

Досліджено вплив складу манганвмісних пірофосфатних електролітів і режимів плазмово-електролітичного оксидування на процеси формування і будову оксидних покривів на сплаві титану VT1-0. Показано шляхи керування топографією поверхні, хімічним і фазовим складом покривів, а також інкорпоруванням у них оксидів мангану. Встановлено, що синтезовані оксидні шари характеризуються підвищеною стійкістю до абразивного зносу і високою каталітичною активністю у реакціях окиснення монооксиду вуглецю

Ключові слова: сплав VT1-0, плазмово-електролітичне оксидування, оксидні покриття, манган, каталітична активність

Исследовано влияние состава марганецсодержащих пирофосфатных электролитов и режимов плазменно-электролитического оксидирования на процессы формирования и строение оксидных покрытий на сплаве титана VT1-0. Показаны пути управления топографией поверхности, химическим и фазовым составом покрытий, а также инкорпорированием в них оксидов марганца. Установлено, что синтезированные оксидные слои характеризуются повышенной стойкостью к абразивному износу и высокой каталитической активностью в реакциях окисления монооксида углерода

Ключевые слова: сплав VT1-0, плазменно-электролитическое оксидирование, оксидные покрытия, марганец, каталитическая активность

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A STUDY OF SYNTHESIS AND PROPERTIES OF MANGANESE-CONTAINING OXIDE COATINGS ON ALLOY VT1-0

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1. Introduction

Titanium and its alloys are justly referred to the most popular construction materials that are diversely used due to their physicochemical and operational characteristics. However, there are several factors limiting the applicability of these materials: in particular, their poor sliding properties entail problems when titanium alloys are used in friction pairs, or high chemical reactivity arises from welding operations. Many problems, however, can be effectively solved due to the surface modification. From this perspective, the most rational approach seems to be based on galvanochemical technologies, including covering the surface with coatings of various composition for different purposes. When it concerns valve metals, the most appropriate coatings seem to be conversion and composite ones [1, 2]. They are important to consider not only because they are able to diversify the functional properties of products but also because they increase the reliability and service life under operating conditions [3, 4].

It is much interesting to consider studies that are aimed at improving the technologies of producing oxide coatings. However, a vast majority of traditional methods can not provide sufficiently strong adhesion, wear resistance and

corrosion resistance combined with a certain set of properties that provide for the functional purposes of materials and products. The method of plasma electrolytic oxidation (PEO), which is also called microarc or anode-spark oxidation, allows creating strong adhesion to the substrate of oxide coatings that have dielectric [5], protective [6], catalytic, anti-friction [7], antiseptic [8], and other properties [9, 10].

A distinctive feature of the PEO method is the possibility to form conversion layers that incorporate both oxides of a refined metal and electrolyte components or products of their electrochemical and thermochemical transformations. The chemical composition of the coatings formed by PEO determine the nature of the oxidizable metal, the process parameters, and the electrolyte components, so that controlling the chemical composition of anode layers can significantly improve their physical and chemical properties [2, 11] as well as significantly expand the functional uses of valve metals and alloys with them.

The relevance of the work in this direction is due to the present lack of effective solutions that would allow combining the advantages of titanium-based alloys as promising carriers and the catalytic activity of manganese oxides in

O–O bond cleavage reactions while ensuring strong adhesion to the substrate. It is especially important in this case to carry out the oxidation process in a single step, eliminating the thermochemical reaction of nitrates decomposition that would release toxic nitrogen oxides.

2. Analysis of previous studies and statement of the problem

To obtain catalytically active functional anti-friction materials, PEO coatings are widely used when based on titanium alloys doped with two-, three- and polyvalent metals. The work carried out in this direction highlights the prospects of synthesis and use of oxide structures. Electrochemical processing of valve metals with a PEO mode in aqueous solutions of salts of different nature and concentration allows obtaining oxide films containing transition metals and mixtures thereof in various combinations. To date, however, there is no common approach or principle in the selection of the electrolyte composition and oxidation mode. In each case, they are selected empirically.

