-containing oxide layers on titanium by the PEO method and to study their composition and photocatalytic activity in the reaction of degradation of Methylene Blue.

MATERIALS AND METHODS

For plasma electrolytic oxidation experiments, plates made of titanium of the VT1-0 grade of a size of 0.5 × 2.5 × 0.1 cm were used. Samples were mechanically polished to remove burrs and defects formed during metal cutting. Thereafter, samples were chemically polished in a mixture of acids HF : HNO₃ = 1 : 3 at 60–80°C for 2–3 s, washed in 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 TER-63/460N thyristor device with a unipolar pulse current waveform was used as a power source. Upon oxidation, samples were washed in distilled water and dried in air.

Compositions of coatings and degrees of Methylene Blue degradation (X , %) in their presence

No.	Electrolyte composition	X , %	Phase composition	Element composition, at %
1	0.1 M Na_3PO_4	32	TiO_2 (anatase, rutile traces)	C 12.8, O 56.0, P 2.7, Ti 28.9
2	0.1 M Na_3PO_4 + 5 g/L ZnF_2	11	TiO_2 (anatase)	C 13.1, O 59.6, Zn 2.3, P 4.0, Ti 20.6
3	0.1 M Na_3PO_4 + 5 g/L $\text{Zn}(\text{CH}_3\text{COO})_2$	25	TiO_2 (anatase)	O 70.1, Zn 1.7, P 5.8, Ti 22.3
4	0.1 M H_2SO_4	17	TiO_2 (anatase, rutile)	O 66.1, S 0.3, Ti 33.6
5	0.1 M H_2SO_4 + 5 g/L $\text{Zn}(\text{CH}_3\text{COO})_2$	23	TiO_2 (anatase, rutile)	O 64.9, S 0.5, Ti 34.6
6	ZnSO_4 + EDTA C (Zn^{2+}) : C (γ^4)=1	19	TiO_2 (anatase, rutile)	C 3.0, O 61.3, N 3.3, Ti 32.5
7	0.1 M CdSO_4	41	TiO_2 (rutile)	C 6.7, O 55.7, Cd 0.5, Ti 37.2

Samples nos. 1–3 were formed for 5 min; samples nos. 4–7 were formed for 10 min.

Treatment was performed in the galvanostatic mode at effective current density $i = 0.1 \text{ A/cm}^2$. For electrolyte preparation, commercially available reagents were used (plus distilled water): H_2SO_4 of “standard titrimetric substance” (STS) grade; Na_3PO_4 of chemically pure grade; ZnF_2 of pure grade; and $\text{Zn}(\text{CH}_3\text{COO})_2$, ZnSO_4 , CdSO_4 , and EDTA of STS grade. The treatment time was 5 or 10 min. Upon PEO completion, samples were washed by distilled water and dried in air at room temperature.

The phase composition was determined by the method of X-ray diffraction analysis (XRD) using a D8 ADVANCE diffractometer (Germany) in $\text{CuK}\alpha$ radiation according to a standard technique. Identification of compounds in the samples under study was performed in the automatic search mode of the EVA software using the PDF-2 database.

The element composition of the coating surface was determined by the method of X-ray spectral analysis (XSA). A Superprobe JXA-8100 microprobe X-ray spectral analyzer (JEOL, Japan) was used, with the surface images being obtained simultaneously. The analyzed layer depth was $\sim 5 \mu\text{m}$. The electrode surface was also studied using a Hitachi S-5500 scanning electron microscope (Hitachi, Japan) with the system of energy-dispersive microanalysis (EDX) (ThermoScientific, United State). The analyzed layer depth was $\sim 1 \mu\text{m}$.

Studies of the photocatalytic properties of the formed coatings were carried out on the example of the reaction of photocatalytic decomposition of the Methylene Blue dye in an aqueous solution.

Ten milliliters of solution of Methylene Blue of a concentration of 10 mg/L and a sample of a size of $0.5 \times 2.5 \text{ cm}$ were placed into a quartz cell. The sample was located right by the reactor wall. A mercury-quartz lamp (DRT-125) was used as a source of ultraviolet irradiation. The distance between the lamp and the sample surface was accurately fixed and equal to 15 cm.

