

Research Article

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Characterization and photocatalytic activity of $\text{Ti}/\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ coatings for azo-dye degradation

Abstract: Anodic oxidation of VT1-0 titanium and E-125 zirconium alloy in aqueous electrolyte solutions based on H_2SO_4 and $\text{K}_4\text{P}_2\text{O}_7$ was used to obtain oxide coatings composed of Zr/ZrO_2 , Ti/TiO_2 , and mixed oxide systems $\text{Ti}/\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$. It was shown that, depending on the electrolyte pH, the films contained from 0.17 to 2.1% wt. of zirconium. The catalytic activity of the synthesized coatings in the oxidation reaction of the methyl orange azo dye under UV irradiation was established. The process rate constants and synergy factors for the mixed systems were calculated.

Keywords: $\text{Ti}/\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ coatings, Electrochemical anodization, Photocatalyst activity, Azo dyes, Methyl orange

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1 Introduction

The current position in development of nanotechnology makes it possible to synthesize materials with unique functional properties, among which a special position is held by the wide-band semiconductor titanium dioxide. Depending on its structure and dispersion degree, TiO_2 can be used for many applications ranging from fabrication of coloring agents, functional dielectric ceramics, gas sensors

to the most advanced applied direction – photocatalysis [1–4].

Photocatalytic processes provide solutions for problems such as decomposition of toxic organic and inorganic compounds in gaseous emissions and waste water, creation of nanophotonic devices, hydrogen production and intensification of the organic synthesis processes [5–7]. However, the practical use of pure TiO_2 is hindered due to its rather low activity of the photocatalyst in the visible spectrum. The effective way to increase the spectral sensitivity of the material is doping the semiconductor nanostructures with transition metal oxides in the quantity of 1–10% wt. [8–13].

The prospective systems include $\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ which has high catalytic activity in various chemical reactions [14–17]. At the same time, the techniques of the synthesis of powder and film systems based on titanium and zirconium oxides, like impregnation, chemical vapor deposition, chemical co-precipitation from solution and sol-gel technology require the use of organic precursors, considerable time and energy consumption [18–20]. Aside from that, the efficiency of the use of powder photocatalysts in liquid-phase processes is reduced due to the additional phase of the powder separation from suspension at the final stage. That is why synthesis of thin films and coatings of $\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ on various substrates seems to be the most expedient.

Among the entire variety of existing methods of obtaining of the film structures, the most interesting is anodic oxidation, which enables formation of the oxide layers with the thickness of several nanometers to hundreds microns on the surface of valve metals and alloys in one phase [21,22]. Adding salts, complexes or colloidal and fine solid particles with the required elements, e.g. zirconium, to an electrolyte composition enables preparation of mixed oxide coatings with different dopant content. In such cases the process of the electrolyte components introduction into the coatings depends on a great number of factors: the nature of the electrolyte, the dopant concentration in the solution, current density, treatment duration, carrier

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composition and material. Therefore, with varying the process parameters, one can obtain coatings with the uniform dopant distribution in the basic oxide (TiO_2) matrix, different porosity, high adhesion to the substrate, wear- and photocorrosion resistance.

This paper is dedicated to the synthesis of titanium dioxide coatings doped with zirconium oxide by anodic oxidation of titanium alloys, as well as the investigation of photocatalytic activity of the obtained systems in the model reaction of the methyl orange (MO) azo dye oxidation.

2 Experimental

Ti/TiO_2 and Zr/ZrO_2 coatings were formed by anodic oxidation of commercial grade VT1-0 titanium and E-125 zirconium alloy respectively using aqueous solutions of electrolytes based on 0.5 M of sulfuric acid and 1 M of potassium pyrophosphate. The composition of alloys is detailed in Table 1. To prepare mixed oxide systems made up of $\text{Ti/Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$, 10 g dm^{-3} of zirconium oxide (Sigma-Aldrich) analytically pure, reagent grade, was added to the electrolyte solutions.

Titanic plates with dimensions of 60x20x5 mm were polished, degreased in sodium carbonate solution, and then etched in the mixture of the fluorhydric and nitric acids (ratio 1:1), washed with distilled water up to pH 7 after each of the above operations. Finally, the samples were dried in air.

