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APPLICATION OF OXIDE-METALLIC CATALYSTS ON VALVE METALS FOR ECOLOGICAL CATALYSIS

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Запропоновано спосіб одержання оксидно-металевих каталізаторів методом одностадійного плазмово-електролітичного оксидування вентильних металів для знешкодження токсидів природного та техногенного походження. Обґрунтовано застосування оксидів мангану та кобальту як легуючих компонентів. Встановлено, що одержані оксидні покриви характеризуються високою каталітичною активністю в модельних реакціях конверсії токсичних компонентів, зокрема відпрацьованих газів двигунів внутрішнього згоряння

Ключові слова: екологічний каталіз, оксидно-металевий каталізатор, плазмово-електролітичне оксидування, каталітична активність

Предложен способ получения оксидно-металлических катализаторов методом одностадийного плазменно-электролитического оксидирования вентильных металлов для обезвреживания токсидов природного и техногенного происхождения. Обосновано применение в качестве легирующих компонентов оксидов мангана и кобальта. Установлено, что полученные покрытия сложными оксидами характеризуются высокой каталитической активностью в модельных реакциях конверсии токсических компонентов, в частности отработанных газов двигателей внутреннего сгорания

Ключевые слова: экологический катализ, оксидно-металлический катализатор, плазменно-электролитическое оксидирование, каталитическая активность

1. Introduction

At the present stage of development of civilization, chemical pollution is considered to be one of the major ecological problems. This is due to the fact that, as a result of natural processes and intensive economic activity, the advanced ecosystems receive a considerable number of chemical agents of different origin. Particularly dangerous in this case are the substances and compounds foreign to the ecosystem itself xenobiotics. As a result of such action, the basic characteristics of air, water, land undergo change, which exerts a generally negative impact on the lives and health of living beings, manufacturing processes, and raw material resources.

The main sources of chemical pollution of the air are the enterprises in power engineering, ferrous and non-ferrous metallurgy, chemical industry, motor transport [1]. Among the most widely-spread air pollutants that should be noted are carbon oxides (CO, CO_2) and nitrogen oxides (NO_x), sulfur compounds (SO_2 SO_3, H_2S), and hydrocarbons (CH_x).

Heavy metal compounds, petroleum hydrocarbons, phenols, synthetic surface-active substances, and pesticides are the main chemical pollutants of hydrosphere. Most of the pollutants enter water basin as a result of technological accidents, discharge of domestic and industrial wastewater.

As a result of contaminating natural environment by chemicals, such negative effects manifest themselves as the “greenhouse effect”, depletion of the ozone layer, emergence of the smog, including photochemical, and breach of food chains. The life cycle of substances in nature leads to the circulation of pollutants in the environment. This contributes to the deterioration in overall environmental situation in the world and necessitates working out activities aimed at removing toxic substances.

Under contemporary conditions, a decrease in the pollution of air and water basins can be achieved employing a scientific approach and applying rational waste-free technologies. The most effective instrument for detoxification of pollutants from gas emissions and wastewater to the level of maximum permissible concentrations is the catalytic reactions [2, 3].

A scientific direction related to the practical use of catalysis for environmental protection of the surroundings from contamination of various origins [4] has been recognized in world practice as the ecological catalysis [5].

Reactions in the ecological catalysis are characterized by a conversion of toxic agents into harmless compounds. This is achieved by the combination of a limited range of transformations of toxicants using highly selective and polyfunctional catalysts. In this case, among the many techniques for purification, the ecological catalysis is attractive from an economic standpoint as well.

Consequently, the development of highly efficient catalytic materials to neutralize substances that pollute the environment is a relevant and promising direction in the implementation of ecological catalysis.

2. Literature review and problem statement

In a general case, the catalyst consists of a matrix (carrier material) and a catalytically-active layer. Catalytic system activity in this case is determined by its composition (number of catalytically-active centers) and the degree of surface development.

For the purposes of environmental catalysis, the most common and technological form of catalyst is the application of a catalytically-active component onto the structured substrate [6]. An example of the practical implementation of such a system is the use of converters of toxic emissions in the internal combustion engines [2, 7].

