COBALT AND MANGANESE OXIDE CATALYTIC SYSTEMS ON VALVE METALS IN ECOTECHNOLOGIES

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The paper discusses the preparation of cobalt and manganese oxide catalytic systems on valve metals (aluminum and titanium alloys) for eco-technologies. Oxide catalysts with d-metals based on aluminum are widely used for reduce the toxic gases emission from internal combustion engines. Catalysts based on Titania doped with transition metal oxides are also widely used in the heterogeneous and especially photo-catalysis. The higher catalytic properties in this case are demonstrated by the nano-structured oxide systems with developed surface both on aluminum and titanium alloys.

From the point of view of the application convenience, better technological forms of a catalyst are the thin-film oxide coatings, formed directly on the metal substrate by the method of plasma-electrolytic oxidizing.

The features of the conversion coatings formation on aluminum and titanium alloys by plasma electrolytic oxidation in alkaline electrolytes are considered. The effect of both the concentration and ratio of the electrolyte components and processing conditions on the composition and the morphology of the surface layers is studied.

The difference in the plasma oxidation parameters of aluminum and titanium alloys is attributed to the various specific electric resistance of matrix metal as well as the alloying elements oxides. The influence of the oxides' composition on the surface relief and their properties is investigated. The factors influencing the catalytic properties of single and mixed oxide systems are established and the prospects for their use in technology of neutralization of toxic substances are discussed.

Intensive economic activity and increase in the production capacities of different sectors of industry lead to the growth of the pollution of air and water basins by toxic substances of different nature and chemical stability. Given this, the organization of removal of natural and technogenic contaminators from air and aqueous medium is impossible without the use of effective and accessible catalysts.

Oxide catalysts with d-metals based on aluminum and its alloys are widely used for reducing the emission of internal combustion engines [1]. At high temperatures, significant advantages are shown by a family of catalysts based on d-metals, which exhibit thermal lability and high oxygen affinity. Non-stoichiometry oxides, in particular cobalt and manganese ones, not only provide the thermal stability of the catalysts but also lead to a significant improvement of their reactivity [2]. In terms of rational designing and effective technology, it seems appropriate to deposit a catalytic layer directly on the surface of ICE pistons manufactured using aluminum alloys with an optimal combination of physical-mechanical and performance properties [3].

In the heterogeneous catalysis the catalysts based on Titania doped with transition metal oxides are also used [4]. Of particular scientific interest are the photo-catalysts based on TiO_2 due to the high chemical inertness, affordability, low toxicity of the products of purification [5, 6].

Higher catalytic properties in this case are demonstrated by the nano-structured oxide systems with developed surface both on aluminum and titanium alloys [7, 8].

It should be noted that from the point of view of the application convenience, a better technological form of a catalyst is the thin-film oxide coatings, formed directly on the main metal-carrier by the method of plasma-electrolytic oxidizing (PEO). PEO of valve metals and their alloys is a proising method for producing nanostructured functional materials with high corrosion protective, mechanical and catalytic properties [9, 10].

The possibility of targeted formation of a surface having specified composition and topography by varying electrolyte composition and electrolysis mode opens new opportunities for creating affordable, high-performance catalysts with significant lifetime, high exploitation and technological characteristics for use in purification technologies from natural and anthropogenic toxic substances.

PEO technologies dissemination requires the establishment of new non-toxic electrolytes, optimizations of conversion coatings formation modes, and also their doping with components, which increase exploitation characteristics [11]. Transition, rare and trace elements, including Mn, Co, Zn, Zr etc., are incorporated in valve metal oxide matrix to provide catalytic properties. Such mixed metal-oxide systems are distinguished by high adhesion to metal substrate, developed surface and a significant number of active catalytic centers [12, 13].

The aim of this paper is to investigate the features of oxide coatings formation using plasma electrolytic oxidation of aluminum and titanium alloys in alkali electrolytes containing transition metal salts, and to study the composition and morphology of the synthesized mixed oxide coatings.

Experimental Procedure

The coatings were formed on substrates of titanium VT1-0 and aluminum AK12M2MgN alloys of composition given in Table 1.

Table 1. Composition of substrates, mass.%

Alloy	Al	Si	Cu	Ni	Mg	Mn	Fe	Zn	Ti	Other elements
VT1–0	–	0.10	–	–	–	–	<0.25	–	99.2–99.7	<0.4
AK12M2MgN	79.0–84.8	11.0–13.0	1.5–3.0	0.8–1.3	0.8–1.3	0.3–0.6	<0.8	<0.5	<0.2	Pb < 0.10 Sn < 0.02 Cr < 0.20

Surface pretreatment of the samples was performed by mechanical cleaning, degreasing, etching and rinsing with distilled water.

