Comparative Analysis of the Composition, Structure, and Catalytic Activity of the NiO−CuO−TiO$_2$ on Titanium and NiO−CuO−Al$_2$O$_3$ on Aluminum Composites

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Abstract—The catalytically active oxide structures based on Al and Ti prepared by plasma-electrolytic oxidation (PEO) and additionally modified by impregnation with an aqueous solution of nickel and copper nitrates followed by annealing were studied. The oxide film−metal composites were studied using X-ray diffraction and X-ray spectroscopic analysis, X-ray electron spectroscopy, and electron microscopy. The catalytic activity of the composites in the reaction of CO oxidation was studied. In spite of differences in the elemental composition and morphology, the initial oxide layers on Al and Ti were comparable in terms of activity. Microgranules of size ~1 μm and formations from tens to hundreds of nanometers in size were detected on the surface of PEO layers. The modified layers contained crystalline CuO, NiO, and Al$_2$O$_3$ or TiO$_2$ phases. The surface layers of the modified structures about 3 nm in thickness on AMg5 aluminum alloy and VT1-0 titanium had the same elemental composition but exhibited different activity in the reaction of CO oxidation to CO$_2$.

INTRODUCTION

Catalysts on metal supports are characterized by high thermal conductivity and mechanical strength, and they can be variously shaped [1]. In many cases, a sublayer or a secondary support, which improves adhesion to the substrate and increases the specific surface area of the catalyst, as compared with that of metal, should be used for the deposition of a catalytically active mass on a metal substrate. This problem can be solved in various manners. For example, a procedure used for the preparation of steel surfaces involved the following three stages [2]: support aluminizing, high-temperature oxidative annealing in a flow of air (in this case, a surface Al$_2$O$_3$ film was formed), and impregnation with an aqueous solution of a salt of the active component (Ni, Cu) followed by oxidative or reductive annealing. This facilitated the generation of a developed contact surface and the formation of active sites on it. Iron alloys containing aluminum can also be used as metal substrates. An aluminum oxide sublayer can be produced by oxidizing these substrates [1]. The solution of this problem is facilitated by the use of valve metals as metal substrates. A secondary support—an anodic oxide film onto which catalytically active mass is supported—is formed on their surface. For example, supporting is performed by the impregnation of M/MO$_x$ composites (M is a metal) with a solution of corresponding salts followed by annealing [3]. Composites as anodized aluminum foil

with supported catalytically active mass are frequently used [4]. The possibility of regulating the coating texture and the size and number of pores by varying anodic treatment conditions belongs to the advantages of an anodized aluminum substrate, and a disadvantage is that the oxide coating consists of only amorphous or partially crystalline aluminum oxide [1, 5].

Plasma electrolytic oxidation (PEO) under the action of electric spark and microarc discharges is used to form oxide layers on valve metals in electrolytes. In the future, this method (which is also referred to as anodic spark deposition, microarc oxidation, anodic treatment at high anodic potentials, and anodic spark electrolysis [6]) can replace currently available techniques for the preparation of both secondary supports [7, 8] and catalytic oxide layers [5, 9, 10] on metal substrates. On the one hand, porous coatings with a certain phase composition of the treated metal oxide can be obtained by regulating the conditions of the PEO formation of a layer (electrolyte, electric parameters, and treatment time). On the other hand, unlike traditional anodic treatment, PEO makes it possible to form structurally complex layers, which include, in particular, catalytically active compounds based on solution components, in a single stage.

Previously [11, 12], we found that oxide layers containing nickel and copper compounds prepared on an aluminum alloy using PEO catalyzed the reaction of CO oxidation to CO$_2$ at temperatures higher than

300°C. In the future, these active oxide coatings can be used in internal combustion engines and industrial processes for the afterburning of discharge gases. Composites of this kind, which are characterized by high thermal and electric conductivity of the metal base, can catalyze reactions that occur with intense heat release or, oppositely, require external heat supply. In particular, they can be used in reactors designed for performing coupled reactions. At temperatures higher than 600°C, it is desirable to use metals such as titanium and zirconium, whose melting temperatures are much higher than those of aluminum and its alloys are, rather than aluminum as a metal base.