A VT1-0 alloy is the main raw material for the manufacture of all types of rolled and compacted semi-finished products (sheets, pipes, and wires), so this alloy is generally used as a model material for the development of a technological mode of metal processing that would have subsequent practical application.

In [12], zinc-containing oxide coatings on the VT1-0 alloy derived from alkali pyrophosphate electrolytes exhibit photocatalytic activity even when the dopant content is 1 wt %.

Polyphosphate electrolytes are also used by researchers [13] for the synthesis of oxide coatings on the aluminum and titanium VT1-0 alloy. The use of polymeric anions facilitates formation of non-stoichiometric oxide systems of increased catalytic activity.

The content of alloying elements in oxide layers on the VT1-0 alloy can be increased by the PEO method followed by subsequent saturating and annealing of the obtained materials [14]. In this case, oxidation of the substrate forms a developed matrix surface, which is subsequently filled with dopants. However, it should be noted that this process is more time-consuming and costly than a single stage PEO treatment mode proposed in [15]. Moreover, synthesized in [15] alloyed oxide coatings are characterized by different content of the base metal and dopant oxides and, hence, different morphology, structure, and phase composition.

In [16], there is a comparative assessment of the processes of formation and the properties of oxide coatings on titanium synthesized in alkaline electrolytes at the same ratio of phosphate and pyrophosphate. It is shown that the use of pyrophosphate contributes to a more developed and rough surface of PEO coating, which improves the functional properties of oxide films.

The research findings in [17] confirm the influence of the initial salt concentration in the electrolyte on an alloying component content in the coating, morphology, structure and characteristics of the surface layer.

The authors of [18] found out that an increase in the catalytic activity of the formed oxide materials can be achieved by surface-forming treatment of the support.

Thus, the PEO of titanium alloys, in particular VT1-0, can be conveniently carried out in alkaline electrolytes that are based on pyrophosphate and the addition of salts of the alloying component. It is essential to substantiate scientifically the composition and the ratio of pyrophosphate electrolyte components as well as to optimize the electrolysis modes and parameters. Successful solution of these tasks will create preconditions for the development of a coating technology for increased service life, chemical resistance to the effects of process fluids and abrasion, enhanced tribological properties, and catalytic activity in heterophase transformations.

3. The purpose and objectives of the study

The purpose of the study is to obtain catalytically active and abrasion-resistant manganese oxide coatings on the VT1-0 alloy in a single step.

The purpose can be achieved through accomplishing the following tasks:

- to justify the choice of the electrolyte components, their rational concentration and the range of current densities for plasma and electrolytic oxidation of the titanium VT1-0 alloy,
- to explore ways to control the surface topography, grain size, chemical and phase compositions of coatings by incorporating manganese oxides into them, and
- to examine the functional properties of synthesized coatings: to study abrasion resistance and catalytic activity in the oxidation reaction of carbon monoxide.

4. A technique of forming oxide coatings on the VT1-0 alloy and a study of their composition, structure, and properties

4.1. Electrolytes and PEO modes

The oxide coatings were formed on the titanium VT1-0 alloy of the following composition, wt %: Ti – 99.2–99.7, Fe<0.25, C<0.07, Si<0.1, N<0.04, O<0.2, and impurities – 0.3. The pre-treatment of the samples included mechanical cleaning from the process contaminants, degreasing in a 0.2–0.3 M NaOH, etching in a mixture of a 0.1–0.3 M HF and 0.3–0.9 M HNO₃, and rinsing with distilled water.

Coatings were formed in an electrolyte based on potassium pyrophosphate with MnSO₄ and KMnO₄ as additives (Table 1). The pre-treatment solutions and the oxidation pyrophosphate electrolytes in the concentration of 0.1–1.0 mol/dm³ were prepared from certified reagents graded as “chemically pure” and “analytical grade” with distilled water.