The samples were preliminarily held in solution under stirring in darkness for 30 min to achieve dye adsorption/desorption equilibrium. Upon completion

of this period, the solution optical density was measured using a spectrophotometer and then used as reference point A_0 . Then, the UV-light source was switched on and directed in a way to make the main illumination part fall on the studied sample surface and the sample was irradiated by the UV-light for 2 h. Changes in the dye concentration were controlled by a spectrophotometer on changes in the intensity of the dye absorption peak. Spectrophotometry measurements were carried out using a Shimadzu UV mini-1240 spectrophotometer (Japan). Measurements of the optical density of Methylene Blue solutions before and after irradiation were carried out at a wavelength of 659 nm (light absorption maximum).

Since the optical density linearly depends on the concentration in accordance with the Bouguer–Lambert–Beer law, the degree of dye decomposition was calculated using the formula

$$X = \frac{A_0 - A}{A_0} \times 100\%.$$

RESULTS AND DISCUSSION

The table shows data on the composition and photocatalytic activity of oxide layers on titanium formed in different electrolytes by the method of plasma electrolytic oxidation.

According to the X-ray spectral-analysis data, the oxide layers on titanium formed in sodium phosphate-based electrolytes (table, nos. 1–3) contain in all cases oxygen, titanium, and phosphorus, while in some cases they contain carbon. The oxide layers formed in the phosphate electrolyte containing in addition zinc fluoride or acetate contain zinc in a quantity of $\sim 2 \text{ at } \%$ and, on the other hand, somewhat larger quantity of phosphorus of smaller quantity of titanium.

The X-ray images of coatings formed in the phosphate electrolyte without addition of zinc salts contain intense peaks corresponding to the anatase modification of titanium oxide and insignificant reflections of its rutile modification (Fig. 1a). The coatings containing just the anatase titanium oxide modification are

formed in electrolytes with sodium phosphate and zinc fluoride or acetate (Figs. 1b, 1c).

Thus, in phosphate electrolytes as with as without zinc salts additives, oxide layers containing the anatase modification of titanium oxide and slightly differing in element composition are formed. Some difference in the morphology of the surface oxide layers formed in the phosphate electrolyte both without additives (Fig. 2a) and with addition of zinc fluoride (Fig. 2b) was established by the method of scanning electron microscopy. In both cases, anodic oxidation yields coatings of heterogeneous structures and porous surface, but the pore sizes are noticeably larger on the surface of oxide layers formed in the electrolyte with zinc fluoride additive.

Analysis of the experimental data showed that, under ultraviolet irradiation, these oxide layers manifested different photocatalytic activity in the reaction of degradation of Methylene Blue. The highest activity is characterized by oxide layers formed in the phosphate electrolyte without addition of zinc salts. The degree of decomposition of Methylene Blue in their presence reaches 32%. In phosphate electrolytes containing in addition zinc fluoride or acetate, oxide layers of lower activity are formed. In other words, embedding zinc into the composition of titanium oxide layers does not result in growth of the photocatalytic properties of oxide layers. In this case, lower photocatalytic activity of Zn-containing oxide layers can be the result of the decrease of the content of titanium (and, therefore, TiO_2) and the increase of the phosphorus content in coatings that is able to form photocatalytically inactive X-ray amorphous compounds with titanium oxide, as well as of the formation of inactive zinc phosphates or titanates or zinc concentrations not on the surface, but in the bulk, of the oxide layer. Moreover, the increase of the size of pores on the surface of oxide layers formed in the phosphate electrolyte with zinc fluoride addition and, as a result, the decrease of the accessible surface can also affect the decrease in the degree of Methylene Blue degradation.