Oxidation was conducted in a standard electrochemical cell according to the two-electrode pattern: the working electrode – titanium alloy plates, the auxiliary electrode – a wire of X18N10T stainless steel. Anodic films $\text{Ti/Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ were formed under the galvanostatic conditions using a B5–50 DC power supply, with the current density $i = 0.5 \text{ A dm}^{-2}$ up to a voltage of 60 V; the treatment duration was 60 minutes. The electrolyte temperature did not exceed 25°C. The coated samples were washed with distilled water and dried in air, then annealed in a muffle furnace at a temperature of 450°C for 4 hours. Such annealing conditions enable conversion of the titanium (IV) oxide amorphous film to the crystalline anatase phase [23].

The described procedure was also used to form individual oxide systems – coatings with individual titanium and zirconium dioxide, which enabled comparative analysis of the properties of the materials obtained. The composition of electrolytes and coatings is shown in Table 2.

Table 1: The composition of titanium and zirconium substrate.

Alloy	VT1-0	E-125
Ti	99.2 – 99.7	–
Zr	–	97.3 – 97.6
Fe	< 0.25	–
C	< 0.07	–
Si	< 0.1	–
N	< 0.04	–
Nb	–	2.4 – 2.7
Impurities	0.3	0.01 – 0.1

Table 2: Composition of electrolytes and coatings.

Nº	Support material	Composition of electrolytes	Composition of coatings
1	VT1-0	H_2SO_4 – 0.5 M	Ti/TiO_2
2	VT1-0	$\text{K}_4\text{P}_2\text{O}_7$ – 1 M	Ti/TiO_2
3	E-125	H_2SO_4 – 0.5 M	Zr/ZrO_2
4	E-125	$\text{K}_4\text{P}_2\text{O}_7$ – 1 M	Zr/ZrO_2
5	VT1-0	H_2SO_4 – 0.5 M; ZrO_2 – 10 g dm^{-3}	$\text{Ti/Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$
6	VT1-0	$\text{K}_4\text{P}_2\text{O}_7$ – 1 M; ZrO_2 – 10 g dm^{-3}	$\text{Ti/Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$

The morphology and composition of the synthesized systems were investigated using a range of physical and chemical methods: scanning electron microscopy (SEM) using a high-resolution microscope “JSM 7500F” (JEOL, Japan), and energy-dispersive X-ray spectroscopy (EDS) using a spectrometer “INCA Penta FET-x3” (Oxford Instruments, Great Britain) with image recording in the secondary electron mode.

Photocatalytic properties of the coatings were tested in the model reaction of the MO azo dye oxidation. The test was conducted in a thermostated photocatalytic reactor at the temperature of 25°C and with continued agitation, the dye concentration was $2 \times 10^{-2} \text{ g dm}^{-3}$. The scheme of photocatalytic reactor is shown in Fig. 1.

The solution with the photocatalyst plates was illuminated with a mercury lamp, emitting soft ultraviolet

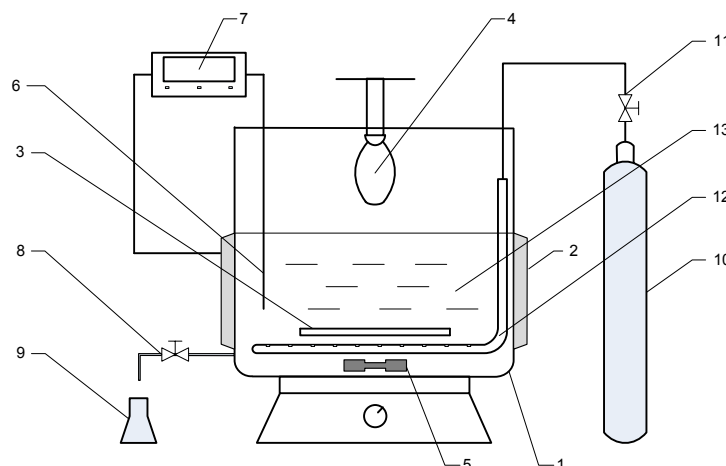


Figure 1: Schematic diagram of the photocatalytic reactor: 1 – photoreactor cowling; 2 – thermal shell; 3 – photocatalyst; 4 – UV irradiation source; 5 – magnetic stirrer; 6 – thermometer; 7 – temperature controller; 8 – sampler; 9 – vessel for test bleed; 10 – bottle with compressed air; 11 – gate for air input; 12 – bubbler; 13 – testing solution.

A. Prior to this, all solutions with the prepared catalysts were stored for 24 hours in the dark to establish the adsorption equilibrium. The MO dye content in the reactor was determined at regular intervals using the photocolormetric technique [24]. In parallel, the process of MO oxidation without ultraviolet was studied. The degree of the azo dye photodegradation on the oxide catalysts TiO_2 and ZrO_2 was assessed in a series of individual tests.