The composition of electrolytes and parameters of oxide systems synthesis are given in Table 2.

Table 2. Composition of electrolytes and the parameters of oxide systems synthesis

N	Substrate	The 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

The acidity of the electrolytes was maintained in the range pH 9–11.5. The electrolytes were prepared from certified reagents graded as "pure grade" and "analytical grade" with distilled water.

The PEO of substrates was conducted using a B5-50 stabilized power supply that maintained voltage up to 300 V. PEO was implemented in an electrolytic cell under conditions of forced cooling of the electrolyte to a temperature of 25–30°C and stirring the electrolyte.

The chemical composition of the coatings was determined by X-ray photoelectron spectroscopy with an INCA Energy 350 energy dispersive spectrometer. X-ray radiation was excited via exposing the samples to a

15-keV electron beam. In addition, X-ray fluorescence analysis was conducted using a SPRUT portable spectrometer with a relative standard deviation of 10^{-3}–10^{-2}; the error in determining the component content was ±1 mass.%.

The surface of the coatings was studied using a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were recorded by the registration of secondary electrons (BSEs) via scanning with an electron beam; this mode made it possible to study the topography with a high resolution and contrast ratio.

The surface morphology and roughness of coatings were studied by an atomic force microscopy AFM using a NT–206 microscope. Scanning was performed using the contact probe CSC-37 (lateral and vertical resolutions 2 and 0.2 nm, respectively; 1024 x 1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm).

The catalytic properties of the oxide systems were studied in the oxidation of carbon (II) oxide to carbon (IV) oxide [14].

Results and discussion

Chronograms of the interelectrode voltage in the PEO formation of oxide coatings on titanium and aluminum alloys have a classic look and are divided into the following characteristic regions (Fig. 1 *a*): pre-spark (I), spark (II) micro-arc (III) and arc discharges (IV). [10, 16]

Forming voltage is growing rapidly in the first 2–3 minutes of PEO process. The dependence $U - t$ is almost linear in the pre-sparc region (Fig. 1 *a*, I) for all electrolytes and substrates through the formation of barrier oxide TiO_2 or Al_2O_3.
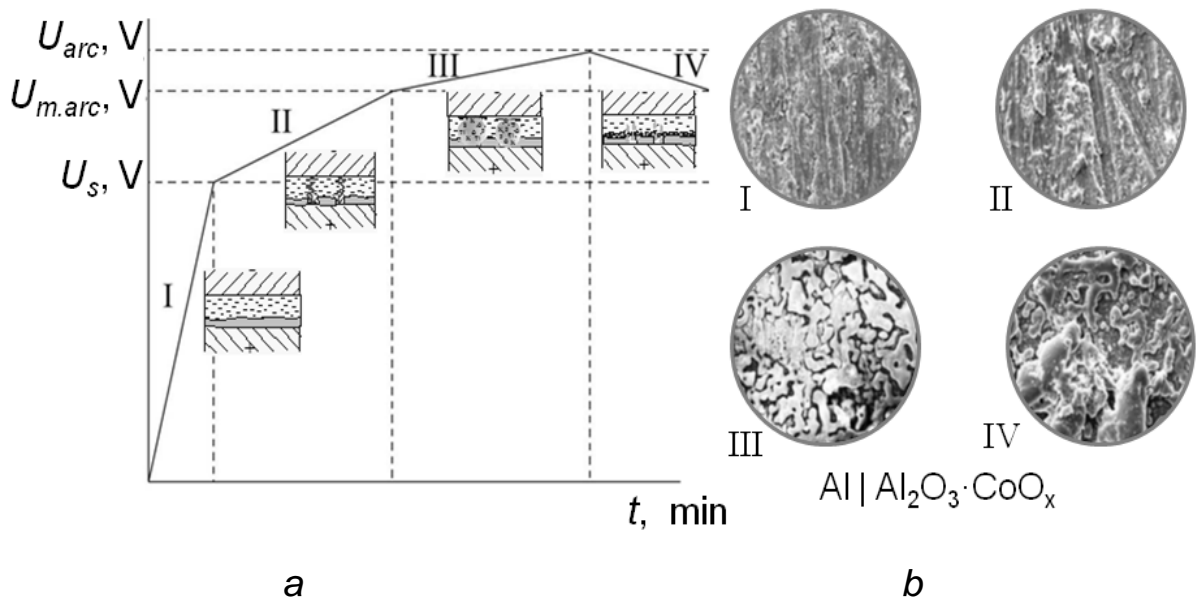