Oxide layers consisting of TiO_2 in rutile and anatase modifications and containing, aside from titanium and oxygen, up to 0.5 at % S are formed in sulfuric-acid-based electrolytes (table, nos. 4, 5). Here, the addition of zinc acetate to such an electrolyte does not affect the composition of the formed layers, and zinc cannot be found in them. As was shown by photocatalytic tests, oxide layers formed in the electrolyte containing 0.1 mol/L H_2SO_4 manifested lower photocatalytic activity than those formed in the phosphate electrolyte. At the same time, addition of zinc acetate to the electrolyte containing H_2SO_4 results in some increase of the degree of Methylene Blue degradation. Possibly, here, in spite of the fact that zinc was not found in coatings, titanium oxide is doped by it, and the photocatalytic activity of oxide layers somewhat increases.

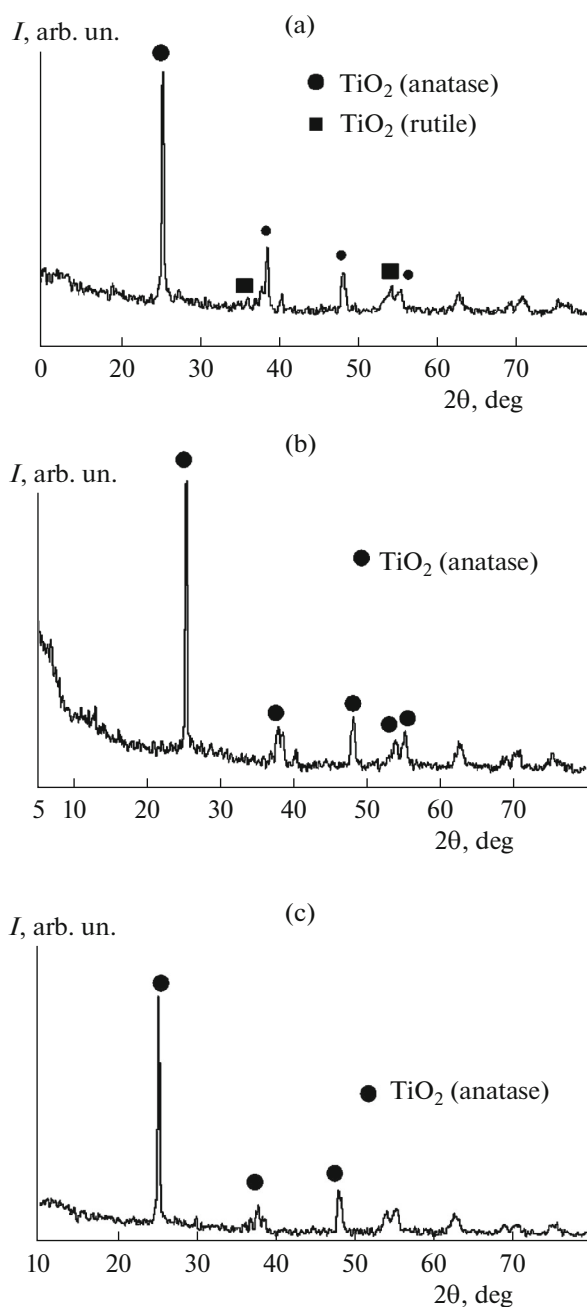


Fig. 1. X-ray images of oxide layers formed for 5 min in 0.1 M solution of Na_3PO_4 (a) without zinc salt addition and with addition of (b) 5 g/L ZnF_2 and (c) 5 g/L $\text{Zn}(\text{CH}_3\text{COO})_2$.

Oxide layers formed in the electrolyte with ZnSO_4 and EDTA ($\gamma^{\text{I-}}$) (table, no. 6) also contain rutile and anatase modifications of titanium oxide and do not contain zinc. The degree of Methylene Blue degradation in their presence is not high and does not exceed 19%.