It was found [5, 13] that both the composition and the nature of valve metals or alloys affect the catalytic properties of the surface structures formed. Thus, Ni- and Cu-containing PEO coatings on Al−Mg (like AMg), Al−Cu−Mg (like D16), and Al−Mn (like AMts) aluminum alloys exhibited different catalytic activities in the reaction of CO oxidation [13], whereas $NiO/MO_x/M$ composites, where M = Al, Mg, or Ti, exhibited different catalytic activities in the reaction of cyclohexane dehydrogenation to cyclohexene [5].

Based on published data [5, 13], we can expect that PEO structures supported on different valve metals under the same conditions in accordance with a previously described procedure [11] will also exhibit different catalytic activity. The aim of this work was to compare the composition, structure, and catalytic properties of nickel- and copper-containing composites on aluminum and titanium supports prepared by a plasma-electrochemical method [11], including composites additionally modified by impregnation followed by annealing.

EXPERIMENTAL

PEO layers were formed on AMg aluminum alloy (4.8−5.8% Mg, 0.02−0.01% Ti, and the balance Al) and VT1-0 titanium (Ti content of >99.6%). Samples of the following two types were used: flat samples of size $20 \times 20 \times 1$ mm were used to determine the elemental and phase composition of the surface and to measure the thickness of coverage, whereas catalytic tests were performed with Al and Ti wire (1.67 and 2 mm in diameter, respectively) samples with a working surface area of 20 cm².

To standardize the surfaces of samples before coating, they were chemically polished to high luster (surface finish class 8−9) in a mixture of concentrated acids. A mixture of $H_3PO_4 : H_2SO_4 : HNO_3 = 4 : 2 : 1$ (by volume) at 110−120°C and a mixture of HF : $HNO_3 = 1 : 3$ (by volume) at 70°C were used for the treatment of aluminum and titanium, respectively [14]. Then, the samples were washed with distilled water and dried in air at 70°C.

The PEO layers containing nickel and copper compounds on aluminum were formed as described else-

where [11, 12] in an aqueous electrolyte containing 0.066 mol/l Na_3PO_4 + 0.034 mol/l $Na_2B_4O_7$ + 0.006 mol/l Na_2WO_4 + 0.08 mol/l $Ni(CH_3COO)_2$ + 0.025 mol/l $Cu(CH_3COO)_2$. In the case of titanium, an analogous electrolyte was used, in which the concentration of $Ni(CH_3COO)_2$ was 0.1 mol/l. Films were formed under galvanostatic conditions using anodic polarization with the effective current density $i = 0.05-0.1$ A/cm² for 5−15 min. A computer-controlled TER4-100/460 homopolar thyristor generator served as a source of current. A stainless steel bath with a cooling water jacket served as a counter electrode. The electrolyte was stirred with a mechanical stirrer; the temperature of solution was no higher than 30°C.

For the modification of samples with PEO coatings formed at $i = 0.1$ A/cm² for 5 min on aluminum and for 10 min on titanium, they were immersed in an aqueous solution containing 1 mol/l $Cu(NO_3)_2$ and 1 mol/l $Ni(NO_3)_2$. The composites based on aluminum and titanium were kept in this solution for 3 min and 1 h, respectively. Thereafter, the samples were dried over an electric heater in air and annealed in a furnace at 500°C for 2−4 h.

The thickness of layers was determined using a vortex-current layer thickness meter. The elemental composition and morphology were determined on a JXA 8100 electron-probe microanalyzer (Japan) with an INCA energy-dispersive system (United Kingdom). Graphite was preliminarily sputtered onto the films in order to prevent surface charging. X-ray diffraction patterns were obtained on a D8 ADVANCE X-ray diffractometer (Germany) using CuK_α radiation. In the course of X-ray diffraction (XRD) analysis, the EVA search program with the PDF-2 data bank was used.

The composition of a surface layer ~3 nm in thickness was analyzed by X-ray electron spectroscopy (XES). The X-ray electron spectra were measured on an ultrahigh-vacuum system from Specs (Germany) with the use of a 150-mm electrostatic hemispherical analyzer. For ionization, MgK_α radiation was used. The spectra were calibrated against the C $1s$ lines of hydrocarbons, the binding energy of which was taken to be 285.0 eV.