3 Results and Discussion

The analysis of the obtained $\text{Ti}/\text{Ti}_{n\text{O}_m} \bullet \text{Zr}_x\text{O}_y$ layers on VT1-0 alloy substrate demonstrates difference in composition and appearance of the surface film. It was found that the samples formed in the H_2SO_4 -based acid electrolyte (Fig. 2a) have a porous structure with the pore size of 50–100 nm and zirconium content in the surface layer ~ 2.1% wt. SEM measurements (Fig. 2b) of the $\text{Ti}/\text{Ti}_{n\text{O}_m} \bullet \text{Zr}_x\text{O}_y$ coating after the thermal treatment at 450°C for 4 hours showed crystal structures with size up to 2 μm on the alloy surface.

An order less zirconium (0.17% wt.) was included in the oxide layer from the alkaline electrolyte based on $\text{K}_4\text{P}_2\text{O}_7$. Crystallites with dimension only up to 1 μm were found on the surface (Fig. 3). It should be mentioned that shift of the solution pH to the alkaline region results in a decrease of the zirconium content in the films. According to [25], zirconium exists only as anionic species, e.g., $[\text{ZrO}(\text{SO}_4)_2]^{2-}$ in sulfuric acid solutions with $[\text{H}^+] = 0.05 - 2 \text{ M}$ and in the process of the electrolysis it

moves to the anode. However in the case of the solution pH in the range 4–11 zirconium exists as a cationic species which causes a low Zr content in the coating.

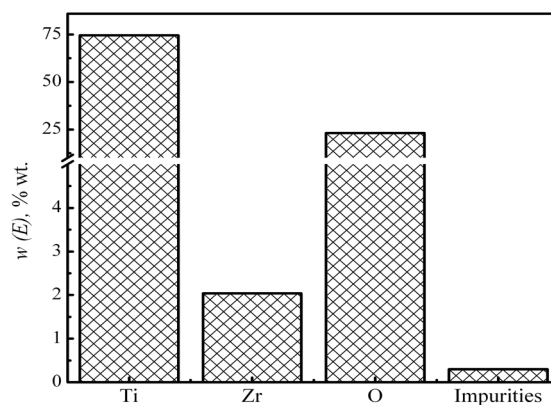
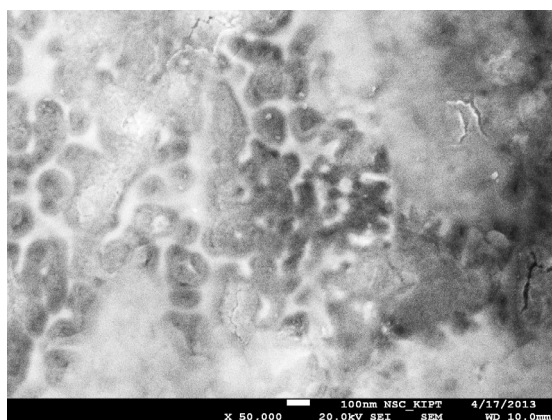
When the coatings are irradiated, the process of the catalyst photoexcitation begins due to formation of electrons (e^-) and holes (h^+), which either directly interact with the dye molecules, or initiate formation of radicals, possessing high reactive capacity. Either way the process of the MO degradation takes place causing the intensive discoloration of the solution (Fig. 4).

Tests of the photocatalytic activity showed that the MO oxidation under the UV irradiation on $\text{Ti}/\text{Ti}_{n\text{O}_m} \bullet \text{Zr}_x\text{O}_y$ coating, obtained from the sulfuric electrolyte, progressed at a higher rate and degradation degree compared to the individual oxide Ti/TiO_2 and Zr/ZrO_2 (Table 3). The mixed oxide compositions formed of $\text{K}_4\text{P}_2\text{O}_7$ showed the lower degree of the dye degradation which can be explained by the low dopant content. To determine the rate constant for the azo dye oxidation under UV irradiation, dependences of concentration changes of MO on time were plotted, where C_t is the MO concentration at a time t [g dm^{-3}] (Fig. 5).

