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Characterization and photocatalytic activity of Ti/$Ti_nO_m \cdot Zr_xO_y$ coatings for azo-dye degradation

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Anodic oxidation of VT1-0 titanium and E-125 zirconium alloy in aqueous electrolyte solutions based on H_2SO_4 and $K_4P_2O_7$ was used to obtain oxide coatings composed of Zr/ZrO_2, Ti/TiO_2, and mixed oxide systems Ti/$Ti_nO_m \cdot Zr_xO_y$. It was shown that, depending on the electrolyte pH, the films contain up 0.17 to 2.1 % wt. of zirconium. Catalytic activity of the synthesized coatings in the oxidation reaction of methyl orange azo dye under UV irradiation was established. The process rate constants and synergy factors for the mixed systems were calculated.

Анодным оксидированием сплава титана марки ВТ1-0 и циркония марки Э-125 в водных растворах электролитов H_2SO_4 и $K_4P_2O_7$ получены монооксидные покрытия состава Zr/ZrO_2, Ti/TiO_2, а также смешанные оксидные системы Ti/$Ti_nO_m \cdot Zr_xO_y$. Показано, что в зависимости от pH электролита, пленки содержат от 0,17 до 2,1 масс. %. циркония. Установлена каталитическая активность синтезированных покрытий в реакции окисления азокрасителя метилового оранжевого под действием УФ-облучения, определены константы скорости процесса и факторы синергизма для смешанных систем.

Характеристика та фотокаталітична активність покриттів Ti/$Ti_nO_m \cdot Zr_xO_y$ для деструкції азобарвників. *М.Д.Сахненко, М.В.Ведь, В.В.Биканова.*

Анодним оксидуванням сплаву титану марки ВТ1-0 та цирконію Е-125 у водних розчинах електролітів H_2SO_4 та $K_4P_2O_7$ одержано монооксидні покриття складу Zr/ZrO_2, Ti/TiO_2, а також змішані оксидні системи Ti/$Ti_nO_m \cdot Zr_xO_y$. Показано, що в залежності від pH електроліту, плівки містять від 0,17 до 2,1 мас. % цирконію. Встановлено каталітичну активність синтезованих покриттів у реакції окиснення азобарвника метилового жовтогарячого під дією УФ-випромінювання, встановлено константи швидкості процесу та фактори синергізму для змішаних систем.

1. Introduction

The present-day stage of nanotechnologies development 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 *t* TiO_2 usable range extends from fabrication of coloring agents, functional dielectric ceramics, gas sensors to the most advanced applied direction — photocatalysis [1–4].

Photocatalytic processes enable solving such problems 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 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 $Ti/Ti_nO_m \cdot Zr_xO_y$, having 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 coprecipitation from solution, sol-gel technology require the use of organic precursors, considerable time and energy consumption [18–20]. Aside from that, an 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 the method of synthesis of thin films and coatings of $Ti/Ti_nO_m \cdot Zr_xO_y$ on various substrates seems to be the most expedient.

Among the entire variety of existing methods of the film structures obtaining, of great interest is anodic oxidation enabling formation of 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 required elements, e.g., zirconium, to an electrolyte composition enables preparation of mixed oxide coatings with different dopant content. The process of the electrolyte components introduction into the coatings in such case depends on a great number of factors: the background electrolyte nature, the dopant concentration in the solution, current density, treatment duration, carrier composition and material etc. Therefore, 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 synthesis of titanium dioxide coatings doped with zirconium oxide by anodic oxidation of titanium alloys, as well as to investigation of photocatalytic activity of the obtained systems in the model reaction of methyl orange (MO) azo dye oxidization.

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, from 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 $Ti/Ti_nO_m \cdot Zr_xO_y$, 10 g/dm^3 of zirconium oxide (Sigma-Aldrich) analytically pure, reagent grade, was additionally added to the electrolyte solutions.

Table 1. Composition of titanium and zirconium substrate

Alloy	VT1-0	E-125
Ti	99.2–99.7	–
Fe	<0.25	–
C	<0.07	–
Si	<0.1	–
N	<0.04	–
O	<0.2	–
Nb	–	2.4–2.7
Impurities	0.3	–

Titanic plates with dimensions of 60×20×5 mm^3 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 $Ti/Ti_nO_m \cdot Zr_xO_y$ were formed under the galvanostatic conditions using a B5-50 dc power supply, with the current density $i = 0.5$ A/dm^2 up to the voltage of 60 V; the treatment duration was 60 min. 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 temperature of 450°C during 4 h. Such annealing conditions enable conversion of titanium (IV) oxide amorphous film to the crystalline anatase phase [23].