The micrographs of film surfaces on titanium were taken on an ULTRA 55 electron microscope equipped with a special detector from Carl Zeiss NTS GmbH (Switzerland), which made it possible to magnify images by a factor of 900 000 with a resolution to 1 nm.

Catalytic tests were performed using a BI-CATflow4.2(A) multipurpose flow system (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Finely cut samples were placed in the active zone of a quartz tube reactor 0.9 cm in diameter and 3 cm in height. The geometric surface area of the outer layer of the catalyst supported on the aluminum or titanium alloy was 20 or 14 cm², respectively (the surface areas were different because of different wire thicknesses). In preliminary tests, we found that the conversion of CO on the metal supports

Table 1. Thickness and elemental and phase compositions of coatings formed on titanium and aluminum according to X-ray spectroscopic data

Composite	h, μm	Phase composition*	Elemental composition, at %							
			Ni	Cu	P	Ti or Al	O	W	Mg	Na
PEO/Ti	40 ± 2	TiO$_2$ (r) TiO$_2$ (a)	11.9	3.2	8.3	9.5	63.4	1.0	–	3.7
PEO/Ti**	40 ± 2	TiO$_2$ (r) TiO$_2$ (a) NiO, CuO	20.8	12.3	4.5	6.2	55.6	0.5	–	–
PEO/Al	18 ± 1	γ-Al$_2$O$_3$	5.9	0.8	1.3	34.9	55.3	0.3	1.4	–
PEO/Al**	15 ± 1	γ-Al$_2$O$_3$ NiO, CuO	10.0	5.5	0.8	30.9	51.3	0.3	1.2	–

 *r and a refer to rutile and anatase, respectively.
**Additionally impregnated and annealed films.

Table 2. Elemental composition of composite surfaces according to XES data

Element	Concentration*, at %			
	PEO/Al		PEO/Ti	
	initial	after impregnation and annealing	initial	after impregnation and annealing
Cu	1.1(2.3)	17.0(22.0)	5.9(9.8)	16.7(18.6)
Ni	1.5(2.8)	19.4(33.2)	5.5(8.8)	21.0(32.9)
O	30.1(53.1)	43.2(37.1)	42.9(47.1)	42.8(35.9)
C	62.4(24.2)	19.5(6.4)	36.3(17.0)	18.0(11.8)
Na	1.6(3.2)	–	1.5(7.8)	–
P	3.2(7.4)	0.9(1.3)	7.5(9.6)	1.5(0.8)

 * The concentrations of elements on the film surfaces after etching are given in parentheses.

without PEO coatings was no higher than 10% in the test temperature range (from 20 to 500°C). The initial reaction mixture contained 5% CO and 95% air. The gas flow rate was 50 ml/min. The outlet concentrations of CO and CO$_2$ were determined using a PEM-2 IR gas analyzer.

RESULTS AND DISCUSSION

A comparative analysis demonstrated that the initial catalysts on metal supports, in which an unmodified PEO coating served as an active component, were noticeably different in terms of phase and elemental compositions (Tables 1, 2) and surface structure peculiarities (Fig. 1). The thickness of the initial coatings (active components) was $h \approx 40$ or ~20 μm on titanium or aluminum, respectively. The weight fractions of coatings in the test systems varied from 1 to 3%, as calculated based on the measurements of sample weights before and after PEO treatment and after modification.

According to XRD data, coatings on titanium contained crystalline TiO$_2$ phases in anatase and rutile modifications, and coatings on aluminum contained the γ-Al$_2$O$_3$ crystalline phase. According to X-ray

spectroscopic analysis data, aluminum and oxygen mainly occurred in the top layer of the active component 2−5 μm in thickness on the aluminum alloy; that is, this layer mainly consisted of aluminum oxide. On the contrary, the top layer of coatings (active component) on titanium contained several times greater amounts of nickel, copper, and phosphorus; consequently, it was mainly composed of compounds based on electrolyte components.

