NEW SUBSTANCES, MATERIALS, AND COATINGS

Catalytically Active Cobalt—Copper-Oxide Layers on Aluminum and Titanium

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Abstract—Oxide coatings modified with cobalt and copper oxides are obtained on titanium and aluminum by means of combining plasma electrolytic oxidation (PEO) in silicate and zirconate electrolytes and impregnation in nitrate solutions followed by annealing. The effect of PEO coatings that were preliminarily formed on aluminum and titanium in different electrolytes on the composition and surface morphology of cobalt—copper oxide composites and their activity with respect to CO oxidation is studied. The maximum total concentration of cobalt and copper is found to be typical of composite layers based on SiO₂ + Al₂O₃/Al, while the minimum content is observed in the case of layers based on ZrO₂ + TiO₂/Ti, the PEO bases being characterized by the highest and lowest water-absorbing capacity, respectively. The effect of PEO coatings on the catalytic activity of cobalt–copper oxide catalysts decreases in the series SiO₂ + TiO₂/Ti > SiO₂ + Al₂O₃/Al > Ce₂O₃ + ZrO₂ + TiO₂/Ti > ZrO₂ + TiO₂/Ti.

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INTRODUCTION

The increasing demands of engineering and the automobile industry for catalysts for the removal of CO and hydrocarbons from exhaust gas emissions makes the development of catalysts that do not involve noble metals, which are critical and expensive materials, a topical task. Catalytic systems based on transition metal oxides, particular spinels, can serve as such catalysts. Copper cobaltites are among the most active spinels [1–3], which, in the opinion of the authors of [3], can be determined by the formation of $CuCo_2O_4$ — Co_3O_4 nonstoichiometric solid solution with a spinel structure.

The deposition of cobalt—copper oxide coatings on metallic substrates taken as grids, corrugated ribbons, porous blocks, etc., promotes the decrease in the gasdynamic resistance and the increase in the heat conductivity of composite materials [4, 5]. For the purpose, one should use a sublayer or a secondary carrier that provides better adhesion of the catalytically active components to the metallic substrate, promotes the formation of a larger specific surface of the catalyst compared to the metal, and induces high dispersity of the active phase.

Such an oxide sublayer on a valve metal can be formed by plasma electrolytic oxidation (PEO), which is a method of anodic or anodic–cathodic treatment of metals in electrolytes under spark or microarc electric breakdowns in the layer near the electrode [6-8]. Particular experimental conditions enable one to synthesize surface layers composed of both oxides of the treated metal in different phase modifications and chemical compounds that involve elements of either the metal and electrolyte or predominantly electrolyte components [9].

As was shown previously, the PEO technique is promising for creating both substrates for catalytically active structures [10, 11] and catalysts themselves [12, 13]. As was found in [14, 15], Co-containing oxide layers on titanium formed by means of combining plasma electrolytic oxidation and impregnation (followed by annealing) are more active than are analogous layers formed as a result of one-stage PEO treatment in the presence of precursors of catalytically active compounds introduced directly into the anodizing electrolyte. Additional introduction of copper oxide in the Co-containing coatings should promote the formation of yet more active composite materials. In this case, the result of impregnation should depend on the composition and characteristics of the preliminarily formed PEO layer, as was shown in [16] by an example of Ni- and Cu-containing composites. The role of the secondary carrier, which is the preliminarily formed PEO layer, is to provide a surface with a certain chemical composition and desirable morphology, as well as stable and strong bonds between the catalytically active components and the metal base, and increase their dispersity.

The object of this work was to study the effect of the characteristics of PEO coatings preliminarily formed on aluminum and titanium in different electrolytes on the composition, surface morphology, and catalytic activity of cobalt–copper-oxide composites produced on their base by impregnation.

EXPERIMENTAL

Co- and Cu-containing composites were formed by combining PEO treatment and impregnation followed by annealing. As PEO layers suitable for covering with cobalt and copper oxides, individual Zr-containing or simultaneously Ce- and Zr-containing layers on titanium and silicate layers on either aluminum or titanium were selected. These systems were previously found to be efficient in the formation of catalytically active composites containing transition metals [14–17].