Table 1

The composition of the PEO electrolytes

Component	Component concentration, mol/dm ³				
	1	2	3	4	5
K ₄ P ₂ O ₇	1.0	1.0	1.0	1.0	1.0
KMnO ₄	–	0.1	0.3	–	–
MnSO ₄	–	–	–	0.1	0.3
pH of the solution	9.15	9.0	9.0	8.65	9.0

The PEO process was performed in a galvanostatic mode, using the B5-50 DC source in a thermostated cell under cooling (the bath temperature did not exceed 25 °C)

and stirring the electrolyte. The current density was varied in the range of 1 to 5 A/dm², the processing time was 30 to 60 min. Since the kinetics of the plasma electrolytic oxidation of metals can vary significantly depending on the acidity of the electrolyte, an important element of the process was monitoring of the electrolytes pH.

4. 2. Research methods

The surface of the samples was studied with using the scanning electron microscope ZEISS EVO 40XVP. The images of the sample surface were obtained through detecting secondary electrons by an electron beam scanning surface, which provided high resolution and contrast in investigating the surface topography. The chemical composition of the surface was determined by analyzing the characteristic X-ray spectrum recorded by the energy-dispersive spectrometer Oxford INCA Energy 350 that was integrated into the software environment SmartSEM. The X-ray excitation was performed by irradiation of the samples with an electron beam of 15 kV.

The phase composition and the structure of the synthesized oxide coatings were analyzed, using the X-ray diffractometer DRON-2.0 in the emission of an iron anode. The diffraction patterns were recorded in a discrete time interval of 0.1° at exposure of 15 to 20 seconds in each point. The elemental composition of the coatings was determined by the X-ray fluorescence method with the use of a portable X-ray spectrometer, which was the universal technical fluorescent device "Sprut", with the relative standard deviation of 10⁻³–10⁻².

The abrasion rate for the materials $\Delta l/\Delta t$ was determined by the Calotte method on the calotester [19].

The catalytic properties of the synthesized PEO coatings were analyzed through using the model reaction of converting CO into CO₂. The experimental study was carried out on a laboratory bench in a tubular flow reactor made of quartz glass with a coaxially wound heating coil. Inside the reactor, there was an inlaid catalyst whose apparent surface area was (4–5)·10⁻² dm². The initial mixture of air with carbon(II) oxide of a 1.0 % concentration was fed to the reactor at a rate of 0.025 dm³ per minute. The reactor temperature was raised from 20 °C to 450 °C at a rate of 1°C per second. The concentration of carbon(II) oxide at the inlet and the outlet of the reactor was measured by using the sensor and analyzer system "Dozor". The catalytic activity was evaluated by the following parameters: the initial temperature of the oxidation process (the ignition temperature, T_i) and the conversion extent (X, %). The extent of conversion was calculated by the following equation:

$$X = \frac{c(\text{CO})_i - c(\text{CO})_f}{c(\text{CO})_i} \cdot 100 \% \quad (1)$$

where $c(\text{CO})_i$ and $c(\text{CO})_f$ are the initial and the final concentrations of carbon(II) oxide, %.

5. The results of forming oxide coatings on the VT1-0 alloy as well as the discussion of their structure, morphology, and properties

The voltage chronograms for the plasma electrolytic oxidation of the titanium alloys (Fig. 1, *a*, *b*) in all the

researched electrolytes have a classic geometry with the division into specific areas: pre-spark, spark, and microarc.

The sections of dependencies that correspond to the pre-spark area of the coatings forming are almost linear, which is explained by the growth of the titania film thickness and a corresponding increase in the resistance. The time before the sparks in all the investigated electrolytes is 1 to 2 minutes at a current density of 2.0–5.0 A/dm².