Fig. 1. Chronograms of interelectrode voltage (a) and morphology of the Al | Al_2O_3·CoO_x oxide coatings obtained by PEO at characteristic regions (b)

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The beginning of the sparking corresponds to the breakdown of dielectric films (Fig. 1 a, I–II). The growth of the voltage is slowed down due to compete processes of breakdown and regeneration of barrier oxide. At this stage thermochemical reactions begin, which provides incorporation of electrolyte components to the forming oxide layer.

The inclusion of the dopants to the oxide systems changes the surface morphology of the synthesized materials (Fig. 1 b.)

The PEO process stabilizes in the region of stable sparking (Fig. 1 a, II). Incorporation of transition metal oxides into the surface layers at the stable PEO manifests itself in the appearance freeform sites of different colors – violet for cobalt and black for manganese.

Percularities of PEO modes for Al and Ti

It is established that the quantitative characteristics of the PEO stages such as the inter-electrode voltage U_f, sparking voltage U_s and maximum forming voltage U_{max} depend on the nature of the treated substrate and the composition of the electrolyte (Fig. 2) [17].

The time to attain the sparking mode and the initial sparking voltage when processing the alloy VT1-0 is lower compared with the similar characteristics for PEO of aluminum alloy AK12M2MgN. This is due to higher electrical resistance of alumina than titania. In addition, a significant amount of alloying components in AK12M2MgN composition, in particular silicon, may change the formation parameters.
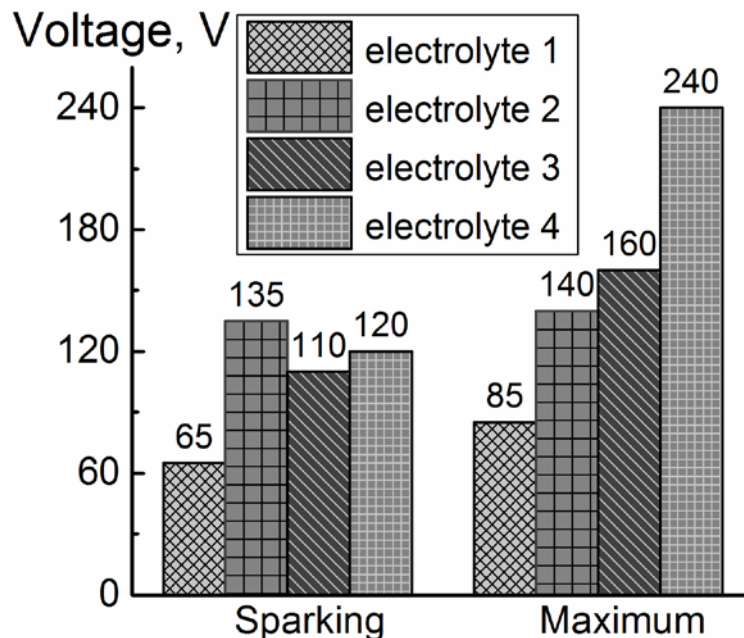

Fig. 2. Voltage characteristics of the PEO stages for electrolytes from Table 2

The most significant inclusions of dopants into the oxide layers (Table 3) are achieved in the microarc mode (Fig. 1 *a*, III).

Table 3. The composition of oxide coatings, mass.%

Oxide system	The contents of components
$TiO_x \cdot CoO_y$	O – 44–56; Ti – 28–35; P – 8–11; Co – 5–7
$TiO_x \cdot MnO_y$	O – 43–54; Ti – 30–40; P – 7–10; Mn – 6–10
$Al_2O_3 \cdot CoO_y$	O – 26–55; Al – 33–49; Si – 1.8–2.8; Co – 8.7–23.6
$Al_2O_3 \cdot MnO_y$	O – 61–62; Al – 2.75–3.85; Si – 0.4–0.9; Mn – 33–36

Transition metal oxides gradually and uniformly cover the surface of the treated sample (Fig. 3). The processing voltage in stage III (Fig. 1 *a*) remains almost unchanged.

It is the microarc mode that is optimal for the synthesis of uniform oxide coatings with the highest content of dopants (Table 3) both for aluminum and titanium alloys.