Planar specimens of sheet titanium of VT1-0 grade and AMg5 aluminum alloy with sizes of $2.2 \times 2.2 \times 0.1$ or $0.7 \times 1.4 \times 0.1$ cm were used, as well as helically twisted titanium and aluminum wires with sections of 1.2 and 1.5 mm, respectively. Planar specimens were used for determining the elemental and phase compositions of the surface layer and measuring the thickness of coatings, while helically twisted specimens were used for catalytic tests.

For removing the surface layer of the metal and standardizing the surface before anodizing, titanium specimens were polished in a mixture of hydrofluoric and nitric acids (HF : HNO₃ = 1 : 3) at 70°C for 2–3 s [18]. Aluminum specimens were polished in a mixture of concentrated nitric, sulfuric, and phosphoric acids (HNO₃: H₂SO₄: H₃PO₄ = 1 : 2 : 4 (vol)) at a temperature of 100–120°C for five or six times at a step exposure of 0.5 min and intermediate rinsing in water until a mirror surface was formed [19]. After the chemical polishing, the specimens were washed in tap water, rinsed in distilled water, and dried in air at 70°C.

Solutions for plasma electrolytic oxidation were prepared from distilled water and commercial analytically pure Na₂SiO₃·9H₂O, chemically pure NaOH and Zr(SO₄)₂ · 4H₂O, and Ce₂(SO₄)₃ (as supplied by ALORICH). Three anodizing electrolytes were used for titanium, namely, (I) 0.1 mol/L Zr(SO₄)₂, (II) 0.05 mol/L Zr(SO₄)₂ + 0.025 mol/L Ce₂(SO₄)₃, and (III) 0.05 mol/L Na₂SiO₃ + 0.05 mol/L NaOH. Plasma electrolytic treatment of aluminum was carried out in alkaline silicate bath III solely.

PEO layers were formed galvanostatically upon anodic polarization (conditions are shown in Table 1) with the use of a computer-controlled multifunctional current source created by Fleron Ltd. (Vladivostok, Russia) on the basis of a commercial TER-4/460N thyristor (Russia). Electrochemical cell for anodizing involved a 1-L glass vessel, a coil hollow pipe made of corrosion-resistant 12Kh8N10T steel served as a cathode, and a magnetic agitator. The temperature of the solution in the course of the treatment did not exceed 50° C.

Specimens covered with PEO coatings were impregnated in an aqueous solution containing $1 \text{ mol/L Cu(NO_3)_2}$ and $1 \text{ mol/L Co(NO_3)_2}$. The duration of exposure to the solution was 1 h in the case of titanium specimens and 3 min for aluminum ones. Then, the specimens were dried over an electric range and annealed in a muffle furnace at 500°C for 4 h in air.

The elemental composition and surface morphology of the specimens were determined with a JXA 8100 X-ray spectral microanalyzer (Japan) with an INCA energy-dispersive supplement (United Kingdom). To avoid the surface charging, the specimens were preliminarily covered with a gold layer (in the case of silicate coatings) or carbon layer (for individual Zr- or combined Zr- and Ce-containing layers).

X-ray patterns were obtained with a D8 ADVANCE X-ray diffractometer (Bruker, Germany) in Cu K_{α} radiation. The EVA computer program with a PDF-2 database was used for X-ray phase analysis (XPA).

Analysis of the surface composition was carried out with the use of X-ray photoelectron spectroscopy (XPS). X-ray spectra were recorded with an ultrahigh vacuum system (Specs, Germany) with a 150-mm electrostatic hemispherical analyzer. Ionization was caused by Mg K_{α} radiation. The working vacuum was 2×10^{-7} Pa. Spectra were calibrated with respect to C1s signal of hydrocarbons, the energy of which was assumed to be 285.0 eV.

The thickness of surface layers was estimated with a VT-201 vortex-current gauge, and the roughness of coatings was determined with an Olympus LEXT confocal laser scanning microscope.

The water-absorbing capacity of oxide films formed on titanium and aluminum alloy was estimated gravimetrically. For the purpose, each specimen was preliminarily weighted on an analytical balance, immersed in a 100-mL glass vessel filled with distilled water for an hour, taken away from water, delicately dried with a filter paper, and weighted. The water-absorbing capacity was estimated as follows:

$$B = [(m_s - m)/m] \times 100\%,$$

where m and m_s are the weights of the specimen before and after the absorption of water.