At the same time, according to XES data, the aluminum concentration on the surface of PEO coatings on an aluminum base (the test layer thickness was ~3 nm) was no higher than 1.5 at %, and magnesium was absent from this surface. Titanium was absent from the surface of coatings (active component) on a titanium base. Thus, the surface of coatings was composed of electrolyte components on both aluminum and titanium. In both cases, considerable amounts of carbon were present on the surface. According to binding energy data, this carbon occurred in both oxidized (C_{CO}) and aliphatic (C_{CC}) states. Copper occurred as Cu$^+$ and Cu^{2+}. After etching the surface with a high-energy argon beam, the carbon content dramatically decreased. In this case, only aliphatic carbon was detected after etching. Copper occurred in
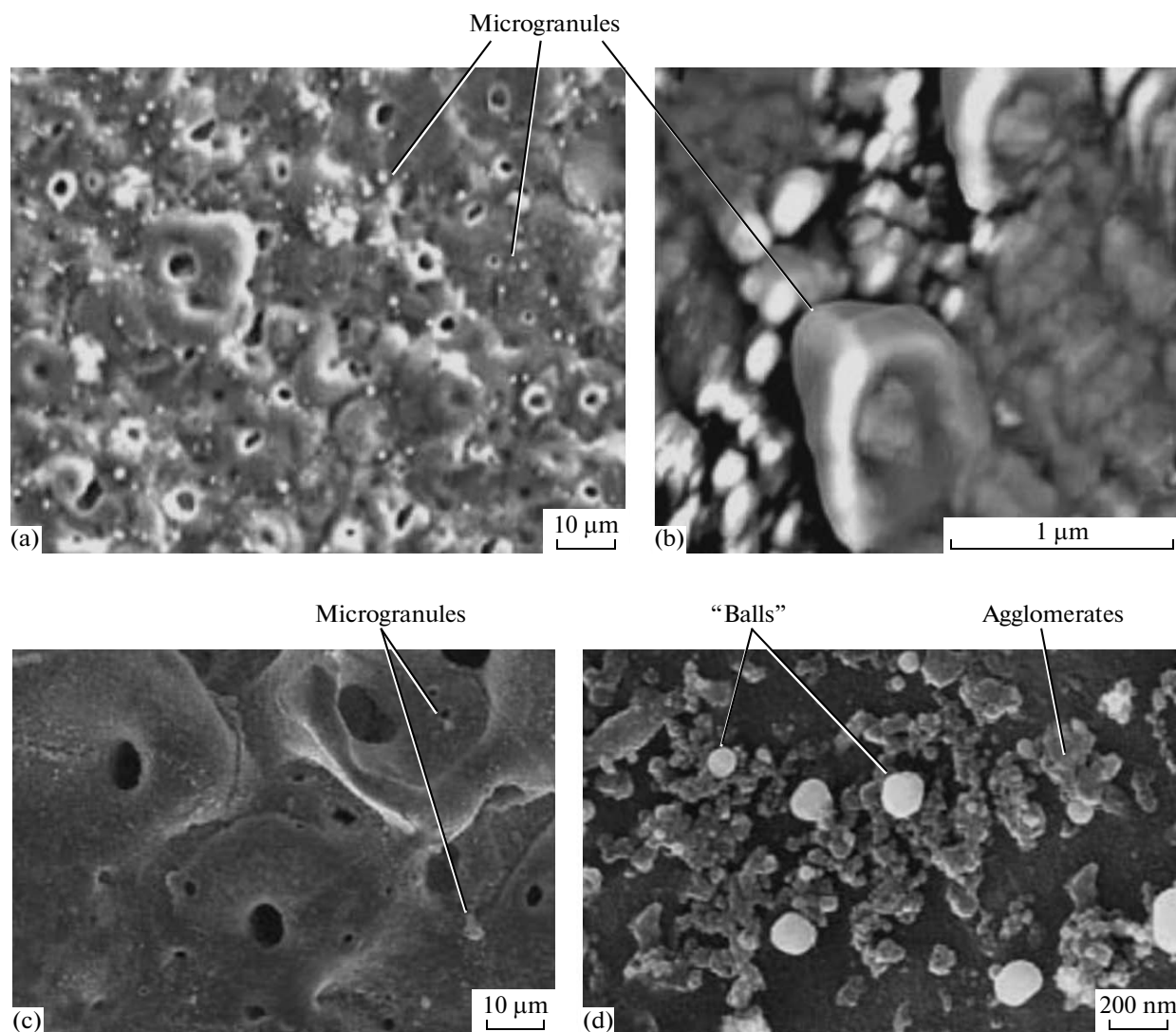
Microgranules

