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**HETEROOXIDE COMPOSITES FOR PHOTOCATALYTIC  
DISINTEGRATION OF TOXICANTS: SYNTHESIS AND APPLICATION**

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**Abstract.** The processes of plasma electrolyte formation of heteroxide coatings on titanium alloys as photocatalytic materials for the decomposition of natural and man-made toxicants have been studied. The coatings were synthesized from aqueous solutions of diphosphate with the addition of dopant metal salts. The surface of  $\text{TiO}_2$  coating is characterized by toroidal mesostructures, and multicomponent compositions have a more developed surface, which has a positive effect on their functional properties, as well as subsequent heat treatment. The photocatalytic properties of the coatings were tested in a model oxidation reaction of the methyl orange azo dye. Among the studied coatings  $\text{TiO}_2 \cdot \text{ZnO}$  is the most catalytically active one.

**Keywords:** plasma-electrolytic oxidation, titanium alloys, photocatalyst, heteroxide coatings, surface morphology.

**Introductions.** The solution to many scientific, technical and environmental problems of today can be implemented with the wide implementation of highly effective methods of transformation of chemical substances - nanosynthesis, nanocatalysis, etc. The chain of such technologies fully includes reagent-free methods of neutralizing toxicants of natural and man-made origin, a clear manifestation of the need for their use is not only significant volumes of solid waste, but also significant pollution of air and water pools with toxicants of various nature. Under such conditions, the problem of ensuring the functioning of vital facilities and mobile means of military and civilian purposes, especially in the areas of military operations, by neutralizing man-made pollution caused by the leakage of toxic substances from destroyed infrastructure facilities, reducing toxic emissions from transport engines, becomes a number of urgent issues. etc. Among the reagentless methods, the methods of heterogeneous catalysis, especially photocatalysis, occupy a prominent place. Photocatalysis belongs to the processes of acceleration of chemical reactions (oxidation or reduction), caused by the activation of a catalyst, usually a metal oxide, by ultraviolet or visible radiation [1].

Recently, it has become a fairly common method for cleaning water and air from organic, and in some cases, inorganic compounds. Semiconductor materials such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{WO}_3$  are primarily considered as photocatalysts, including modified with various elements both in volume and on the surface, and composites based on them [2]. Among the above photocatalysts, titanium (IV) oxide ( $\text{TiO}_2$ ) is the most attractive due to its chemical inertness, high corrosion resistance and non-toxicity. Creation of a catalyst based on titanium (IV) oxide with increased efficiency is an important scientific and practical task, the solution of which involves determining the conditions for the synthesis of a material with a highly developed surface, a reduced band gap, and an increased resource under operational conditions. A comprehensive solution to this problem can be seen in the development of the scientific basis for the controlled synthesis of coatings with heterooxide and/or doped oxides of titanium (IV) on the surface of metal carriers, with the dominant use of

titanium alloys as carriers, in particular porous ones, using electrochemical technologies.

**Materials and methods.** Titanium (IV) oxide coatings and heterooxide compositions were synthesized by plasma-electrolytic oxidation (PEO) on VT1-0 titanium alloys [3] from aqueous diphosphate solutions. PEO was carried out at  $i=4.0 \text{ A/dm}^2$  and the formation voltage  $U \geq 150 \text{ V}$  for 30 min. Heat treatment of the samples was carried out at  $500^\circ\text{C}$  for 20 minutes. The photocatalytic properties of the coatings were tested in a model oxidation reaction of the methyl orange (MO) azo dye. The research was carried out in a thermostated photocatalytic reactor at a temperature of  $25^\circ\text{C}$  and continuous stirring.

**Results and discussion.** It was established that uniform binary and ternary heterooxide coatings ( $\text{TiO}_2 \cdot \text{MO}_x$ , where M is W, Mo, Zr, Zn, Cu, etc) were synthesized on titanium samples by plasma-electrolytic oxidation in diphosphate electrolytes with the addition of dopant metal salts (oxides of d-elements) with high adhesion to the carrier metal and a developed surface. The process took place in the regime of thermal/electrical breakdown of the oxide layer of the coating, where the temperature in the reaction zone reached  $2000^\circ\text{C}$ . The presence of compounds of d-elements in the electrolyte ensured the incorporation of metal oxides into the composition of the coating, thereby causing an increase in the specific surface area of the depositions, which, a priori, favorably changed their photocatalytic activity.

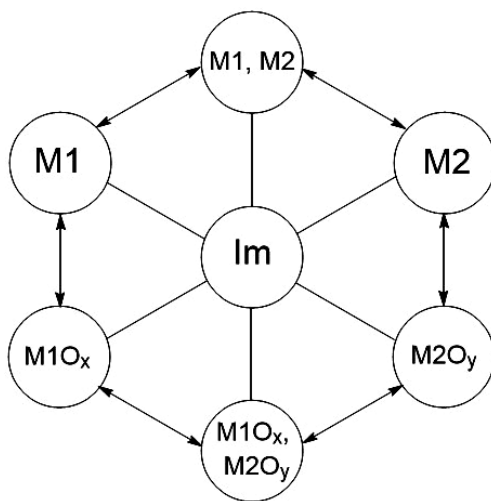
In the process of synthesis of heterooxide composites (HOC) in PEO regimes, it was established that the voltage of formation of HOC changed in a rather wide interval, due to the difference in the specific electrical resistance of the oxides of dopant metals, which were incorporated into the composition of the heterooxide matrix [4].