Catalytic tests were carried out in a BI-CATflow4.2(A) universal flow-type system (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Wire specimens covered with PEO coatings (with a geometric surface area of the coating of 20 cm²) and cut in segments of 4–7 mm were placed in the active zone (with a diameter of 0.9 cm and a height of 3 cm) of the pipe quartz reactor. The initial reaction mixture contained 5% CO and air. The gas consumption was 50 mL/min. The exit concentration of CO and CO₂ was measured with a PEM-2 infrared gas analyzer. The studied temperature range was 20– 500°C.

	Conditions of for	rmation					Cha	racteristics of	of coatings	oatings	
Oxide coating/Ti (Al) composite	Electrolyte C mol/I	i,	t,	U _f ,	h,	R _a ,	W,	phase	Cat %	<i>T</i> ₅₀ °C	
	Electoryce, c, mor E	A/cm ²	min	V	μm	μm	%	tion	C, at 70	s T_{50} 1 $-$ $\frac{483}{448}$ $\frac{491}{451}$	2
$\frac{\text{ZrO}_2 + \text{TiO}_2}{\text{Ti}}$	0.1 Zr(SO ₄) ₂	0.2	20	240	14	0.44	0.4	$c-ZrO_2$ ZrTiO ₄ TiO ₂ (r)	6.3 Zr 24.8 Ti 68.9 O		—
$\frac{\text{Ce}_2\text{O}_3 + \text{ZrO}_2 + \text{TiO}_2}{\text{Ti}}$	$0.05 \operatorname{Zr}(\operatorname{SO}_4)_2 + 0.025$ Ce ₂ (SO ₄) ₃	0.2	20	209	20	0.37	1.0	$\begin{array}{c} Ce_2O_3,\\ ZrO_2\\ ZrTiO_4\\ TiO_2\left(r\right) \end{array}$	2.2 Ce 7.8 Zr 21.9 Ti 68.1 O	Ι	_
<u>SiO₂+TiO₂</u> Ti	0.05 Na ₂ SiO ₃ + 0.05 NaOH	0.1	10	250	13	1.42	1.3	$TiO_2(r),$ $TiO_2(a)$	0.4 Na 17.1 Si 10.4 Ti 72.1 O	$\frac{483}{448}$	$\frac{483}{448}$
$\frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{Al}}$	0.05 Na ₂ SiO ₃ + 0.05 NaOH	0.1	10	360	9	1.03	3.4	γ-Al ₂ O ₃	0.9 Na 13.1 Si 23.8 Al 1.5 Mg 60.7 O	<u>491</u> 451	<u>491</u> 451

|--|

i is the current density, *t* is the duration of formation, U_f is the final voltage on electrodes, *h* is the thickness of the layer formed, R_a is the roughness of coatings, *W* is the water-absorbing capacity, *C* is the concentration of elements in the coatings according to the X-ray spectrum analysis, and T_{50} is the temperature of the 50% conversion of CO in the (1) first and (2) second cycles of catalytic tests at increasing (numerator) and decreasing (denominator) temperature, (r)—rutile, (a)—anatase, c—cubic modification.

RESULTS AND DISCUSSION

Conditions of the formation of PEO coatings on titanium and aluminum alloy, as well as their phase and elemental compositions, thickness, roughness, and water-absorbing capacity, are listed in Table 1. Note that in weakly acidic sulfate solutions, the conditions of the process were severer (longer formation at a higher current density) than in the case of alkaline-silicate baths. In this case, the thickest coatings on titanium (about 20 μ m) were formed in Ce- and Zr-containing electrolyte, while the thinnest ones (about 9 μ m) were formed in a silicate bath.

The largest surface roughness is typical of silicate coatings on titanium, which agrees with the data of scanning electron microscopy (SEM). As can be seen in the images shown in Fig. 1, the largest fragments of the surface relief (pores and protuberances) are present on the coatings formed on aluminum and titanium in 0.05 M Na₂SiO₃ + 0.05 M NaOH solution, while the fine porous structure with pore diameters of

 $1-3 \,\mu\text{m}$ is typical of the coatings formed on titanium in Zr-containing electrolytes.

The maximum water-absorbing capacity is observed in the case of silicate coatings on aluminum. The low water absorption of zirconate coatings on titanium confirms once again their hydrophobicity, which was discovered previously [20] based on their wetting angles (close to $\sim 90^{\circ}$).