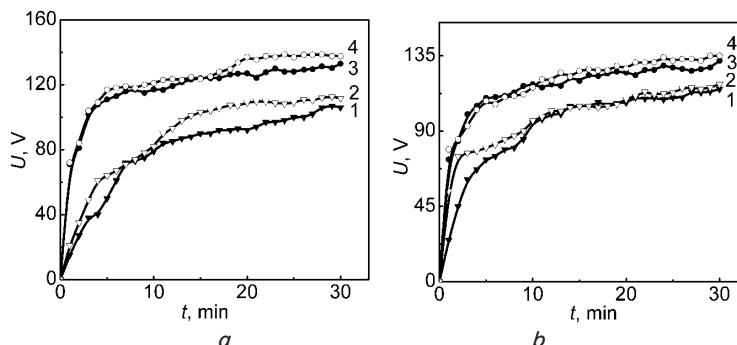


Fig. 1. The voltage chronograms to PEO at VT1-0 alloy in a pyrophosphate electrolyte: *a* – KMnO₄ and *b* – MnSO₄ with different concentrations of manganese salts, mol/dm³: 1.3–0.1 and 2.4–0.3 for *i*; A/dm²: 1.2–2.0 and 3.4–4.0

The pre-spark area for oxide films that are formed in a pyrophosphate electrolyte have a light gray color corresponding to the titanium(IV) oxide. The sparking voltage is in the range of 55 V to 65 V, and the PEO process stabilization occurs at the voltages of 120 V to 140 V (Table 2).

Table 2

Parameters of the coating formation process

Process parameters	Electrolyte				
	1	2	3	4	5
Sparking voltage U _i , V	55	65	65	65	65
Process voltage U _{PEO} , V	120	130	140	130	120

In the transition to the sparking section, the U, t dependence stops being linear, and the voltage growth slows down significantly, apparently due to the inclusion of the electrolyte components into the coating. This is particularly evident in the formation of coatings in manganese-containing solutions when black freeforms begin to appear in the anode areas, primarily occurring at sharp edges and in defect surface sites. On the basis of the color gamut of MnO_y (Table 3), we can confidently assert that the dark areas are formed by manganese oxides of different oxidation number.

In the microarcs mode, the amount of inclusions increases, and they gradually cover the entire surface of the electrode, wherein the process voltage practically remains unchanged; however, in all U, t dependencies there are observed small oscillations that appear to be associated with different electrical resistivities of the produced mixed oxides (Table 3).

When synthesized in the pyrophosphate electrolyte, oxide coatings on VT1-0 resemble enamel (Fig. 2, *a*): on their surface areas of blue and golden-yellow colors appear, which correspond to the oxides of TiO₂, Ti₃O₅, and TiO. The results of the X-ray analysis confirm that the coatings in the conversion layer contain a mixture of the titanium oxides: Ti₃O₅, TiO₂, and TiO (Table 4) [20].

Table 3

The electrical resistivity and thermal stability of the oxides

Oxide	Electrical resistivity ρ (Om-cm) at 293 K	Color	Conductivity type	Thermal stability
Ti				
TiO _x ($x=0.92-1.26$)	$3 \cdot 10^{-3}$	light bronze metal	metallic	1,198–1,298 K $3TiO_2+Ti \rightarrow 2Ti_2O_3$
Ti ₂ O ₃	10^5	purple	s/c* n-type	1,698–1,798 K $TiO_2+Ti \rightarrow 2TiO$
TiO _{1.75-1.97} TiO _{1.98-2.00}	10^5-10^{13}	from blue-steel through dark blue and straw-yellow to white	s/c n-type	1,198–1,598 K $6TiO_2 \rightarrow 2Ti_3O_5+O_2$
TiO ₂ (anatase and rutile)	10^{13}	light gray	s/c n-type	1,698–2,298 K $6TiO_2 \rightarrow 2Ti_3O_5+O_2$
Mn				
MnO	10^9-10^{12}	green	dielectric	–
Mn ₂ O ₃	10^5	brown	s/c	1,238–1,388 K $6Mn_2O_3 \rightarrow 4Mn_3O_4+O_2$
Mn ₃ O ₄	10^4-10^5	Black-brown	s/c p-type	1,858 K $2Mn_3O_4 \rightarrow 6MnO+O_2$
MnO ₂	$10^{-1}-2.8 \cdot 10^{-3}$	black	s/c n-type	828–883 K $4MnO_2 \rightarrow 2Mn_2O_3+O_2$