Fig. 1. Surfaces of PEO films on (a, b) aluminum and (c, d) titanium.

the oxidation state of Cu^+ after etching, and the concentrations of copper, nickel, and phosphorus increased. The reduction of copper to Cu^+ can also be a consequence of processes occurring in the course of etching.

The details of the surface relief of coatings (active component) on titanium were noticeably coarser than those on aluminum (Figs. 1a, 1c). On titanium, the sizes of coarse pores (electric breakdown channels) and flowed formations around pores and cavities were greater. Scattered fine particles of size about 1 μm occurred on the coating surface of aluminum. At a higher magnification, it can be seen that these particles (microgranules) were regularly shaped as tapered polyhedral tubes. They were concentrated at surface defect sites. The composition of microgranules was determined by X-ray spectroscopic analysis upon sputtering gold onto the films and concentrating the probe beam at a spot about 1 μm in diameter (Table 3).

A comparison between data given in Tables 1 and 3 indicated that the concentrations of nickel, copper, and other solution components in microgranules here higher and the concentrations of aluminum and oxygen were lower than the average values on the surface of the oxide coating.

On the coating surface on titanium, the concentration of particles of size about 1 μm was noticeably smaller. In high-resolution micrographs, it can be seen that, in this case, scattered particles tens and hundreds of nanometers in size occurred on the surface of flowed formations (Fig. 1d). Formations of the following two types were present: spherical ones and irregularly shaped agglomerates. The use of special attachments to the instrument allowed us to determine elemental composition at particular points on the surface. In this case, analysis was performed by concentrating the probe beam on an area of about 50×50 nm. The elemental composition of agglomerates

Table 3. Elemental composition of microparticles on the surface of PEO films

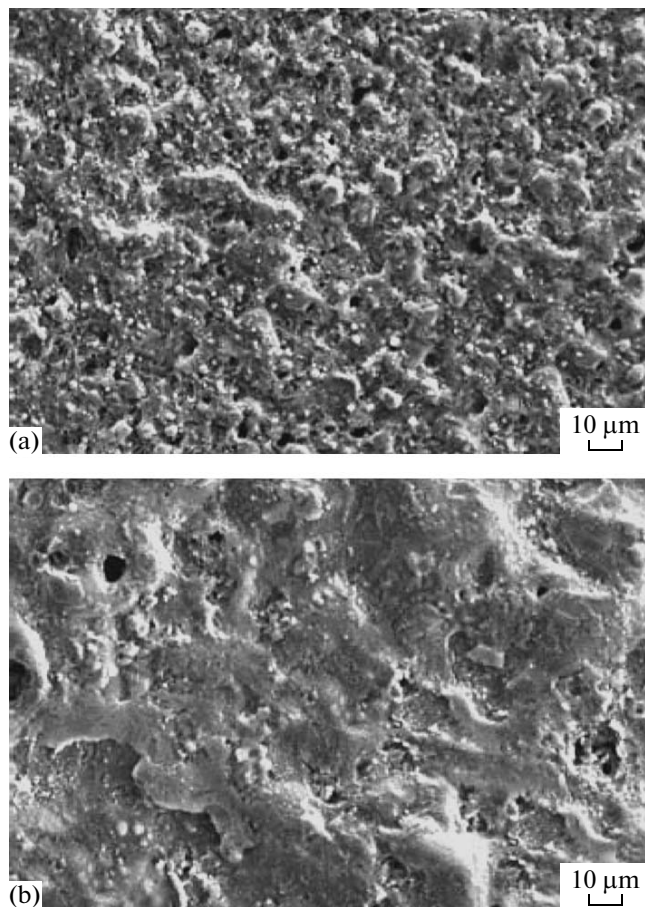| Element	Concentration, at %	
	microgranules on Al	balls on Ti
C	38.4	19.5
O	38.4	46.6
Mg	0.9	–
Al	14.3	–
W	–	0.6
P	–	4.0
Ni	8.2	6.0
Cu	1.8	17.1
Ti	–	2.9

was found similar to the composition of bulk films. Spherical formations (balls) mainly contained elements added with the electrolyte, and the amount of carbon and copper was greater than the amount of the other elements (Table 3). As judged from the elemen-