According to the XPA data (Table 1), all the coatings involve oxides of the metal treated, namely titanium and aluminum. In addition to titanium oxide (with rutile structure), Zr-containing coatings contain crystalline zirconium oxide and titanate. Ce- and Zrcontaining coatings also involve crystalline oxide of trivalent cerium. At the same time, despite the high silicon content in PEO coatings formed on aluminum and titanium in a silicate electrolyte (13–17 at % according to X-ray spectrum analysis (XSA), silicon oxide was not found with XPA. Silicon is present in the coatings in the form of amorphous silica (an amor-



Fig. 1. SEM images of the surfaces of PEO coatings formed on (a-f) titanium and (g, h) aluminum in electrolyte solutions (M): (a, b) 0.05 Zr(SO₄)₂, (c, d) 0.05 Zr(SO₄)₂ + 0.025 M Ce₂(SO₄)₃, and (e-h) 0.05 Na₂SiO₃ + 0.05 NaOH. Images were obtained in (a, c, e, g) relief and (b, d, f, h) phase-contrast modes.

phous halo typical of SiO_2 can be seen in X-ray patterns).

Impregnation of specimens in cobalt and coppernitrate solutions followed by annealing affects the thickness of coatings insubstantially (Table 2). The thickness of impregnated Zr-containing coatings is slightly smaller than that of the original ones, while silicate coatings on aluminum become thicker upon modification.

According to the XPA data (Table 2), the modification results in the appearance of crystalline cobalt and

Composite	h um	Phase	C at %	Co + Cu,	Co + Cu	<i>T</i> ₅₀ , °C	
composite	n, pill	composition	0, <i>ut</i> 70	at %	Σ (Ti, Zr, Ce, Si, Al, Mg)	1	2
$\frac{\frac{\text{Co}_3\text{O}_4 + \text{CuO}}{\text{ZrO}_2 + \text{TiO}_2}}{\text{Ti}}$	10	CuOZrO2, ZrTiO4TiO2(r)	3.2 Co, 1.8 Cu 8.9 Zr, 18.7 Ti 67.4 O	5.0	0.18	245 279	$\frac{269}{270}$
$\frac{\frac{\text{Co}_3\text{O}_4+\text{CuO}}{\text{Ce}_2\text{O}_3+\text{ZrO}_2+\text{TiO}_2}}{\text{Ti}}$	19	$\begin{array}{c} \text{Co}_{3}\text{O}_{4}, \text{CuO}\\ \text{Ce}_{2}\text{O}_{3}, \text{ZrO}_{2}\\ \text{ZrTiO}_{4}\\ \text{Ti}_{0.928}\text{O}_{2}\left(r\right) \end{array}$	2.4 Co, 6.4 Cu 1.6 Ce, 5.8 Zr 17.2 Ti, 66.7 O	8.8	0.36	$\frac{237}{236}$	$\frac{243}{241}$
$\frac{\frac{\text{Co}_3\text{O}_4 + \text{CuO}}{\text{SiO}_2 + \text{TiO}_2}}{\text{Ti}}$	12	Co_3O_4 , CuO TiO ₂ (r), TiO ₂ (a)	3.8 Co, 3.9 Cu 8.7 Si, 20.0 C 8.4 Ti, 55.7 O	7.7	0.45	<u>186</u> 165	$\frac{201}{200}$
$\frac{\frac{\text{Co}_3\text{O}_4 + \text{CuO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}}{\text{Al}}$	12	$\begin{array}{c} \text{Co}_3\text{O}_4, \text{CuO}\\ \gamma\text{-Al}_2\text{O}_3 \end{array}$	6.8 Co, 6.8 Cu 8.1 Si, 11.0 C 14.5 Al, 1.2 Mg, 51.5 O	13.6	0.57	<u>249</u> 274	<u>223</u> 243

Table 2. Characteristics of Co- and Cu-containing composite films deposited on PEO layers of different compositions

(r)—rutile, (a)—anatase.

copper oxides in the coatings (Co_3O_4 is not found in Zr-containing coatings alone), which agrees with the literature data [21].