Transition of the oxidation process to the arc discharge region (Fig. 1 *a*, IV) causes the oxide layer destruction by arcs of high-intensity fields.

$Ti \mid TiO_2 \cdot CoO_y$ $\quad$ $Ti \mid TiO_2 \cdot MnO_y$ $\quad$ $Al \mid Al_2O_3 \cdot CoO_y$ $\quad$ $Al \mid Al_2O_3 \cdot MnO_y$
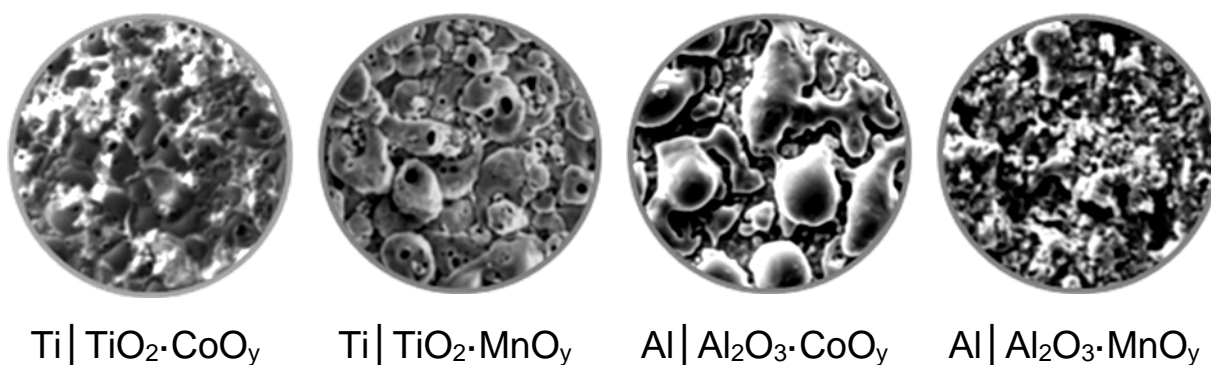
Fig. 3. Morphology of oxide systems obtained from the electrolytes of Table 2 during 30 min of PEO treatment. Magnification x 1000

Varying the operating current density also affects the change in the morphology of the surface coatings (Fig. 4). This is explained by appropriate changes in oxidation rate and duration of PEO stages.

The high degree of oxide coatings surface development during the PEO of aluminum and titanium alloys is confirmed by the results of surface topography analysis using scanning probe microscopy [3, 14].

Ceramics-like mosaic surface structure of mixed oxides obtained on the AK12M2MgN alloy in the electrolyte 3 consists of agglomerates