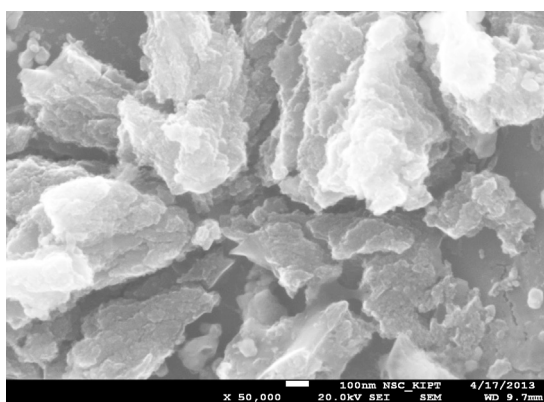
The character of concentration changes indicates that the MO photocatalytic oxidation is the pseudofirst order reaction and its rate w is given by:

$$w = -\frac{dC}{d\tau} = k_{\text{exp}} \cdot C_t \quad (1)$$

where k_{exp} – rate constant [min^{-1} ; C_t] – concentration of MO in the given time [g dm^{-3}].



(a)



(b)

Figure 2: The morphology and composition of coatings $\text{Ti}/\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ obtained from the sulfuric electrolyte: a) before and b) after thermal treatment $t = 450^\circ\text{C}$, 4 hours. Both photographs magnified 50000x.

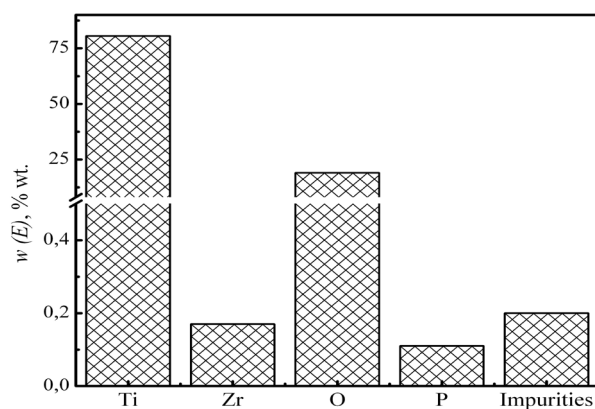
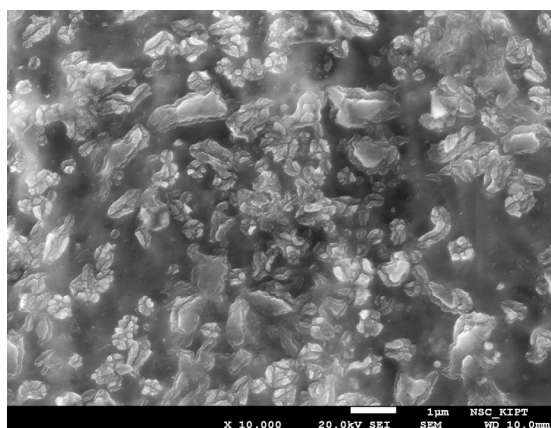


Figure 3: The morphology and composition of coatings $\text{Ti}/\text{Ti}_n\text{O}_m \bullet \text{Zr}_x\text{O}_y$ obtained from the alkaline electrolyte. Photograph magnified 10000x.

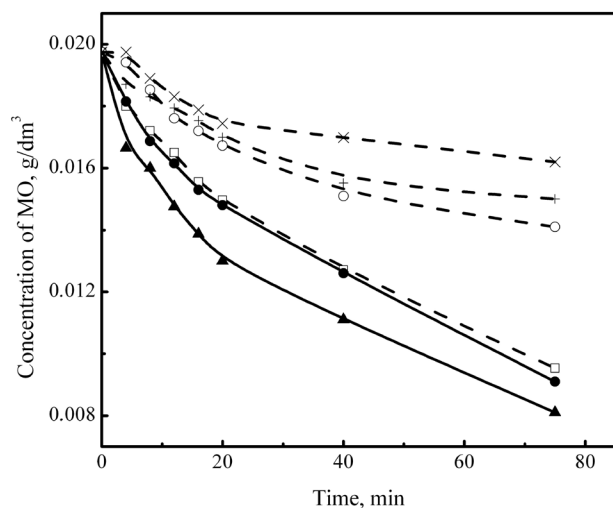


Figure 4: Photocatalytic destruction of MO under UV irradiation for coatings: 1 (o); 2 (□); 3 (+); 4 (x); 5 (▲); 6 (●). Conditions: $t = 25^{\circ}\text{C}$; $C_0 = 2 \times 10^{-2} \text{ g dm}^{-3}$, pH 7.