An important methodological aspect of our work was the search for an adequate description and organization of the synthesis processes of metal oxide composites, including HOC, using electrochemical technologies. The reason was that such HOC can be obtained, firstly, by varying the composition and ratio of components in electrolyte solutions, and, secondly, by using certain electrolysis

modes, which could significantly increase the stability of electrolytes and did not require the involvement of additional equipment for the implementation of processes in the case of colloidal solutions, hydrosols, etc.

We developed such a methodological approach for binary systems [5], the formation of which can occur due to oxidation, in particular PEO, cathodic or electrophoretic deposition, electrokinetic and other processes of an electrochemical nature, the course of which led to the formation of a metal oxide composite matrix. Under such conditions of the formation of HOC, the terms "matrix" and "second phase" were transformed, which led to their inversion (Fig. 1).

The intensities of the transitions between the individual vertices of the graph in Fig. 1 there are electrochemical reactions, the rates of which are determined by a significant number of factors. Among them are the nature, composition and ratio of electrolyte components, the nature of polarization (anode, cathode, reversible), electrolysis mode (stationary, non-stationary, pulsed, programmable, etc.), as well as its amplitude and time parameters [6].



**Fig. 1. Graph for states of bimetallic metal oxide system**

An important element of the graph of states is the element **Im** - which unites the set of the intermediates of reactions that take place in the studied systems with the formation of HOC. It is the combination of these and a significant number of other factors ultimately determine not only the composition of the consolidated material or coating, but also its structure and morphology, the degree of localization of individual phases, their distribution by material thickness, and finally properties and areas of

application. It is clear that for the formalization of polymetallic, in particular ternary systems, as noted in [7], visualization in this way is difficult to do, here will be useful scientific work of physical chemistry on the topological description of multicomponent silicate systems.

The scheme shown in Fig. 1 has a deep philosophical connotation, as it represents some physico-chemical “avatar”, as the embodiment of the relationship and interdependence of processes with their internal content and the beauty of external manifestation.

We paid special attention to the creation of HOCs, in which the oxide component was formed in the process of electrolysis, which did not require the introduction of phase oxides into the composition of electrolytes, which significantly increased the stability of solutions, and therefore simplified technological processes [8].

As a result of the studies of HOC, samples with a varied composition of titanium-based oxide matrices were obtained. According to the data of X-ray phase analysis, the obtained metal-oxide coatings consist of an amorphous matrix with the inclusion of crystalline phases of oxides of variable composition, in particular: CuO, Cu<sub>2</sub>O, ZnO, CoO, Co<sub>2</sub>O<sub>3</sub> and others. It was found that the photocatalytic properties depend on the electrolysis mode and electrolyte composition. Thus, two-component oxide matrices – TiO<sub>2</sub>·CuO and TiO<sub>2</sub>·CoO have a fairly uniform surface morphology and high adhesion to the substrate. In the case of the formation of a three-component oxide system, the surface morphology changes and acquires a mesoglobular character.

Comparison of the photocatalytic activity of the samples in the reactions of decomposition of the MO azo dye showed that the highest index was recorded in zinc-containing systems - binary Ti<sub>n</sub>O<sub>m</sub>·Zn<sub>x</sub>O<sub>y</sub> and ternary Ti<sub>n</sub>O<sub>m</sub>·Zn<sub>x</sub>O<sub>y</sub>·CuO, and for TiO<sub>2</sub> monoxide and two-component CECs – TiO<sub>2</sub>·CuO, TiO<sub>2</sub>·CoO, TiO<sub>2</sub>·SnO, Ti<sub>n</sub>O<sub>m</sub>·Zr<sub>x</sub>O<sub>y</sub> etc, the degree of MO photodestruction was lower.

There are several probable reasons for the inhibition or synergistic increase in the photocatalytic activity of such compositions - the difference in the content of

metals - dopants in the composition of the HOC, which is determined by the nature of the dopant, the conditions and modes of formation of the heterooxide coating, as well as the geometric factor - zinc-containing coatings are characterized by the most developed surface.

Subsequent thermal treatment in the modes indicated earlier did not have a significant effect on the photocatalytic activity of the synthesized systems. Nevertheless, the positive effect of heat treatment was manifested in an increase in the activity resource of metal oxide systems, which, in particular, increased by 2 times for  $\text{TiO}_2 \cdot \text{CuO}$  and  $\text{TiO}_2 \cdot \text{CoO}$ , and by 4 times for  $\text{TiO}_2 \cdot \text{CuOZnO}$ , while the degree of photodegradation MO practically remained unchanged.

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