Fig. 2. Surface morphology of modified PEO coatings on (a) aluminum and (b) titanium.

tal composition, the agglomerates were composed of the electric discharge erosion products of the bulk films. It is likely that spherical formations, as well as microgranules, were formed based on electrolyte components in accordance with a mechanism considered previously [15] at sites where the solution became locally supersaturated under the action of electric discharges in the near-electrode space.

After additionally impregnating the samples with a solution of copper and nickel nitrates followed by annealing, a layer (shell) was formed on the surface to smoothen the relief of the initial coatings of an active component (Fig. 2). In this case, the NiO and CuO oxides were the constituents of the active component in addition to support metal oxides. Because titanium, aluminum, phosphorus, tungsten, and magnesium (see Table 1), which were absent from the impregnating solution, occurred in the test layer (2−5 μm) after modification, it is believed that the resulting shell either was nonsolid or had a thickness of 2−5 μm or smaller. It is likely that both of these factors make their contributions. In this context, note that the total thickness of the initial coating with the shell did not increase as a result of modification (Table 1). Poor adhesion between the shell and the surface should also be noted. The supported layer spread and partially crumbled away upon cutting or sharply bending the samples. In this case, the shorter the impregnation time (i.e., the smaller the shell thickness), the stronger the adhesion.

According to XRD data (Table 1), the constituents of the active component (shell + coating) of modified catalysts on titanium or aluminum supports were crystalline NiO, CuO, and TiO_2 in rutile and anatase modifications or NiO, CuO, and γ-Al_2O_3, respectively.

According to XES data, the surface compositions of active components on both aluminum and titanium (shell + coating) after impregnation were almost the same (Table 2), although the durations of this procedure were different. As compared with the initial PEO coating, the surface concentrations of copper and nickel (in a layer of ~3 nm in thickness) increased by a factor of tens on aluminum or several times on titanium. In both cases, the major portion of copper occurred as Cu^+ and entered into the composition of X-ray amorphous compounds because the crystalline phases of univalent copper compounds were not detected by XRD analysis. Tungsten, sodium, and magnesium were absent from the surface of impregnated samples, whereas the phosphorus content decreased several times. However, as well as on the surface of the initial films, oxidized and aliphatic carbon occurred on this surface. Carbon-containing compounds were absent from the impregnating solution, and the relatively large amount of carbon on the surface may be explained by the following reasons: surface contamination, the sorption of carbon-containing compounds from air, and the formation (or encapsulation) of carbon-containing compounds in the

course of the formation of oxide structures. After etching the impregnated samples, as well as the initial PEO films, the carbon content decreased, and only aliphatic carbon remained in the surface layer.

A common feature of both of the catalytic structures (coating or shell + coating) is a noticeable increase in the nickel content after the removal of a top layer several tens of angstrom units in thickness by etching. In this case, the change in the nickel content of the modified structures caused by etching was approximately consistent with the change in the carbon content. It is likely that the decreased nickel content of the surface layer was due to the sorption of carbon-containing compounds at nickel-containing sites; these carbon-containing compounds were removed by etching to make nickel compounds accessible.