The procedure as set forth 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.

The morphology and composition of the synthesized systems were investigated using complex of physical and chemical methods: scanning electron microscopy (SEM) using a

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	$K_4P_2O_7$ — 1 M	Ti/TiO_2
3	E-125	H_2SO_4 — 0.5 M	Zr/ZrO_2
4	E-125	$K_4P_2O_7$ — 1 M	Zr/ZrO_2
5	VT1-0	H_2SO_4 — 0.5 M; ZrO_2 — 10/dm^3	$Ti/Ti_nO_m{\cdot}Zr_xO_y$
6	VT1-0	$K_4P_2O_7$ — 1 M; ZrO_2 — 10/dm^3	$Ti/Ti_nO_m{\cdot}Zr_xO_y$

high-resolution microscope "JSM 7500F" (JEOL, Japan), and energy-dispersive X-ray spectroscopy (ERS) using a spectrometer "INCA Penta FET-x3" (Oxford Instruments, Great Britain) with image recording in the second electrons 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 $2{\cdot}10^{-2}$ 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 A. Prior to this, all solutions with the prepared catalysts were kept within 24 hours in dark to establish the adsorption equilibrium. The MO dye content in the reactor was determined at regular intervals using the photocolorimetric 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.

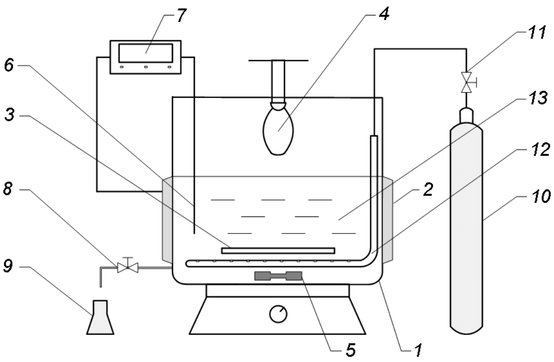
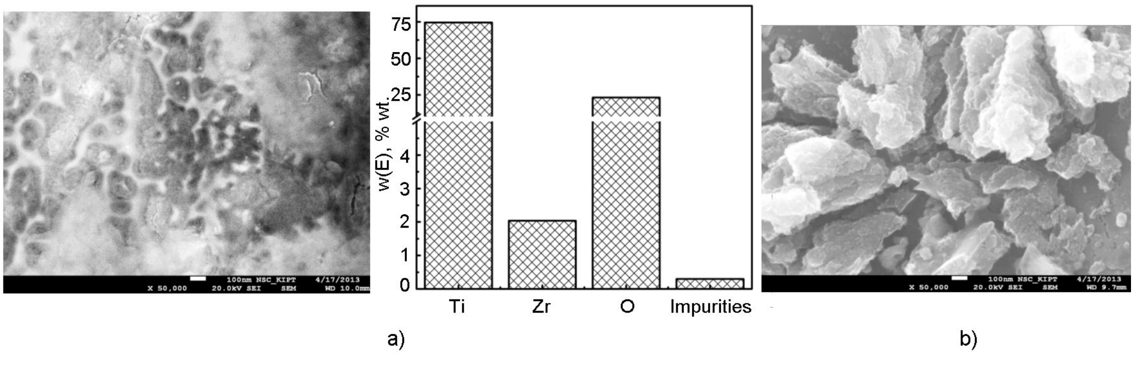


Fig. 1. Schematic diagram of the photocatalytic reactor: *1* — photoreactor cowling; *2* — thermal shell; *3* — photocatalyst; *4* — UV irradiation source; *5* — magnetic stirred; *6* — thermometer; *7* — thermocontroller; *8* — sampler; *9* — vessel for test bleed; *10* — bottle with compressed air;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

3. Results and discussion

Analysis of morphology and composition of the prepared materials $Ti/Ti_nO_m{\cdot}Zr_xO_y$ on VT1-0 alloy demonstrates the different composition and texture of the film surface. It was found that the samples, formed in H_2SO_4-based acid electrolyte (Fig. 2, a), have a porous structure with the pore size of 50...100 nm and zirconium content in the surface layer ~ 2.1 wt.%. The findings of the SEM of the coating $Ti/Ti_nO_m{\cdot}Zr_xO_y$ after the thermal treatment at 450°C during 4 h (Fig. 2, b) up to 2 μm on the alloy surface.