sphere-like islet structures of non-stoichiometric cobalt oxides (Fig. 5 *a*). The PEO treatment of AK12M2MgN alloy in electrolyte 4 (Fig. 5 *b*) allows a surface layer of micro-globular structure containing non-stoichiometric manganese oxides [3].
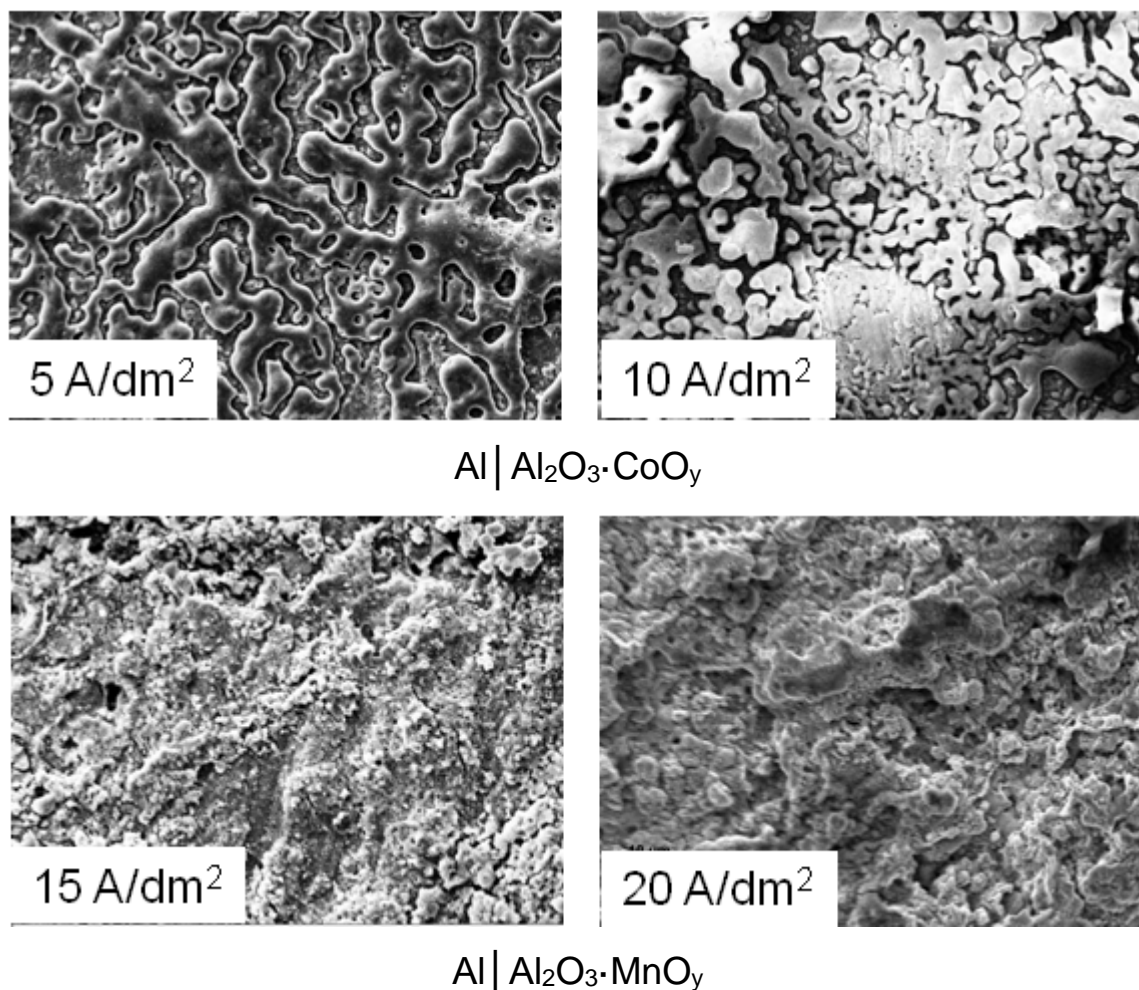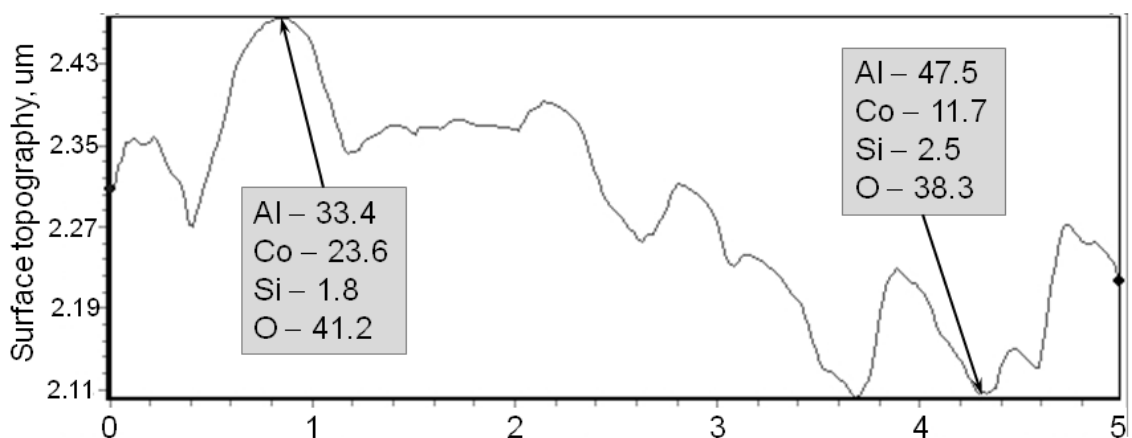