A promising class of compounds used in the ecological catalysis is the oxide-metallic systems. Such catalysts have high catalytic activity due to inhomogeneity of chemical composition, for example, a deviation from stoichiometry, introduction of admixtures, as well as local chemical formations. They also maintain working ability for a long time under the action of high temperatures and pressure, which is often characteristic of the neutralization processes of toxic components. Good indicators of corrosion resistance, mechanical strength, and capability to regenerate provide such materials with a long operational lifecycle.

The most affordable and promising one among the techniques for obtaining oxide-metallic systems on highly developed structured carriers is the plasma- electrolytic oxidation (PEO) of valve metals [8]. PEO implies surface oxidization under the action of short-lived electric discharges at high voltage in aqueous electrolytes. A special feature of PEO is that it is possible over one technological process to obtain both a highly developed surface of the carrier material and a catalytically-active layer. This is the way in which an oxide-metallic catalytic system forms [9].

A change in the composition of employed solutions and treatment conditions makes it possible to flexibly manage the process for obtaining catalysts and to change chemical composition of the materials over a wide range. In addition, when treating the carrier material with PEO, it is possible to form a catalytically active layer on parts with significant dimensions and of geometrically complex shape. This considerably expands the scope of application range of such catalytic systems. Simple equipment employed during electrochemical treatment, as well as non-toxicity of the used electrolytes, position PEO as an ecologically safe resource-saving technology of catalysts with a broad scope of application [8].

PEO coatings on valve metals, particularly aluminum and titanium, possess catalytic properties and are widely used in the heterogeneous catalysis [10, 11]. Titanium oxide is also a photocatalyst for the reactions of neutralization of toxicants in the gaseous medium and solutions [12, 13]; the effectiveness of separate oxides, however, is not high enough.

Introducing to the composition of oxide systems TiO_2 and Al_2O_3 additional components increases efficiency of the catalytic activity of oxide-metallic systems. Incorporation occur both through direct capture of composite particles from electrolyte in the process of oxide layer growth and at the expense of thermochemical and electrochemical transformations of the working solution's components [14, 15]. The composition of oxide surface layers can be introduced with compounds of transient, noble, rare and dispersed elements, as well as non-metals.

In paper [16], by applying the method of PEO, the oxide catalytically-active coatings on titanium were obtained from aqueous electrolytes. In order to form a PEO-coating, the authors used an electrolyte based on sodium tetraborate with the addition of manganese acetate. The surface oxide layer after treatment consisted of titanium oxide and a mixture of manganese oxides. The given oxide coating shows catalytic activity in the oxidation reaction of CO to CO_2. It is noted, however, that the catalytic activity of such system depends on the concentration and surface distribution of manganese, as well as the surface layer morphology.

Authors of [17] synthesized a mixed oxide-metallic PEO-coating with a high content of manganese on the aluminum alloy AL25. The given system consists of nonstoichiometric manganese oxides and is effective in the oxidation reaction of carbon (II) oxide to CO_2. It was shown that the oxide-metallic coating had a micro-globular structure of the surface. This is a prerequisite for high catalytic activity in the redox reactions involving oxygen.

PEO-systems based on titanium oxide, doped with iron, possess a higher photocatalytic activity in comparison with pure TiO_2 [18]. In order to form the coatings, the authors used an electrolyte based on sulfuric acid with the addition of Fe^{3+} ions. Destruction of rhodamine V under the action of UV on the obtained catalyst, in the authors' opinion, is predetermined by a change in the parameters and structure of titanium oxide due to the inclusion of iron ions into it. The issue of control over catalytic activity of such a system, however, remained unresolved.

Photocatalytic properties are also inherent for the TiO_2 systems, which incorporated in their structure cerium oxides [19], vanadium oxides [20], tungsten oxides [21], and zirconium oxides [22]. They are effective for the destruction of organic compounds. It should be noted, however, that such catalysts are fairly expensive, which is why preference is to be given to the more affordable catalytic materials based on transition metals.

Thus, in paper [23], authors studied the properties of mixed oxide-metallic coatings of titanium with the metals of iron triad (Fe, Co, Ni). It is shown that the introduction of dopants affected the structure and surface morphology of the synthesized oxide-metallic systems. The formed PEO-coatings are characterized by high catalytic activity in the conversion reaction of carbon (II) oxide. Given this, such materials may be used for catalytic systems of air- and water purification. It should be noted that the catalytic activity of the considered PEO-coatings relative to the destruction of toxicants remained unexplored.