Note: * – s/c – semiconductor

Table 4

The phase composition of the coatings

The electrolyte composition of PEO, mol/dm ³	The phase composition of the coatings
K ₄ P ₂ O ₇ – 1	TiO, TiO ₂ , and Ti ₃ O ₅
K ₄ P ₂ O ₇ – 1 KMnO ₄ – 0.3	TiO, TiO ₂ , Ti ₃ O ₅ , MnO _{1.88} , MnO, MnO ₂ , and Mn ₂ O ₃
K ₄ P ₂ O ₇ – 1 MnSO ₄ – 0.3	TiO, TiO ₂ , Ti ₃ O ₅ , MnO _{1.88} , Mn ₃ O ₄ and Mn ₂ O ₃

The inclusion of manganese oxides in the coating leads to a change in the surface morphology (Fig. 2, b). On the surface of the oxide systems that were formed by a plasma electrolytic oxidation in a solution of 1 M potassium pyrophosphate, sufficiently large areas of the amorphous glassy film alternate with tubular porous sections (Fig. 2, a, b). The surfaces of the coatings with mixed oxides TiO_xMnO_y are more uniform; they clearly display visible spheroidal grains, and a 5,000 magnification reveals the oxides' tubular structure (Fig. 2, b, d).

The dependencies of the thickness of coatings on the PEO current density in the researched electrolytes are linear (Fig. 3). The specific thickness increment per unit of the current density in the pyrophosphate electrolyte $dh/di=5 \text{ mkm}/(\text{A} \cdot \text{dm}^{-2})$ is less than in manganese-containing electrolytes, which is $9 \text{ mkm}/(\text{A} \cdot \text{dm}^{-2})$ for KMnO₄ and $12 \text{ mkm}/(\text{A} \cdot \text{dm}^{-2})$ for MnSO₄ during the same time of the electrolysis.

The influence of the electrolyte composition on the coating thickness obtained at the same current density relates to the formation of mixed oxide systems; moreover, in MnSO₄-containing electrolytes, the thickness and, consequently, the oxidation rate for the same final synthesis voltage, are higher. The inclusion of manganese oxides into conversion coatings that are based on titanium alloys naturally affects the field strength E_{gk} in the coating (Table 5).

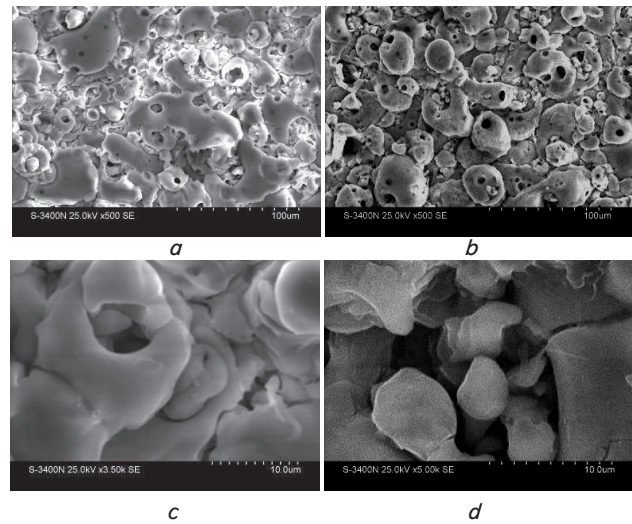


Fig. 2. The morphology of PEO coatings on the VT1–0 alloy obtained from solutions, mol/dm³: a and c – K₄P₂O₇ – 1; b and d – K₄P₂O₇ – 1, and KMnO₄ – 0.1. Magnification: a and b – 500; c and d – 5,000