Thermal decomposition of cobalt (II) and copper (II) nitrates can be described by the following reactions [21]:

$$3\text{Co(NO}_3)_2 \xrightarrow{260^\circ\text{C}} \text{Co}_3\text{O}_4 + 6\text{NO}_2 + \text{O}_2.$$

$$2\text{Cu(NO}_3)_2 \xrightarrow{300^\circ\text{C}} \text{CuO} + 4\text{NO}_2 + \text{O}_2.$$

At 400°C, cobalt and copper oxides can interact with each other to produce spinel [2]:

$$3CuO+2Co_3O_4+\frac{1}{2}O_2 \xrightarrow{400^\circ C} 3CuCo_2O_4$$

And, at 500°C, the spinel decomposes onto the original oxides. The X-ray patterns of Co_3O_4 and $CuCo_2O_4$ are close [2], and the formation of $CuCo_2O_4$ along with Co_3O_4 is quite possible in our case. The composition of the active layer may be $CuO + Co_3O_4 + CuCo_2O_4$.

According to the data of XSA, secondary layers can be arranged in the following series of descending total concentration of transition metals in the coatings: $SiO_2 + Al_2O_3/Al > Ce_2O_3 + ZrO_2 + TiO_2/Ti > SiO_2 + TiO_2/Ti > ZrO_2 + TiO_2/Ti$, in which the maximum and minimum incorporation of Co and Cu is typical of the layers with the highest and lowest water-absorbing capacity (*W*) respectively (cf. Tables 1 and 2). If the total content of cobalt and copper is normalized to the total concentration of inactive substrate elements (neglecting oxygen and carbon), a similar series of the decreasing reduced total concentration looks as follows: (Co + Cu)/(Si + Al + Mg) = 0.57 > (Co + Cu)/(Si + Ti) = 0.46 > (Co + Cu)/(Ce + Zr + Ti) = 0.36 > (Co + Cu)/(Zr + Ti) = 0.18 (Table 2) and coincides with the series of decreasing water-absorbing capacity of the films (Table 1, Fig. 2). Note also that the concentration of copper is higher than that of cobalt in Ce- and Zr-containing composites on titanium.

Comparing the SEM images shown in Figs. 1 and 3, one can see that the surface morphology of the preliminarily applied PEO layer is preserved upon deposition of transition metal oxides. When silicate PEO coatings on aluminum and titanium are used as secondary substrates, a shell composed of cobalt and cop-



Fig. 2. Correlation between the water-absorbing capacity of PEO layers and the reduced concentration of active components in Co- and Cu-containing coatings.



Fig. 3. SEM images of the surfaces of cobalt-copper-oxide composites: (left column) relief and (right column) phase modes.

per oxides seals the surface irregularities and makes the surface relief smoother.

All PEO-layer/Ti (Al) and $(Co_3O_4 + CuO)/PEO-layer/Ti$ (Al) composite materials were tested as catalysts in a model reaction of CO oxidation to CO₂. The change in the conversion of CO depending on temperature was taken as the measure of catalytic activity (Fig. 4). Among composite specimens that do not involve transition metals, a 50% conversion of CO is reached under the considered experi-

mental conditions on silicate coatings alone (Table 1, Fig. 4a). The coatings formed on titanium are more active than those on aluminum alloy. The secondary substrates can be arranged in the following series of descending catalytic activity:





Fig. 4. Temperature dependences of the conversion of CO on PEO layer/titanium (aluminum alloy) composites (a) before and (b, c) after the deposition of cobalt and copper oxides in the (a, b) first and (c) second cycles of catalytic tests.

Upon deposition of cobalt and copper oxides, the temperature of 50% conversion on silicate coatings decreased by 250–300°C. In the first cycle of catalytic tests on all cobalt–copper-oxide catalysts, a counterclockwise hysteresis loop is observed (Fig. 4b), which may indicate the activation of specimens during their contact with the reaction-gas mixture [22], where CO plays the role of an activator. However, already in the second cycle, the catalysts are stabilized (Fig. 4c). According to the X = f(T) plots, the cobalt–copper-oxide catalysts used can be arranged in the following series of descending catalytic activity in the first cycle of catalytic tests:

$$\frac{\boxed{Co_{3}O_{4}+CuO}}{\underbrace{SiO_{2}+TiO_{2}}{Ti}} > \left[\frac{\underbrace{Co_{3}O_{4}+CuO}}{\underbrace{Ce_{2}O_{3}+ZrO_{2}+TiO_{2}}{Ti}} \right]$$
$$> \left[\frac{\underbrace{Co_{3}O_{4}+CuO}}{\underbrace{ZrO_{2}+TiO_{2}}{Ti}} \right] \approx \left[\frac{\underbrace{Co_{3}O_{4}+CuO}}{\underbrace{SiO_{2}+Al_{2}O_{3}}{Al}} \right]$$