Cobalt-containing oxide coatings on titanium [24] were obtained from a silicate electrolyte with the addition of cobalt acetate. However, an increase in the catalytic activity of the received materials in the oxidation reaction of CO was achieved by the additional impregnation and subsequent annealing of the obtained oxide systems.

In article [25], catalytic materials on titanium and aluminum were received over one stage by the method of PEO, as well as over two stages by combining the PEO-modification of base metal with subsequent impregnation in the solutions of salts of catalytically active components. By employing such a technique, the authors obtained oxide-metallic systems doped with the oxides of transition metals (Mn, Fe, Co, Ni), which were tested in the model reaction of CO oxidation. The need for conducting additional technological operations was predetermined by the low content of dopants and uneven distribution of catalytic components in the surface layers.

Thus, it follows from an analysis of the scientific-technical literature that the effective catalysts for the purposes of ecological catalysis are mixed oxide-metallic systems. In order to receive such systems on valve metals, particularly aluminum and titanium alloys, it would seem appropriate to apply the plasma electrolytic oxidation. Such a technique of synthesis makes it possible to form catalytically active materials with high content of dopants and a broad scope of application. At the same time, unresolved issues of control over the morphology of coatings, choice of dopants, the need to use impregnation with salts followed by thermolysis to enhance catalytic activity of coatings, as well as a limited range of the studied toxicants, hamper development of technology for the ecological catalysis.

3. The aim and objectives of the study

The aim of present work is to obtain oxide-metallic catalysts with a high content of dopants on valve metals (aluminum and titanium). This will enable creation of the highly efficient catalytic materials for the ecological catalysis over a one-stage technological process.

To achieve the aim, the following tasks have been set:

– to substantiate a technique for obtaining oxide-metallic catalysts on valve metals, taking into account basic requirements for catalytic materials;

– to examine the composition and surface morphology of the obtained catalytic systems;

– to explore catalytic activity of the obtained catalytic materials in the neutralization reactions of toxic components.

4. Procedure for obtaining oxide-metallic catalysts on valve metals; study of the composition, morphology, and properties

4. 1. Technique for obtaining

We demonstrated previously that obtaining oxide-metallic systems with a high content of dopants was possible in the process of one-stage plasma-electrolytic oxidation of titanium alloys [26] and aluminum alloys [27] when using complex electrolytes. The synthesized materials did not require further treatment and possessed a broad range of functional properties, including those catalytic. This very approach to the formation of catalytic coatings underlies the present research as a working hypothesis.

Oxide-metallic catalysts were obtained by the method of PEO on valve metals (titanium and aluminum). A catalytically active layer on the samples (alloys VT1-0 and AK12M2MgN) was formed by the PEO method under galvanostatic mode using the direct current source B5–50. Current density of the formation was 1–20 A/dm^2, voltage – up to 240 V. Electrochemical treatment was carried out at constant agitation of working solutions for 30–60 minutes in alkaline solutions whose composition was introduced with manganese or cobalt cations (Table 1). The temperature was maintained by the flow circulation cooling in a range of 25–30 °C.

Table 1

Composition of electrolytes and synthesis parameters of oxide-metallic catalysts

No.	Substrate	Composition of electrolyte		Current density i, A/dm^2
		Components	Concentration, mol/dm^3	
1	Titanium alloy VT1-0	$K_4P_2O_7$ $Na_3C_6H_5O_7$ $CoSO_4$	0.3 0.1 0.1	1.0–5.0
2		$K_4P_2O_7$ $KMnO_4$	0.1 0.1–0.3	
3	Aluminum alloy AK12M2MgN	$K_4P_2O_7$ $CoSO_4$	0.4 0.1	3.0–5.0
4		NaOH $KMnO_4$	0.005–1.0 0.05–0.2	10.0–20.0

Preparation of the samples' surface for the application of catalytically active layer included mechanical cleaning from fat and technological pollutions, degreasing, etching, rinsing with water.