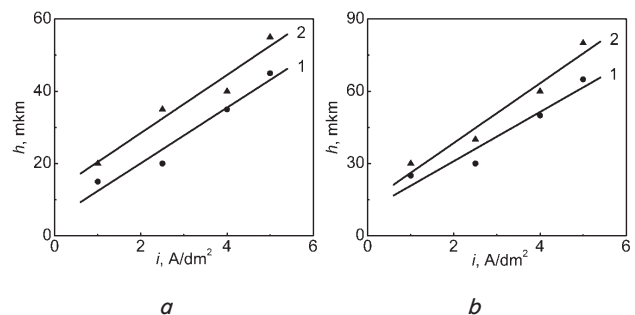


Fig. 3. The dependence of the coating thickness on the current density in the pyrophosphate electrolyte, which contains: a – KMnO₄, b – MnSO₄ with different concentrations of manganese salts, mol/dm³: 1 and 3 – 0.1; 2 and 4 – 0.3

Table 5

The field strength in the PEO coatings obtained in different electrolytes at $j=5 \text{ A/dm}^2$

Electrolyte	1	2	3	4	5
$U_k, \text{ V}$	120	130	140	130	120
$h \cdot 10^6, \text{ m}$	45	55	45	65	80
$E_{gk} \cdot 10^{-6}, \text{ V/m}$	2.67	2.36	2.27	2	1.75

The observed decrease in the field strength E_{gk} depends on the presence, besides titanium, of manganese and phosphorus, which are fairly evenly distributed throughout the thickness of the coating (Fig. 4, *a, b*), and also of trace quantities of potassium.

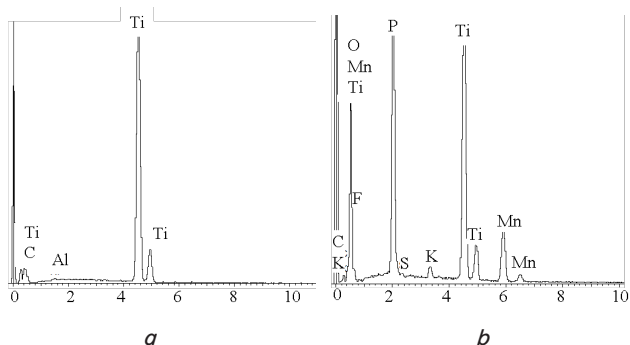


Fig. 4. The radiographs and the VT1-0 alloy composition, wt%: *a* – before the PEO: C – 0.13; O – 0.27; Ti – 99.60; *b* – after the PEO in the solution, mol/dm³: $K_4P_2O_7$ – 1.0, $MnSO_4$ – 0.1; $i=1.5 \text{ A/dm}^2$: C – 4.62; O – 48.69; P – 14.36; K – 0.96; Ti – 20.34; Mn – 11.03.

It is particularly noteworthy that the content of phosphorus in all coatings is higher at the oxide – solution interface versus lower deep down to the oxide – Ti boundary, whereas the content of titanium regularly increases in the same direction (Fig. 5).

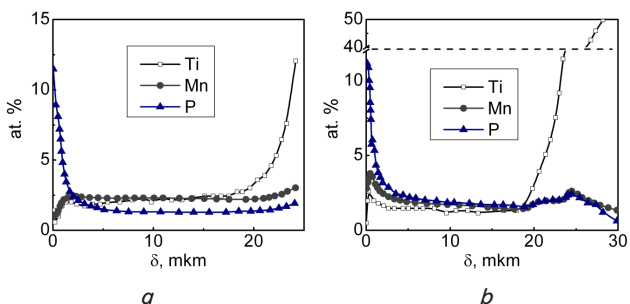
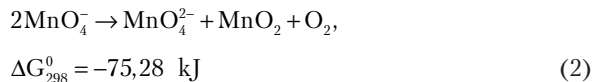


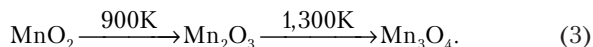
Fig. 5. The distribution of the major components throughout the thickness of the PEO coatings produced in a pyrophosphate electrolyte that comprises: *a* – $KMnO_4$ and *b* – $MnSO_4$, with up to 100 % of oxygen. The coordinate $\delta=0$ corresponds to the coating surface