The results of studies of degradation of Methylene Blue under UV radiation showed that the highest photocatalytic activity was manifested by oxide layers

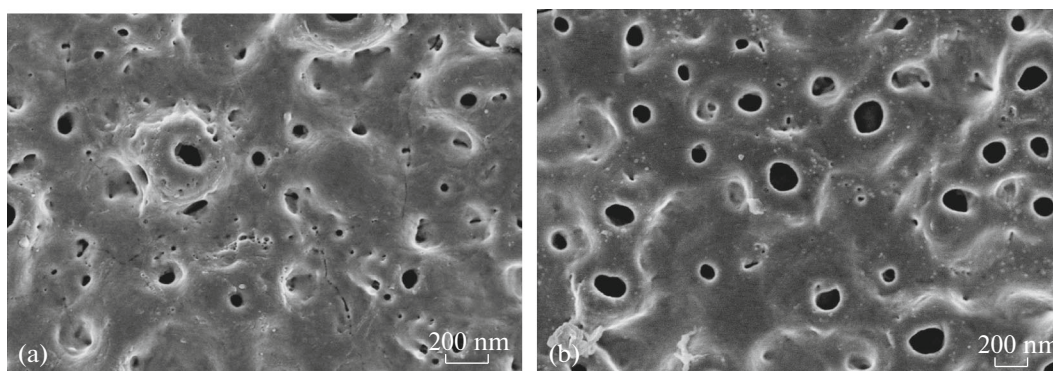


Fig. 2. SEM images of the surface of oxide layers formed for 5 min in 0.1 M solution of Na_3PO_4 (a) without additives and (b) with addition of 5 g/L ZnF_2 .

formed in the electrolyte containing cadmium sulfate. The degree of dye degradation with participation of such oxide layers attains 41%, which is noticeably higher than that for other layers under study.

According to the X-ray spectral-analysis data, the composition of oxide layers formed in the electrolyte containing cadmium sulfate includes—in addition to carbon, titanium, and oxygen—up to 0.5 at % of cadmium (table, no. 7). The X-ray image of the coating obtained in the electrolyte containing cadmium sulfate and shown in Fig. 3 allowed identification of the titanium oxide crystalline phase only in the rutile modification. No traces of metallic cadmium or any of its binary oxide compounds were detected.

One can assume that, at such a low concentration of cadmium, it dopes titanium dioxide, since chemical modification and formation of new crystalline compounds occur at higher metal concentrations.

CONCLUSIONS

Thus, it was established in the present work that, under UV irradiation, all the formed coatings dis-

played photocatalytic activity in the reaction of Methylene Blue degradation. Therefore, the studied sulfate and phosphate electrolytes are promising as bases for the development of other electrolytes in which photocatalytically active oxide layers on titanium may be obtained. The photocatalytic activity of oxide layers depends on their phase and element compositions and morphology, but, in some cases, samples differing in photocatalytic activity have virtually identical phase and element compositions.

In the series of phosphate electrolytes, the highest photocatalytic activity in the reaction of Methylene Blue degradation characterizes oxide layers formed in electrolytes containing just sodium phosphate. Zinc embedding into such layers does not increase, but, in opposite, somewhat decreases their photocatalytic activity, which can be caused both by the formation of inactive X-ray amorphous zinc and titanium phosphates and zinc concentrating in bulk layers rather than on the surface.

The highest photocatalytic activity in the reaction of Methylene Blue degradation is manifested by titanium oxide coatings doped with cadmium. Under the experimental conditions, the degree of Methylene Blue degradation with participation of Cd-containing coatings reaches 41%.

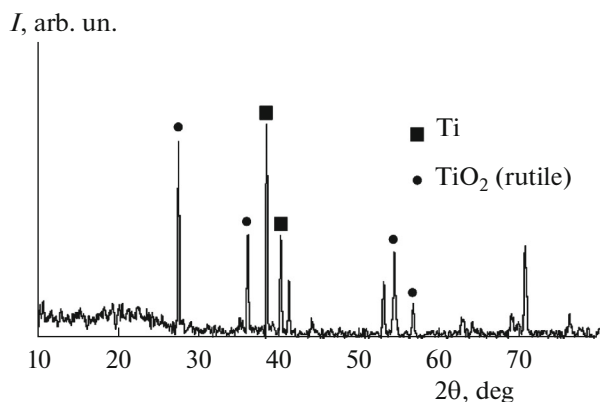


Fig. 3. X-ray image of the oxide layer formed in the electrolyte containing 0.1 M CdSO_4 .

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Translated by D. Marinin