An order less zirconium (0.17 wt. %) is included in the oxide layer from the alkaline electrolyte based on $K_4P_2O_7$, and the surface is covered with crystallites with dimension of up to 1 μm (Fig. 3). It should be



a)

b)

Fig. 2. Morphology and composition of coatings $Ti/Ti_nO_m{\cdot}Zr_xO_y$ obtained from the sulfuric electrolyte before (×50000, *a*) and after (×50000, *b*) thermal treatment t = 450°C, 4 h.

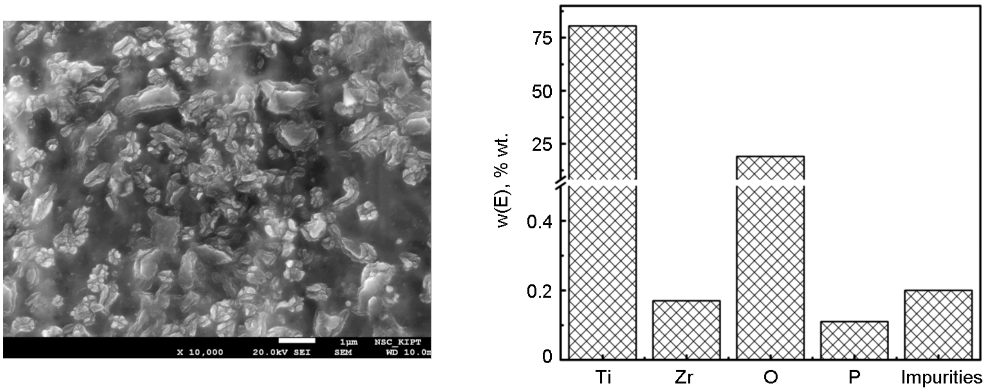


Fig. 3. Morphology and composition of coatings $Ti/Ti_nO_m{\cdot}Zr_xO_y$ (×10000) obtained from the alkaline electrolyte.

Table 3. Results of photocatalytic activity testing of different coatings

No	MO degradation (%) after 75 min illumination	Rate constant, $k{\cdot}10^{-2}$, 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	1.01
6	53.92	1.45	0.71

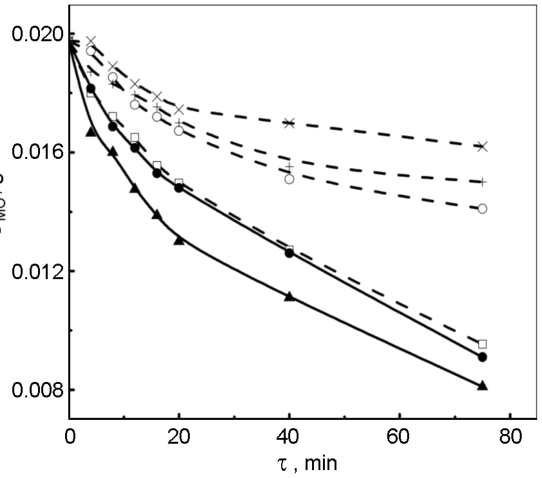


Fig. 4. Photocatalytic destruction of MO under UV irradiation for coatings: *1* (○); *2* (□); *3* (+); *4* (×); *5* (▲); *6* (●). Conditions: t = 25°C; $C_0 = 2{\cdot}10^{-2}$ g/dm^3, pH 7.

mentioned that pH shift to the alkaline region results not only in reduction of zirconium content in the films, but in growth of the titanium content. Such behavior is explained by acidic nature of zirconium and titanium oxides, whose chemical stability in the alkaline medium is reduced. The low content of impurities in the coatings can be explained by the high purity of VT1-0 alloy.