4. 2. Research methods of oxide-metallic catalysts

Study of the surface morphology of the obtained oxide-metallic catalytic systems was carried out using the scanning electron microscope ZEISS EVO 40XVP (Germany). Topography of the catalysts surface was studied applying the atomic force microscope NT-206, probe CSC-37, and cantilever V. In order to determine chemical composition of the surface oxide layers of catalysts, we employed the energy dispersion spectrometer Oxford INCA Energy 350 (Great Britain) with the integrated programming environment SmartSEM.

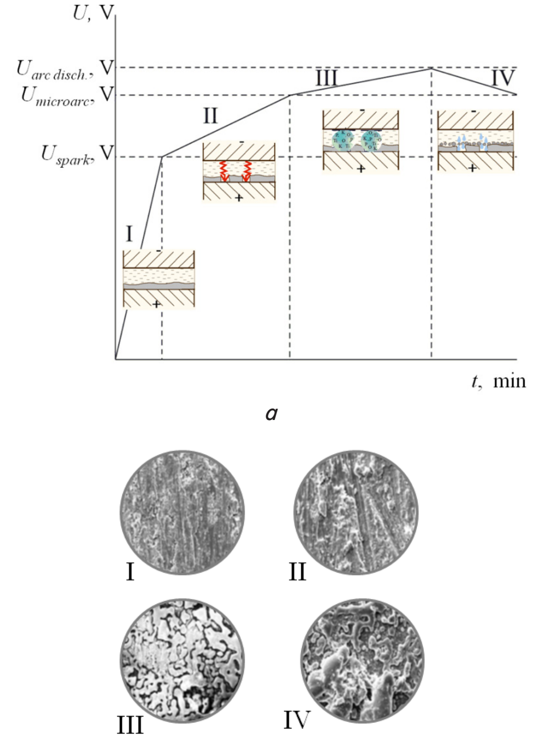
Catalytic activity of the oxide systems was tested in a model oxidation reaction of CO into CO$_2$. Experimental research was conducted at a laboratory bench in a tubular flowing reactor, as specified in paper [26].

Oxide-metallic coatings on AK12M2MgN were additionally tested during combustion and catalytic transformation of toxic substances in the cylinder of an internal combustion engine. For this purpose, the coating was directly formed on the piston cover of a single-cylinder aspirated diesel engine [28].

5. Results of obtaining oxide-metallic catalysts on valve metals

As was previously demonstrated [23], the introduction of cations of iron triad into the composition of electrolytes for PEO-treatment of titanium alloys makes it possible to obtain oxide systems with a different content of dopants in the surface layer. In this case, using the complex electrolytes particularly helps to improve the stability and operational lifecycle of working solutions [17, 29], and contributes as well to a more uniform distribution of doping components on the surface of the treated material.

It was established that the chronograms of forming voltage for the mixed oxide-metallic catalytic coatings on titanium and aluminum acquired a classic shape and were divided into specific regions (Fig. 1, *a*): pre-spark (I), spark (II), microarc (III), arc discharges (IV).



a

b

Fig. 1. Characteristic of stages of PEO-treatment of valve metals: *a* — chronograms of inter-electrode voltage, *b* — surface morphology of the system Al | Al_2O_3·CoO_x at different stages of PEO. Magnification ×1000

The inclusion of dopants into the composition of the synthesized oxide systems changes surface morphology of the treated materials. As an example, we show dynamics of change in the morphology of AK12M2MgN during treatment in electrolyte 3 (Fig. 1, *b*) at each stage of PEO.

The study results helped to establish that the characteristics of stages of PEO-treatment of valve metals to form catalytically active layers depend on the nature of the treated material and the electrolyte composition [23, 27].

Important for a technique of obtaining oxide-metallic catalysts on aluminum and titanium alloys are the characteristics of voltage during oxidation of the base metal (Fig. 2).

Under the specified conditions (Table 1), uniform oxide-metallic coatings (Fig. 3) with a content of dopants to 36 % by weight for manganese, and 23.6 % by weight for cobalt, were obtained on the titanium and aluminum alloys.