The amount of manganese in the oxide systems depends on the nature of the dopant: the electrolyte $K_4P_2O_7+KMnO_4$ was used to form coatings with an even distribution of Mn throughout the thickness at the level of 2.5–2.7 at. %, and it did not exceed 1 at. % on the surface $\omega(Mn)$. The electrolyte $K_4P_2O_7 + MnSO_4$ was used to obtain oxide systems containing manganese in the surface layer at 3.8–4.0 at. %, which was more conducive to the implementation of catalytic reactions.

Of course, the reason of this difference is the diversification of the base metal and Mn(II) oxidation routes, whereas in the $KMnO_4$ -contained solutions manganese can be included in the coating only after thermochemical reactions in the arcing zone [21]:



and high temperature conversions



It should be noted that the composition and structure of the complex oxide coatings are significantly affected by the current density of the forming. As can be seen from Fig. 6, *a*, PEO at current density of 1 A/dm² provides uniform microporous oxide coatings, and at 1.5 A/dm² the morphology changes: the roughness of the surface and the number of toroid-like coating sections increase (Fig. 6, *b*). Thus, an increase in the current density during PEO allows obtaining materials with a more developed surface area, which creates conditions for increasing the catalytic activity of the materials.

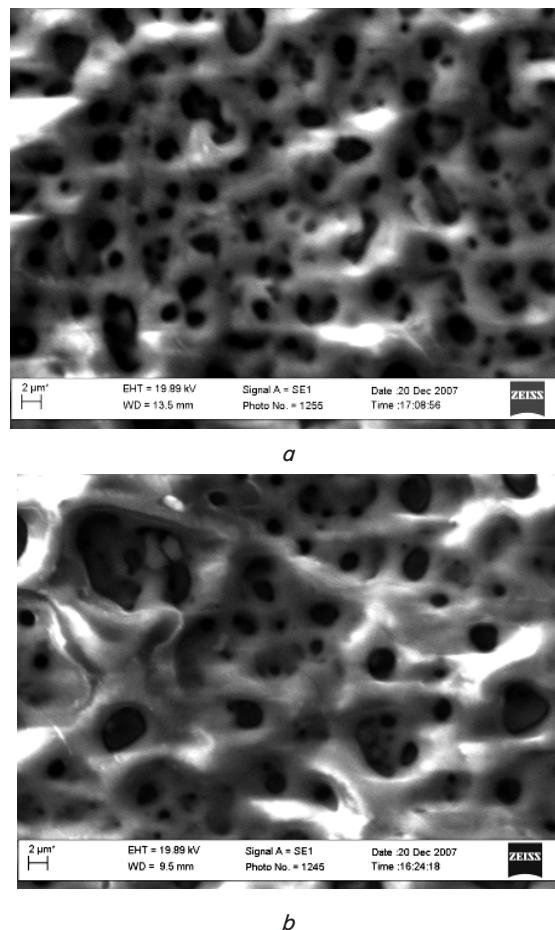


Fig. 6. The photomicrographs of the surface $TiO_x \cdot MnO_y$ formed at current densities, A/dm^2 : *a* – 1.0 and *b* – 1.5. Magnification by 2,000

The results of testing the catalytic activity of the coatings with the mixed manganese-based oxides show that the

ignition temperature T_i corresponding to the top efficient operation of a catalyst for the synthesized $TiO_x \cdot MnO_y$ systems is in the range from 250 °C to 270 °C, which is slightly higher than for platinum-based ones (200 °C), and the complete conversion of CO is achieved at 400 °C (Table 6).