When the coatings are irradiated, process of the catalyst photoexcitation due to formation of electrons e^- and holes h^+, which either directly interact with the dyer molecules, or initiate formation of radicals $OH^\bullet$, possessing high reactive capacity. Therefore, the process of MO degradation with the intensive discoloration of the solution take place (Fig. 4).

Testing the photocatalytic activity showed that MO oxidation under action of UV irradiation on $Ti/Ti_nO_m{\cdot}Zr_xO_y$ coating, obtained from the sulfuric electrolyte, progressed at a higher rate and degradation degree as compared to the individual oxide Ti/TiO_2 and Zr/ZrO_2 (Table 3). The mixed oxide compositions, formed of $K_4P_2O_7$, showed the lower degree of the dye degradation, which can be explained by the low dopant content. To determine the rate constants for the azo dye oxidation under UV irradiation, dependences of $\ln C_t/C_0$ on time were plotted, where C_t is the MO concentration at a time φ (Fig. 5).

The character of dependences indicates that the MO photocatalytic oxidation is the first order reaction, and its rate w is given by the expression:

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

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

The values obtained make possible evaluation of influence of TiO_2 doping with zirconium oxide on the photocatalytic oxidation rate through the synergy factor [25]:

$$R = \frac{w_{\exp(Ti/Ti_nO_m \cdot Zr_xO_y)}}{w_{\exp(Ti/TiO_2)} + w_{\exp(Zr/ZrO_2)}}, \quad (2)$$

where $w_{\exp(Ti/Ti_nO_m \cdot Zr_xO_y)}$ — rate of MO photocatalytic oxidation for the $Ti/Ti_nO_m{\cdot}Zr_xO_y$ coating, min^{-1}; $w_{\exp(Ti/TiO_2)}$ — rate of MO photocatalytic oxidation for the Ti/TiO_2 coating, min^{-1}; $w_{\exp(Zr/ZrO_2)}$ — rate of MO photocatalytic oxidation for the Zr/ZrO_2 coating, min^{-1}.

The values of rate constants and synergy factor (Table 3) show that the mixed oxide systems $Ti/Ti_nO_m{\cdot}Zr_xO_y$ have higher catalytic activity as compared to individual oxide ones.

However, it should be mentioned that systems $Ti/Ti_nO_m{\cdot}Zr_xO_y$ are not synergistic (for coatings obtained from H_2SO_4 $R = 1.01$, and for coatings obtained from $K_4P_2O_7$ $R = 0.71$), they rather bear an additive character, which reflects the contribution of individual oxides, proportional to the content in the mixed oxide system.

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 $Ti/Ti_nO_m{\cdot}Zr_xO_y$ with the porous and micro-crystalline surface structure and zirconium content of up to 2 wt. %. It is established that increase of the electrolyte pH area results in a considerable reduction of zirconium content in the films. It is shown that the contact masses of Ti/TiO_2, Zr/ZrO_2 and $Ti/Ti_nO_m{\cdot}Zr_xO_y$ after thermal treatment at 450°C during 4 hours possess the photocatalytic reactivity in the reaction of methyl orange degradation when exposed to UV-irradiation, moreover, the mixed coatings $Ti/Ti_nO_m{\cdot}Zr_xO_y$, formed of the sulfuric acid electrolyte have higher catalytic reactivity as compared to both individual oxides and $Ti/Ti_nO_m{\cdot}Zr_xO_y$ of $K_4P_2O_7$. It is established that methyl orange photooxidation on the synthesized coatings is the first-order reaction, and the system $Ti/Ti_nO_m{\cdot}Zr_xO_y$, formed of H_2SO_4 has the highest value of the synergy factor $R = 1.01$ as related to the coatings of the individual titanium dioxide and zirconium oxide. The obtained data can be used for wastewater purification of the organic aromatic compounds.

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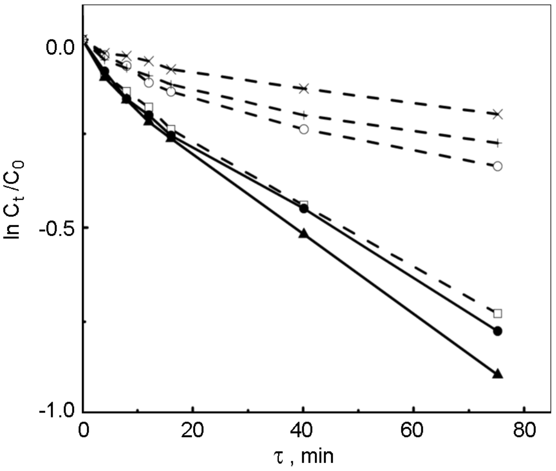

Fig. 5. First-order linear transforms $\ln C/C_0 = f(\varphi)$ for coatings: *1* (○); *2* (□); *3* (+); *4* (×); *5* (▲); *6* (●). Conditions: t = 25°C; $C_0 = 2{\cdot}10^{-2}$ g/dm^3, pH 7.