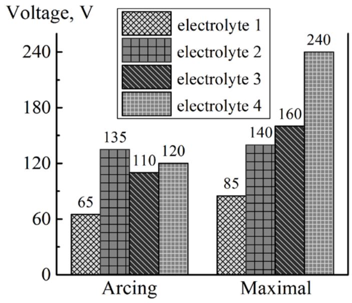


Fig. 2. Voltage characteristics at the stages of PEO for electrolytes 1–4 (Table 1)

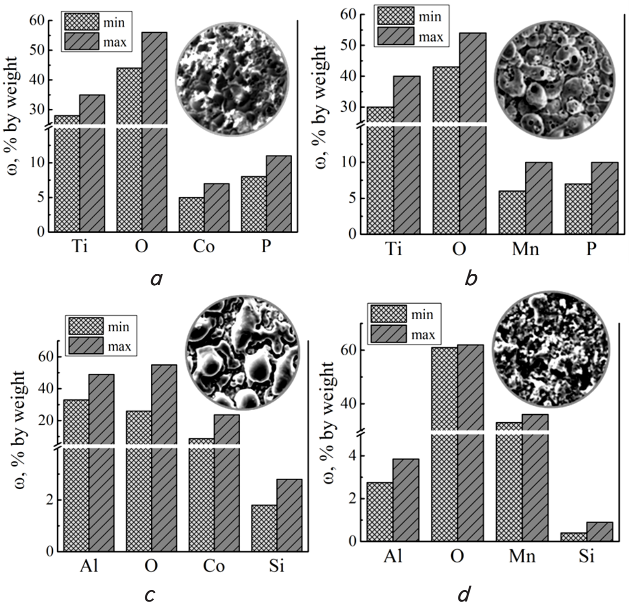


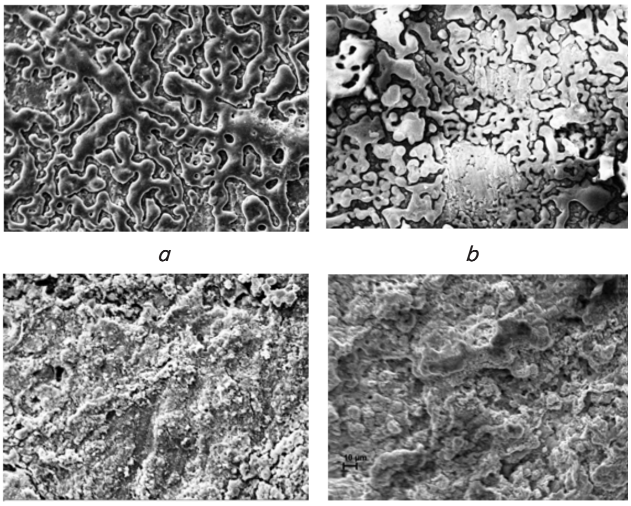
Fig. 3. Composition and surface morphology of the oxide-metallic catalytic systems: *a* — Ti | TiO_2·CoO_y, *b* — Ti | TiO_2·MnO_y, *c* — Al | Al_2O_3·CoO_y, *d* — Al | Al_2O_3·MnO_y. Magnification ×500

Variation of the working current density affects a change in the surface morphology of the obtained oxide-metallic coatings (Fig. 4).

The high level of surface development of oxide coatings during PEO of titanium and aluminum alloys is confirmed by the results of surface topography analysis using a scanning probe microscopy (Fig. 5).

Catalytic activity testing of manganese- and cobalt-containing oxide-metallic catalysts on titanium and aluminum was held in a model oxidation reaction of carbon (II) oxide. It was established that ignition temperature T_i, which corresponds to the onset of effective work of the catalyst, is in a range of 250–280 for PEO coatings on titanium, and 170–230 – on aluminum.