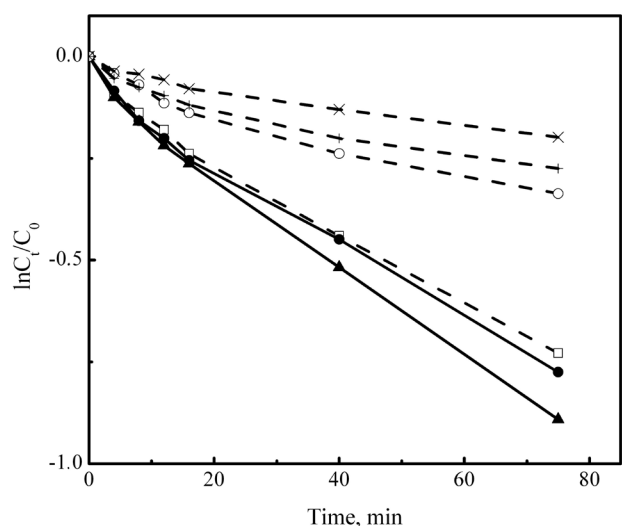


Figure 5: Pseudo first-order linear transforms $\ln C/C_0 = f(t)$ for coatings: 1 (o); 2 (□); 3 (+); 4 (x); 5 (▲); 6 (●). Conditions: $t = 25^{\circ}\text{C}$; $C_0 = 2 \times 10^{-2} \text{ g dm}^{-3}$, pH 7.

The values obtained make possible evaluation of the influence of TiO_2 doping with zirconium oxide on the photocatalytic oxidation rate through the synergy factor [26]:

$$R = \frac{k_{\exp(\text{Ti/Ti}_{n\text{O}_m}\cdot\text{Zr}_x\text{O}_y)}}{\% \text{Ti} \cdot k_{\exp(\text{Ti/TiO}_2)} + \% \text{Zr} \cdot k_{\exp(\text{Zr/ZrO}_2)}} \cdot 100\%, \quad (2)$$

where $k_{\exp(\text{Ti/Ti}_{n\text{O}_m}\cdot\text{Zr}_x\text{O}_y)}$, $k_{\exp(\text{Ti/TiO}_2)}$, $k_{\exp(\text{Zr/ZrO}_2)}$ – rate constant of MO photocatalytic oxidation for the $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$, Ti/TiO_2 , Zr/ZrO_2 coating, min^{-1} .

Table 3: Results of photocatalytic activity testing of different coatings.

Nº	MO degradation (%) after 75 min illumination	Rate constant, $k \times 10^{-2}, \text{min}^{-1}$	Synergy factor
1	28.61	0.88	–
2	51.75	1.39	–
3	24.05	0.80	–
4	18.00	0.66	–
5	59.00	1.69	1.924
6	53.92	1.45	1.044

The values of rate constants and synergy factor (Table 3) show that the mixed oxide systems $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ have higher catalytic activity as compared to individual oxide ones. The systems $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ are synergistic (for coatings obtained from H_2SO_4 $R = 1.924$, and for coatings obtained from $\text{K}_4\text{P}_2\text{O}_7$ $R = 1.044$).

It is also experimentally found that the catalyst system suffers no loss of activity for at least 6 cycles of operation.

4 Conclusions

Anodic oxidation of VT1-0 alloy in aqueous solutions of sulfuric and pyrophosphate electrolytes enables preparation of the mixed nanostructured oxide systems composed of $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ with the porous and microcrystalline surface structure and zirconium content up to 2% wt. It is established that the increase of the electrolyte pH area results in a considerable decrease of the zirconium content in the films.

It was shown that the surface of the Ti/TiO_2 , Zr/ZrO_2 and $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ after thermal treatment at 450°C for 4 hours possess photocatalytic activity in the reaction of methyl orange degradation when exposed to the UV-irradiation. Doped coatings $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$, formed in the sulfuric acid electrolyte have higher catalytic activity as compared to both individual oxides and $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ from $\text{K}_4\text{P}_2\text{O}_7$ solution.

It was also established that the methyl orange photooxidation on the synthesized coatings is the pseudo first-order reaction. The coatings $\text{Ti/Ti}_{n\text{O}_m} \cdot \text{Zr}_x\text{O}_y$ are synergistic, the synergy factors for oxide systems formed in H_2SO_4 and $\text{K}_4\text{P}_2\text{O}_7$ are 1.924 and 1.044, respectively, as resulted from the calculations.

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