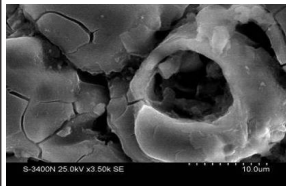
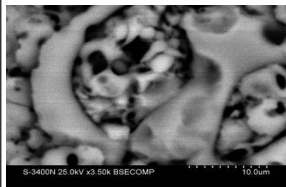
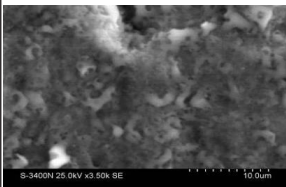
Table 6

The indicators of the catalytic activity of the materials in the oxidation reaction of CO

Catalyst material	The content of the active ingredient ω , wt %	Conversion extent X, %	Ignition temperature T_i , °C
Pt [22]	100	100	200
Pt _{exp}	100		
TiO _x ·MnO _y	$\omega(Mn)=7.5$	100	250

An important operational characteristic of functional materials that defines their service life under operating conditions is resistance to external influences. One of the most important indicators of reliability is resistance of coatings to abrasion, which essentially depends on their composition and surface morphology [23]. It has been determined that higher contents of manganese and titanium in mixed oxide systems decrease the grain size and facilitate formation of a microglobulin surface (Table 7) due to randomization of electrochemical and thermochemical reactions throughout the surface and inside the oxide layer.

The resistance of the oxide coatings to abrasion

Electrolyte composition, mol/dm ³	Photomicrographs of the coating surface, $\times 2,000$	The coating composition*, at. %	Abrasion rate, $\Delta l/\Delta t$, mkm/h
$K_4P_2O_7 - 1$		Ti – 31.28 O – 53.40 P – 11.53 K – 3.79	2.50
$K_4P_2O_7 - 1$ $MnSO_4 - 0.05$		Ti – 40.11 Mn – 1.00 O – 48.75 P – 8.42 K – 1.72	1.85
$K_4P_2O_7 - 1$ $MnSO_4 - 0.1$		Ti – 40.73 Mn – 3.17 O – 47.42 P – 8.05 K – 0.63	0.81

The tendency to a reduced abrasive wear rate really coincides with the observed grain refinement and smoothing of the surface layers (Table 7). Certainly, the tribological properties of the oxide systems also increase in case of a lower content of potassium, as it is known [24] that inclusion of alkali metal oxides loosens the structure of mixed oxides.

Thus, the process of plasma-electrolytic oxidation in a Mn (II)-containing solution on the surface of titanium alloys results in the formation of the complex oxide layers $TiO_x \cdot MnO_y$. These are the mixed oxides of titanium TiO , Ti_3O_5 , and TiO_2 with manganese MnO_2 , Mn_2O_3 , and Mn_3O_4 , as evidenced by the results of studying the phase composition of the coatings.

6. Conclusion

1. The study has rationalized the choice of electrolyte components and their advisable concentrations and determined the current density range for the PEO of the VT1-0 alloy. The analysis of the forming dependencies in a plasma electrolytic oxidation mode has revealed that the VT1-0 alloy oxidation happens by the classical scheme, which comprises the steps of forming a barrier layer, spark oxidation, and microarc oxidation.

2. It has been shown that the plasma electrolytic oxidation of the VT1-0 alloy in pyrophosphate solutions facilitates the formation of enamel-like oxide coatings of a microglobular morphology; according to the results of the X-ray analysis, such coatings include a mixture of the titanium oxides Ti_3O_5 , TiO_2 , and TiO . By varying the concentration of the electrolyte and the current density for forming, it is possible to control the chemical and phase compositions of coatings as well as the topography of the surface and the grain size. The study has proved the possibility of including manganese into oxide coatings by incorporating the components of the electrolyte into the growing oxide phase and subsequent chemical and thermal transformations, which allows forming mixed conversion compositions on the VT1-0 alloy surface.

3. The research findings have determined that coatings formed in the PEO mode with reduction of the grain size and formation of a microglobular structure have an increased abrasion wear resistance and an intense catalytic activity in carbon monoxide oxidation reactions. Thus, there is a prospect of using such coatings in the industrial systems of catalytic purification of exhaust gases of industrial plants and power system facilities.

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