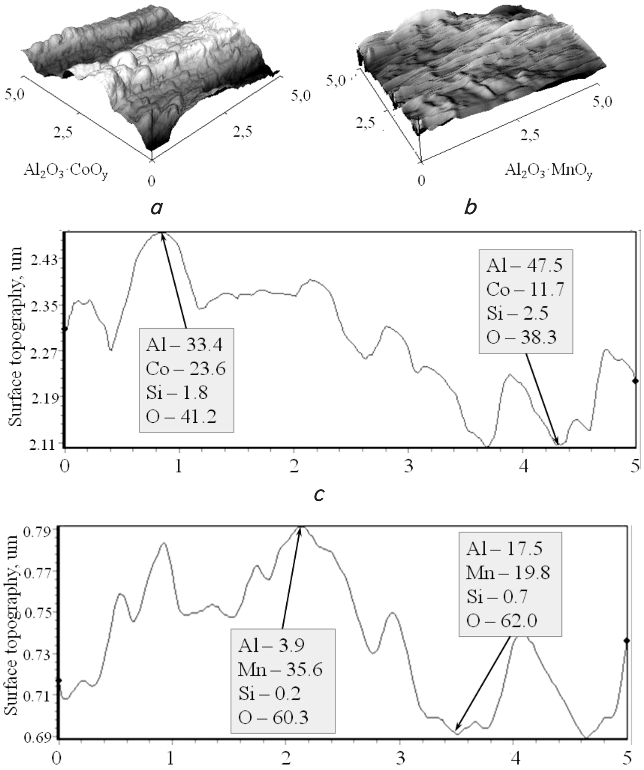
The oxide-metallic systems TiO_x·MnO_y and Al_2O_3·MnO_y enable the CO conversion degree at the level of 70–100 %, while for the oxide catalysts TiO_x·CoO_y and Al_2O_3·CoO_y this value is in a range of 68 81 % (Table 2).



a *b*

c *d*

Fig. 4. Impact of current density on surface morphology of the oxide-metallic catalytic systems on AK12M2MgN: *a* – Al | $Al_2O_3{\cdot}CoO_y$ 5 A/dm^2, *b* – Al | $Al_2O_3{\cdot}CoO_y$ 10 A/dm^2, *c* – Al | $Al_2O_3{\cdot}MnO_y$ 15 A/dm^2, *d* – Al | $Al_2O_3{\cdot}MnO_y$ 20 A/dm^2



a *b*

c

d

Fig. 5. 3D maps and cross-section profiles of the oxide-metallic systems: *a*, *c* – Al | $Al_2O_3{\cdot}CoO_y$, *b*, *d* – Al | $Al_2O_3{\cdot}MnO_y$. Scanning area is 5×5 μm

For the bench testing of a single-cylinder diesel engine, we synthesized the oxide-metallic coatings $Al_2O_3{\cdot}MnO_y$ and $Al_2O_3{\cdot}CoO_y$ on the surface of the combustion chamber of the piston. The results obtained from tests clearly indicate that the application of the synthesized PEO-systems leads to a reduction in fuel consumption within 3 %. The amount of toxic emissions from engine under forced operation modes also decreased [28].

Table 2

Characteristics of coatings by the mixed oxides

Electrode material	Content of alloying component ω, % by weight	Conversion degree *X*, %	Ignition temperature T_i, °C
Pt [30]	100	100	200
Pt_{exp}	100		
$TiO_x{\cdot}CoO_y$	Co – 7.7	68	280
$TiO_x{\cdot}MnO_y$	Mn – 7.5	100	250
$Al|Al_2O_3{\cdot}CoO_y$	Co – 25	81	170
$Al|Al_2O_3{\cdot}MnO_y$	Mn – 33	70	230

6. Discussion of the composition, morphology, and properties of oxide-metallic catalysts

The difference in the parameters of plasma-electrolytic treatment of valve metals during formation of the oxide-metallic catalytic coatings on titanium and aluminum alloys (Fig. 1, *a*) is explained by the different electric resistance of oxides of carrier materials in the catalytically active layer (Al_2O_3 and TiO_2). In addition, the alloy AK12M2MgN has a significant amount of alloying components in its composition, which also affects characteristics of the PEO stages [31]. That is why oxidation of the alloy VT1-0 is characterized by a less period for entering the sparking regime and by lower voltages during treatment process (Fig. 2).

The most intense formation of a catalytically active layer in the catalysts occurs under a microarc mode (Fig. 1, *b*, section 3). This is explained by the implementation of thermochemical reactions that enable inclusion of the electrolyte components into the oxide layer being formed. In this case, the surface morphology of the treated material changes subsequently.

