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SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF $Ti/Ti_nO_m \cdot Zr_xO_y$ COATINGS FOR AZO-DYE DEGRADATION

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Anodic oxidation of BT1-0 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 $Ti/Ti_nO_m \cdot Zr_xO_y$ with synergetic effect. It was established mixed oxide materials contain from 0.17 up 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 shown. The process rate constants and synergy factors for the mixed systems were calculated.

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, the TiO_2 usable range extends from fabrication of coloring agents, functional dielectric ceramics, gas sensors to the most advanced applied direction – photocatalysis [1]. The prospective systems include $Ti_nO_m \cdot Zr_xO_y$ has high catalytic activity in various chemical reactions [2]. 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. That is why synthesis of thin films and coatings of $Ti_nO_m \cdot Zr_xO_y$ 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 the anodic oxidation, which enabling 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. 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. This paper is dedicated to the 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 the methyl orange (MO) azo-dye oxidization.

Experiment

Ti/TiO_2 and Zr/ZrO_2 coatings were formed by anodic oxidation of commercial grade BT1-0 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. 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 added to the electrolyte solutions. 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 minutes. The composition of electrolytes and coatings is shown in Table 1.

Table 1. Composition of electrolytes and coatings

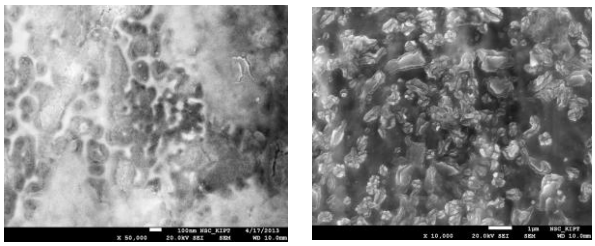
№	Support material	Composition of electrolytes	Composition of coatings
1	BT1-0	H_2SO_4 – 0.5 M	Ti/TiO_2
2	BT1-0	$K_4P_2O_7$ – 1 M	Ti/TiO_2
3	E-125	H_2SO_4 – 0.5 M	Zr/ZrO_2
4	E-125	$K_4P_2O_7$ – 1 M	Zr/ZrO_2
5	BT1-0	H_2SO_4 – 0.5 M; ZrO_2 – 10/dm^3	$Ti/Ti_nO_m \cdot Zr_xO_y$
6	BT1-0	$K_4P_2O_7$ – 1 M; ZrO_2 – 10/dm^3	$Ti/Ti_nO_m \cdot Zr_xO_y$

The morphology and composition of the synthesized systems were investigated using a complex 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 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.

Results and Discussion

The analysis of the obtained $Ti/Ti_nO_m \cdot Zr_xO_y$ layers on BT1-0 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 (Figure 1, a) have a porous structure with the pore size of 50–100 nm and zirconium content in the surface layer ~ 2.1% wt. SEM measurements of the $Ti/Ti_nO_m \cdot Zr_xO_y$ coating after the thermal treatment at 450ºC for 4 h showed crystal structures with size up 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 $K_4P_2O_7$. Crystallites with dimension only up to 1 μm were found on the surface (Figure 1, b). It should be mentioned that shift of the solution pH to the alkaline region results in decreasing of the zirconium content in the films. According to [3], zirconium exists only as anionic species, e.g., $[ZrO(SO_4)_2]^{2-}$ in sulfuric acid solutions with $[H^+]$ = 0.05-2 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.



a *b*

Fig. 1. The morphology of coatings $Ti/Ti_nO_m \cdot Zr_xO_y$ obtained from the sulfuric (50000, a) and alkaline electrolyte (50000, b).

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 constant for the azo-dye oxidation under UV irradiation, dependences of on time were plotted, where C_t is the MO concentration at a time t, g/dm^3 (Figure 2).

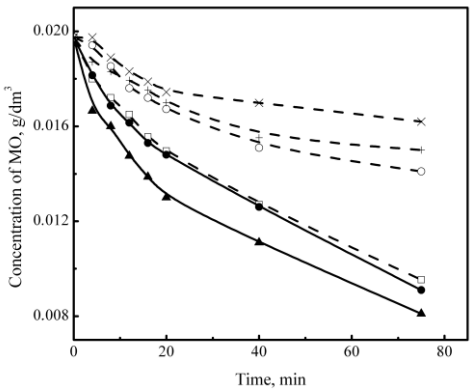


Fig. 2. Photocatalytic destruction of MO under UV irradiation for coatings: 1 (o); 2 (□); 3 (+); 4 (x); 5 (▲); 6 (●). Conditions: t = 25 °C; $C_0 = 2 \cdot 10^{-2}$ g/dm3, pH 7.

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 up to 2% wt. Dopped coatings $Ti/Ti_nO_m \cdot Zr_xO_y$, formed in the sulfuric acid electrolyte have higher catalytic activity as compared to both individual oxides and $Ti/Ti_nO_m \cdot Zr_xO_y$ from $K_4P_2O_7$ solution. It is established that the methyl orange photooxidation on the synthesized coatings is the pseudofirst-order reaction. It is calculated that the coatings $Ti/Ti_nO_m \cdot Zr_xO_y$ are synergetic, the synergy factors for oxide systems formed in H_2SO_4 and $K_4P_2O_7$ are 1.924 and 1.044, respectively.

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СИНТЕЗ ТА ФОТОКАТАЛІТИЧНА АКТИВНІСТЬ ПОКРИВІВ $Ti/Ti_nO_m \cdot Zr_xO_y$ ДЛЯ ЗНЕШКОДЖЕННЯ АЗОБАРВНИКІВ

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Анодним оксидуванням сплаву титану марки ВТ1-0 та цирконію марки Е-125 у водних розчинах електролітів H_2SO_4 й $K_4P_2O_7$ одержано оксидні покриви складу Zr/ZrO_2, Ti/TiO_2, а також змішані оксидні системи $Ti/Ti_nO_m \cdot Zr_xO_y$ з синергетичним ефектом. Встановлено, що змішані оксидні матеріали містять від 0,17 до 2,1% мас. цирконію. Визначено каталітичну активність синтезованих покривів у реакції окиснення азобарвника метилового жовтогарячого під дією УФ-випромінювання, визначені константи швидкості процесу та фактори синергізму для змішаних систем.

Ключові слова: азосполуки, електрохімічне анодування, покриви $Ti/Ti_nO_m \cdot Zr_xO_y$, синергізм, фотокаталітична активність.