References

1. L.Zhao, Y.Liu, L.Wang, H.Zhao, *Indust.Eng. Chem.Res.*, **53**, 70 (2014).
2. S.Marinel, D.H.Choi, R.Heuguet, D.Agrawal, *Ceram. Intern.*, **39**, 299 (2013).
3. J.Nisar, Z.Topalian, A.De Sarkar, L.Osterlund, *ACS Appl.Mater.Interf.*, **5**, 8516 (2013).
4. M.Fujishima, Q.Jin, H.Yamamoto, H.Tada, *Phys.Chem.Chem.Phys.*, **14**, 705 (2012).
5. M.Klare, G.Waldner, R.Bauer, H.Jacobs, *Chemosph.*, **38**, 2013 (1999).
6. J.Kim, D.Monllor-Satoca, W.Choi, *En.Environ.Sci.*, **5**, 7647 (2012).
7. Y.Shen, C.S.Friend, Y.Jiang, D.Jakubczyk, *J. Phys.Chem.B*, **104**, 7577 (2000).
8. S.Chai, G.Zhao, P.Li, Y.Lei, *J.Phys.Chem.C*, **115**, 18261 (2011).
9. Z.Zhang, Y.Yuan, Y.Fang, L.Liang, *Talanta*, **73**, 523 (2007).
10. E.Garcia-Ramirez, M.Mondragon-Chaparro, O.Zelaya-Angel, *Appl.Phys.A: Mater. Sci. Proc.*, **108**, 291 (2012).
11. J.Zhu, D.Yang, J.Geng, D.Chen, *J.Nanopart. Res.*, **10**, 729 (2008).
12. M.R.Bayati, F.Golestani-Fard, A.Z.Moshfegh, *Catal.Lett.*, **134**, 162 (2010).
13. M.Hirano, K.Ota, *J.Amer.Ceram.Soc.*, **87**, 1567 (2004).
14. Q.Luo, Q.Cai, X.Li, Z.Pan, *Trans..Nonfer. Metals Soc.China*, **23**, 2945 (2013).
15. K.Maver, U.L.Stangar, U.Cernigoj et al., *J. Photochem.Photobiol.*, **8**, 657 (2009).
16. Yu.I.Gnatyuk, V.I.Yatskiv, N.P.Smirnova, V.M.Granchak, *Theor.Exper.Chem.*, **41**, 371 (2005).

17. H.Liu, G.Liu, Q.Zhou, *J.Solid State Chem.*, **182**, 3238 (2009).
18. S.Qiu, T.L.Starr, *J.Electrochem.Soc.*, **154**, 472 (2007).
19. M.D.Hernandez-Alonso, I.Tejedor-Tejedor, J.M.Coronado, *Thin Solid Films*, **502**, 125 (2006).
20. A.A.Ismail, D.W.Bahnemann, *J.Mater.Chem.*, **21**, 11686 (2011).
21. J.L.Zhao, X.H.Wang, R.Z.Chen, L.T.Li, *Solid State Commun.*, **134**, 705 (2005).
22. J.M.Macak, L.V.Taveira, H.Tsuchiya, K.Sirotna, *J.Electroceram.*, **16**, 29 (2006).
23. D.A.Buldakov, D.I.Petyhov, I.V.Kolesnic, *Rossiisk.Nanotech.*, **4**, 78 (2009).
24. A.B.Isaev, G.A.Magomedova, N.A.Zakargaeva, *Kinet.Catal.*, **52**, 204 (2011).
25. C.G.Silva, Synthesis, Spectroscopy and Characterization of Titanium Dioxide Based Photocatalysts for the Degradative Oxidation of Organic Pollutants, Universidade do Porto, Spain (2008).