Plasma electrolytic oxidation of the alloy VT1-0 in electrolytes 1 and 2 enables formation of the enamel-like uniform surface (Fig. 3, *a*–*c*). The surface consists of spheroidal grains alternating with tubular microporous structure characteristic of TiO_2 [23].

The surface of mixed oxides applied onto the alloy AK12M2MgN in electrolyte 3 consists of agglomerates of spherical islet structures of nonstoichiometric cobalt oxides (Fig. 3, *c*). PEO-treatment of the alloy AK12M2MgN in electrolyte 4 (Fig. 3, *d*) allows obtaining a surface layer of micro-globular structure [31].

An analysis of elemental composition of the obtained oxide systems (Fig. 3) indicates incorporation of the alloying components of alloys to the matrix of titanium and aluminum oxides. The content of dopants (mangan and cobalt) in oxide-metallic coatings increases with an increase in the current density of forming.

It was established in the course of conducted experiments that the variation of PEO conditions makes it possible to control the process of synthesis of oxide-metallic composition in the matrix of oxide of the base metal. High densities of the oxidation current results in the formation of a more developed structure of the catalyst surface (Fig. 4, *b*, *d*). This is also an additional factor in the formation of a better developed surface of catalysts by modifying energy parameters of the oxidization process.

The results of employing atomic force microscopy confirm this assumption. Surface of the obtained oxide systems consists of agglomerates of grains in a nanometer range. The cobalt-containing coatings differ by a globular structure (Fig. 5, *a, c*). The oxide-metallic coatings with manganese are characterized by the presence of sharp edges and a smoothed surface relief (Fig. 5, *b, d*).

The composition, morphology, and topography of surface of the oxide-metallic systems on the titanium and aluminum alloys are a prerequisite for the high catalytic activity of materials during redox reactions [32].

An analysis of results of testing catalytic activity of the synthesized oxide materials allows us to conclude that they are not inferior to the contacts that contain precious metals, and, in some cases, they outperform them for such critical parameters as ignition temperature and degree of conversion. Among the investigated systems, the most efficient in a model carbon monoxide oxidation reaction are the manganese-containing oxide catalysts.

Applying the oxide-metallic coating of the piston of an internal combustion engine leads to a reduction in the ignition temperature of fuel mixture. Consequently, the phase of uncontrollable fuel burning, as well as time of its combustion, decrease, while a combustion temperature reduction excludes the possibility of participation of nitrogen in the gas-phase reactions. The specified features of the combustion process, considering catalytic processes on the surface of the oxide-metallic coating of piston, enable reducing the amount of toxic emissions from the engine with exhaust gases.

Thus, the manganese- and cobalt-containing oxide-metallic systems, formed by the method of PEO could find application in the technology of ecological catalysis for the disposal of toxic components when used in the systems of air and water purification.

Promising direction for employing oxide-metallic coatings when applied directly on the parts of piston group of ICE is the use of catalytic materials for the intra-cylinder catalysis in order to reduce toxicity of engine emissions.

7. Conclusions

1. We substantiated a technique for obtaining the oxide-metallic catalysts on valve metals using a PEO method in complex electrolytes with the addition of manganese and cobalt salts. It was established that the proposed technique of synthesis makes it possible to form within one technological process catalytically active materials with a developed surface and a high content of dopants. The introduction to the composition matrices of TiO_2 and Al_2O_3 of manganese and cobalt oxides contributes to the enhancement of catalytic activity of the obtained oxide-metallic systems.

2. The composition and surface morphology of the obtained catalytic systems were studied. It was found that the proposed method makes it possible to apply uniform highly-developed oxide-metallic coatings onto titanium and aluminum alloys containing up to 36 % by weight of manganese and 23.6 % by weight of cobalt. Varying the PEO conditions enables control over the process of synthesis of oxide-metallic layer on the matrix of base metal oxide.

3. The obtained manganese- and cobalt-containing oxide-metallic coatings on the alloys of titanium and aluminum are characterized by a high catalytic activity in the conversion reaction of carbon (II) oxide and a reduction in the toxicity of gas emissions from internal combustion engines. Therefore, the proposed oxide-metallic systems could find effective application in the technologies of ecological catalysis during neutralization of toxic components in the systems of air and water purification.

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