(Fig. 4b). In the second cycle, the series changes as follows:

$$\begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{SiO_{2}+TiO_{2}}\\Ti \end{bmatrix} > \begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{SiO_{2}+Al_{2}O_{3}}\\Al \end{bmatrix}$$
$$> \begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{Ce_{2}O_{3}+ZrO_{2}+TiO_{2}}\\Ti \end{bmatrix} > \begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{ZrO_{2}+TiO_{2}}\\Ti \end{bmatrix}$$

(Fig. 4c); this is chiefly because of the activation of coatings formed on aluminum. We can state that the deposition of a catalytically active layer produces nearly no effect on the order of the decrease in the catalytic activity of the PEO-layer/Ti (Al) supports.

It is worth noting that according to the data of [23], by contrast, in the case of the deep oxidation of methane, zirconium dioxide used as a substrate for cobalt and copper oxides enables one to increase the activity of the catalyst compared to the specimens based on MSM-41 and SBA-15 mesoporous silica molecular sieves. In that work, catalysts were produced as a result of impregnation of supports in cobalt and copper formate solutions followed by thermal decomposition. The authors of [23] believe that the higher catalytic activity of a specimen based on zirconium dioxide compared to silicon-oxide catalysts may be due to a certain contribution of the activity of individual ZrO_2 along with the activity of applied 3d metal oxides, whereas mesoporous silica is widely used as a support due to its larger specific surface area.

Comparing the results of catalytic tests to the SEM images shows that composite structures with more strongly developed surfaces are more active both as secondary carriers and in the case of impregnated coatings. Small pores $(1-3 \mu m)$ in individual Zr and combined Ce- and Zr-containing PEO layers can confine the surface sites that contain cobalt and copper oxides and decrease their accessibility. At the same time, the developed surface of silicate coatings promotes the formation of extended surface parts (Figs. 3e-3h), which seem to be more active with respect to the oxidation of CO. The supposition is indirectly confirmed by the results of [24], which indicate the existence of a relation between the catalytic activity and the character of the cobalt ion distribution in Co/SiO_2 and Co/Al_2O_3 systems, namely, the activity of deposited Co systems increases when the distribution of cobalt changes from individual ions to clusters.

Comparison of the results of catalytic tests to the data of XSA does not allow us to draw a conclusion regarding the correlation between the total concentration of active elements in the coatings and their cata-

Composite	Elemental composition, at %.									
Composite	Cu	Со	0	С	Ti (Al)	Zr	Si	S	Cu+Co	C0/Cu
$\frac{\frac{\text{Co}_3\text{O}_4+\text{CuO}}{\text{ZrO}_2+\text{TiO}_2}}{\text{Ti}}$	$\frac{17.9}{26.7}$	$\frac{13.9}{22.1}$	$\frac{48.9}{41.5}$	$\frac{14.8}{5.8}$	$\frac{1.0}{1.5}$	$\frac{1.5}{2.3}$	_	$\frac{1.9}{0}$	$\frac{31.8}{48.8}$	$\frac{0.78}{0.83}$
$\frac{\underline{Co_3O_4+CuO}}{\underline{Ce_2O_3+ZrO_2+TiO_2}}_{Ti}$	$\frac{20.1}{25.6}$	$\frac{14.5}{25.9}$	$\frac{46.7}{36.8}$	$\frac{15.8}{10.9}$	$\frac{0.4}{0}$	$\frac{0.5}{0.8}$	_	$\frac{2.0}{0}$	$\frac{34.6}{51.5}$	$\frac{0.72}{1.01}$
$\frac{\frac{\text{Co}_3\text{O}_4+\text{CuO}}{\text{SiO}_2+\text{TiO}_2}}{\text{Ti}}$	$\frac{13.4}{22.8}$	$\frac{13.1}{30.1}$	$\frac{40.2}{37.9}$	$\frac{33.4}{9.2}$	_	_	_	_	$\frac{26.5}{52.9}$	$\frac{0.98}{1.32}$
$\frac{\frac{\text{Co}_3\text{O}_4 + \text{CuO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}}{\text{Al}}$	$\frac{17.6}{22.2}$	$\frac{16.7}{26.2}$	$\frac{44.2}{46.7}$	$\frac{21.4}{4.8}$	_	_	_	_	$\frac{34.3}{48.4}$	$\frac{0.95}{1.18}$