Figure 3 shows data on the catalytic activity of the resulting composites on Ti and Al in the reaction of CO oxidation to CO_2. As can be seen, the initial (unmodified) composites exhibited almost the same activity under the experimental conditions. However, a difference between them appeared after additional impregnation. Thus, the temperatures of the 50% conversion of CO (T_{50}) on the initial aluminum and titanium samples were 410−460 and 410−450°C, respectively, or 310−320 and 210−240°C, respectively, on the modified samples. Thus, in spite of the differences in the elemental and phase compositions and surface structures, the initial composites based on titanium and aluminum exhibited approximately the same activity in the reaction of CO oxidation to CO_2. At the same time, modified layers on both titanium and aluminum supports were different in terms of activity; according to XES data, the external layers contacting with a gas atmosphere had the same elemental composition. This can be due to both differences in surface morphologies and the effect of the bulk compositions of the coatings. Layers on titanium contained a TiO_2 phase in the bulk, whereas layers on aluminum contained the γ-Al_2O_3 phase. At this stage of studies, it is difficult to explain why the initial layers on aluminum and titanium had the same activity, although their elemental and phase compositions were different. This may be due to the presence of the same active surface sites in approximately the same concentrations. It is likely that, in the PEO films on titanium containing several times greater amounts of nickel and copper, a portion of these elements occurred as the constituents of catalytically inactive phosphates, and this facilitated the equalization of active oxide concentrations in both of the catalysts. This problem should be studied additionally.

Thus, the composites formed on titanium and aluminum by the PEO method under identical conditions with the use of an electrolyte containing nickel and copper compounds were different in terms of the thickness, composition, and morphology of oxide layers. On the surface of the coatings, microgranules
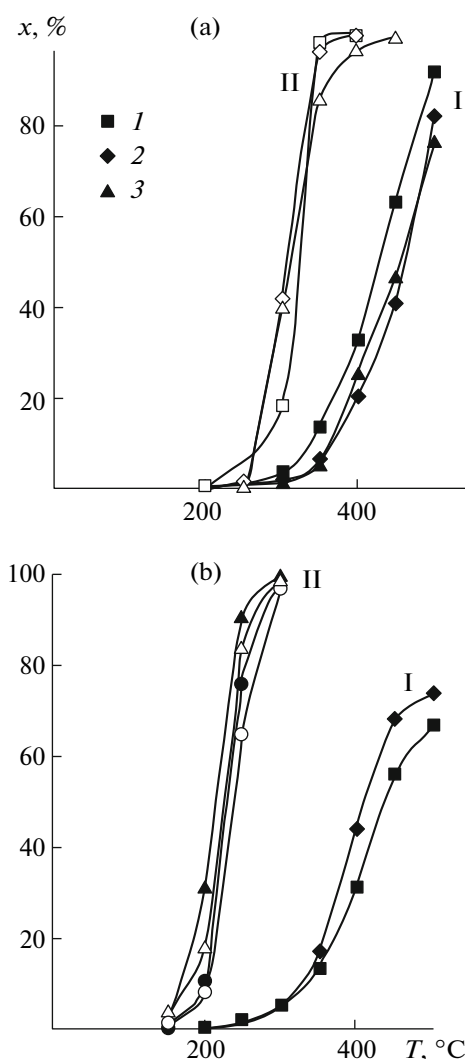
Fig. 3. The temperature dependence of (x) CO conversion into CO_2 on (a) aluminum and (b) titanium composites. Light points refer to the initial PEO coatings; dark points refer to the modified PEO coatings on aluminum obtained under the following conditions: (*1*) $i = 0.1$ A/cm^2, $t = 5$ min; (*2*) $i = 0.1$ A/cm^2, $t = 10$ min; and (*3*) $i = 0.05$ A/cm^2, $t = 15$ min. All of the PEO coatings on titanium were obtained at $i = 0.1$ A/cm^2 for 10 min. Curves IIa, Ib, and IIb were obtained in different cycles of catalytic tests.

about 1 μm in size and particles from tens to hundreds of nanometers in size were present. The composition of the microgranules and nanosized particles was characterized by an increased concentration of the elements that were the electrolyte constituents. It is likely that dispersed formations were responsible to an extent for the catalytic activity of the oxide structures. To 35−60 at % carbon occurred in the surface layer of the coatings. The modified active layers (shell + coating) contained CuO and NiO phases along with the crystalline phases of TiO_2 or Al_2O_3. In spite of differences in the composition and morphology of the initial

PEO structures on AMg5 aluminum alloy and VT1-0 titanium, their activity in the reaction of CO oxidation to CO_2 was approximately the same. Modification noticeably increased the catalytic activity.

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