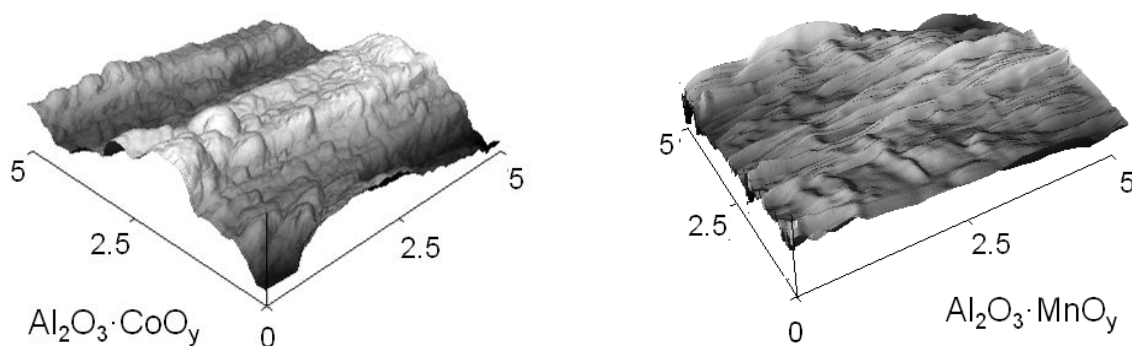Al│Al$_2$O$_3$·CoO$_y$

Al│Al$_2$O$_3$·MnO$_y$

Fig. 4. Effect of current density on the coatings surface morphology. Magnification x 500

Plasma-electrolytic oxidation of the alloy VT1-0 in electrolytes 1 and 2 provides the formation of enamel-like uniform surface. It consists of spheroid grains alternating with tubular micro-porous structure which is typical for TiO$_2$ [12, 15].
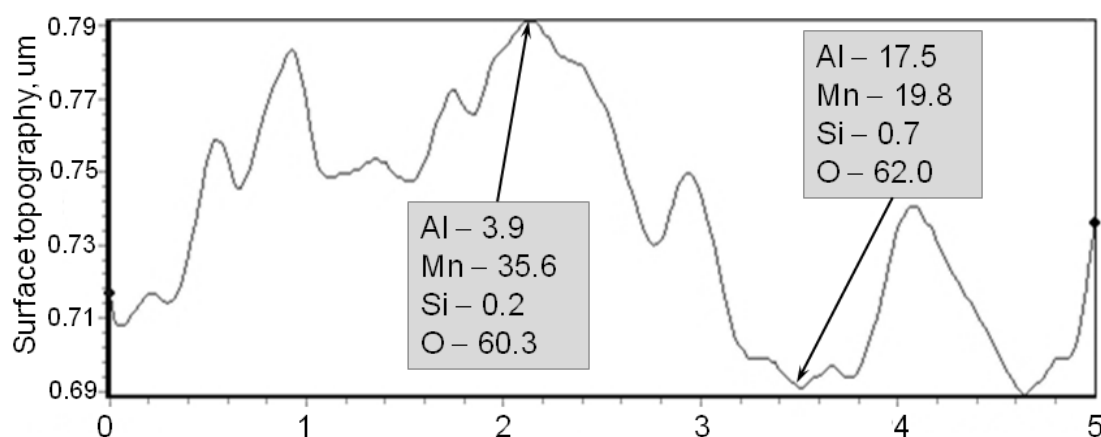
The composition, morphology and surface topography mixed oxide systems Ti│TiO$_2$·MnO$_y$, Ti│TiO$_2$·CoO$_y$, │Al$_2$O$_3$·CoO$_y$, Al│Al$_2$O$_3$·MnO$_y$ predetermine high catalytic activity in red-ox reactions.

The synthesized oxide materials are tested in model reactions of CO and benzene oxidation, and their high catalytic activity, which is not inferior to those containing noble metals, is proved [18]. This is explained by a high affinity of manganese and cobalt non-stoichiometric oxides to oxygen and a corresponding decrease in the activation energy of the double bond O=O destruction.

The Al$_2$O$_3$·CoO$_y$, Al$_2$O$_3$·MnO$_y$ systems were formed on the surface of the piston of combustion chamber of a KamAZ truck. Stand tests of the single-cylinder diesel engine with catalytic coatings show a reduction in hourly fuel consumption and toxic emissions at forced modes of engine operation.

a

b

Fig. 5. 3D maps and profiles of the surface for mixed oxide systems:
a – Al│Al$_2$O$_3$·CoO$_y$; b – Al│Al$_2$O$_3$·MnO$_y$.
Scanning area 5 × 5 µm

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Conclusions

1. Plasma-electrolytic oxidation of titanium and aluminum alloys in alkaline electrolytes with addition of manganese and cobalt salts allows obtaining mixed oxides coatings of different composition.

2. The composition and morphology of the oxide coatings are regulated by the ratio of electrolyte components and operating current density. Mixed oxide systems are characterized by developed micro-globular surface, and the surface relief depends both on the substrate and dopants oxides nature.

3. Synthesized mixed oxide systems revealed high catalytic activity in CO and benzene oxidation, which is not inferior to that of noble metals. This allows one to recommend them for the removal of toxicants of various origins.

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