Table 3. Elemental composition of the surface (numerator) and subsurface (denominator) layers of $Co_3O_4 + CuO/PEO$ layer/Ti (Al) composites according to XPS data

lytic activity. For example, despite the fact that the maximum concentration of cobalt and copper is typical of the composites based on silicate coatings on aluminum, the highest catalytic activity is actually observed in the case of silicate coatings on titanium. At the same time, the series of descending reduced total content of cobalt and copper—namely, (Co + Cu)/(Si + Ti) = 0.46 > (Co + Cu)/(Ce + Zr + Ti) = 0.36 > (Co + Cu)/(Zr + Ti) = 0.18—coincides with the series of descending catalytic activity of cobalt—copper-oxide coatings, at least on titanium:

$$\begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{SiO_{2}+TiO_{2}}\\Ti \end{bmatrix} > \begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{Ce_{2}O_{3}+ZrO_{2}+TiO_{2}}\\Ti \end{bmatrix}$$
$$> \begin{bmatrix} \frac{Co_{3}O_{4}+CuO}{ZrO_{2}+TiO_{2}}\\Ti \end{bmatrix}.$$

The catalytic properties of composite materials are known to be affected by the surface concentration of active components (Table 3). The X-ray electron spectra of the surface layers upon etching with argon are shown in Fig. 5. The general X-ray spectra of all composites are nearly identical. According to the XPS data (Table 3), the total concentration of copper and cobalt in the surface layers of the composite structures is 26.5-34.4 at %, while that in the subsurface layers is 48.4–52.9 at %. Note that the concentration of copper in the surface layers of individual Zr and combined Ce- and Zr-containing composites is higher than that of cobalt. At the same time, in the surface layers of Sicontaining composites, the concentrations of copper and cobalt are equal. On the whole, there is a correlation between the Co/Cu ratio and the catalytic activity of the composite materials-namely, the higher the Co/Cu ratio in the subsurface layer (Table 3), the lower the temperature of the 50% conversion (Table 2) and, hence, the higher composite activities in CO oxidation. In addition, there is no element of the PEO layer, such as silicon, aluminum, and titanium, in the surface layers of silicate coatings on aluminum and titanium, which indicates the formation of a continuous shell of cobalt and copper oxides on the surface. The presence of sulfur, which is a poison for the catalysts of oxidation reactions, in the surface layers of the composite structures based on individual Zr- or combined Ce- and Zr-containing coatings on titanium is caused by the conditions of plasma-electrolytic oxidation carried out in sulfate electrolytes. The higher activity of $Co_3O_4 + CuO/SiO_2 + TiO_2/Ti$ composites can be due to the highest Co/Cu ratio in the subsurface layer, the formation of a continuous shell of cobalt and copper oxides on the surface, and the absence of poisoning components.

Thus, combining plasma–electrolytic oxidation in a number of electrolytes and impregnation in aqueous solutions of Co(II) and Cu(II) nitrates followed by annealing enabled us to produce $Co_3O_4 + CuO/PEO$ layer/Ti (Al) cobalt–copper oxide composites on aluminum and titanium. The maximum total concentration of cobalt and copper was found to be typical of the composite based on SiO₂ + Al₂O₃/Al, while the minimum one was on ZrO₂ + TiO₂/Ti, i.e., on the PEO layers with the highest and lowest water-absorbing capacity, respectively. The secondary carriers formed as a result of PEO treatment can be arranged in the following series of descending effect on the catalytic activity of cobalt–copper composites:





$$SiO_2 + TiO_2/Ti > SiO_2 + Al_2O_3/Al > Ce_2O_3$$
$$+ ZrO_2 + TiO_2/Ti > ZrO_2 + TiO_2/Ti.$$

Copper–cobalt oxide catalysts based on silicate PEO coatings on titanium are found to be most promising materials for further investigations.

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