Composites with transition metal oxides on aluminum and titanium and their activity in CO oxidation

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ABSTRACT

Plasma electrolytic oxidation (PEO) technique and impregnation in nitrate solutions with next air calcinations have been used to obtain the composites with binary oxides of transition metals on aluminum and titanium. The general composite formula is as follows: $CuO + M_xO_y$/PEO-layer/Ti(Al), where M_xO_y is oxide of transition metal (Mn, Fe, Co, Ni). Solutions of $Zr(SO_4)_2$ and of $Zr(SO_4)_2 + Ce_2(SO_4)_3$ as well as of $Na_2SiO_3 + NaOH$ have been used for PEO treatment of titanium, with the last one being used for aluminum treatment alone. The composites have been investigated by XRD, XSA, SEM and XPS. Catalytic tests in oxidation of CO into CO_2 showed that both metal substrate and PEO layer composition impact the composites' catalytic activity. The results were compared with the catalytic test data of aluminum coatings obtained by one-stage PEO technique with precursors of transition metal oxides being added directly into forming solutions.

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1. Introduction

Supported binary oxides of transition metals are known to be of potential use as catalysts in redox reactions [1–3]. Application of metal substrates instead of ceramic monoliths gives to such compositions higher mechanical resistance and thermal conductivity as well as the possibility of obtaining various sophisticated forms adapted to a wide variety of problems and uses [4]. One of the ways to obtain such compositions supported on valve metals (Al, Ti, Zr, Mg, and others) is electrochemical formation of oxide ceramic-like surface structures by spark or arc discharges under anodic or anodic–cathodic polarization (plasma electrolytic oxidation; hereinafter, PEO). 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 [5]) can replace currently available techniques for preparing both secondary supports [6] and catalytic oxide layers [7,8] on metal substrates.

Previously [8], we found that Cu-containing aluminum-supported composites produced by one-stage PEO technique display low CO oxidation activity. Meanwhile, the composites simultaneously containing compounds of copper and other transition metals have higher activity and thermal stability. Based on their decreasing catalytic activity, formed oxide compositions were ranged as: Cu–Ni > Cu–Co > Cu–Fe > Cu–Mn (Fig. 1) [9].

In the works above one-stage PEO method was used, when precursors of catalytic active compounds were directly involved in forming electrolyte. The additional modification of Ni- and Cu-containing

PEO-coatings on aluminum and titanium by impregnation in an aqueous solution of nickel and copper nitrates was followed by annealing results with dramatic temperatures decrease of CO half-conversion [10]. Thus the temperatures of 50% CO conversion (T_{50}) on the initial aluminum and titanium samples were 410–460 and 410–450 °C or 310–320 and 210–240 °C, respectively, on the modified samples.
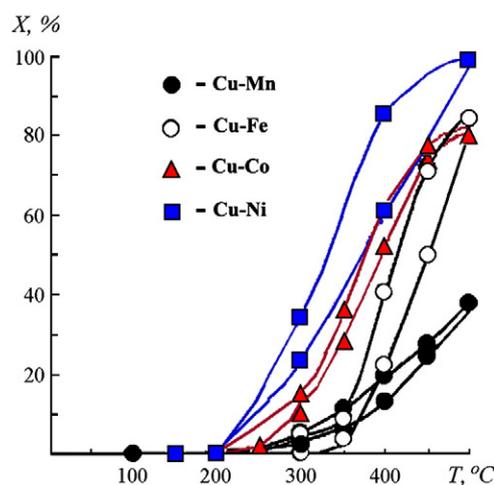
Fig. 1. Temperature dependences of CO conversion (X) for oxide composites on AMg5 aluminum alloy formed by one-stage PEO technique. The precursors of transition metal oxides (acetates of Mn, Co, Ni, Cu(II) and oxalate of Fe(III)) were added directly into phosphate–borate–tungstate electrolyte (PBW-electrolyte). Borrowed from [9].

Table 1
The formation conditions and the characteristics of PEO coatings.

Substrate	Formation conditions				Coating characteristics			
	Electrolyte compositions	i, A/cm^2	τ, min	U_f, V	h, μm	R_a, μm	Phase composition	Elemental composition, at.%
VT1-0	0.1 M Zr(SO$_4$)$_2$	0.2	20	240	14	1.42	TiO$_2$(r) ZrTiO$_4$ c-ZrO$_2$	6.3 Zr 24.8 Ti 68.9 O
VT1-0	0.05 M Zr(SO$_4$)$_2$ + 0.025 M Ce$_2$(SO$_4$)$_3$	0.2	20	209	20	0.37	ZrTiO$_4$ TiO$_2$(r) Ce$_2$O$_3$ ZrO$_2$	7.8 Zr 2.2 Ce 21.9 Ti 68.1 O
VT1-0	0.05 M Na$_2$SiO$_3$ + 0.05 M NaOH	0.1	10	250	13	0.44	TiO$_2$ (r) TiO$_2$ (a)	0.4 Na 17.1 Si 10.4 Ti 72.1 O
AMg5	0.05 M Na$_2$SiO$_3$ + 0.05 M NaOH	0.1	10	360	9	1.03	γ-Al$_2$O$_3$	0.9 Na 13.1 Si 23.8 Al 1.5 Mg 60.7 O

Legend:
(r) is rutile, (a) is anatase, and c-ZrO$_2$ is cubic modification of zirconia.
U_f stands for the final formation voltage.
h is the thickness of PEO coatings.
R_a indicates a surface roughness, determined from microscope measurements.

The objective of the present work is to modify various PEO-layers on aluminum and titanium with binary oxides of transition metals to study their elemental and phase composition as well as their activity in CO oxidation to be able to compare the activity lines of modified composites with the similar lines for composites obtained by one-stage PEO technique.

2. Experimental

2.1. Materials

The PEO layers were formed on AMg5 aluminum alloy (4.8–5.8% Mg, 0.02–0.01% Ti, and the balance Al) and VT1-0 titanium (Ti content > 99.6%). Two types of samples were used: flat samples of 20 × 20 × 1 mm were used to determine the elemental and phase composition of the surface and to measure the thickness of coatings, whereas catalytic tests were performed with Al and Ti wire (1.67 and 1.2 mm in diameter, respectively) samples with a working surface area 20 cm^2.
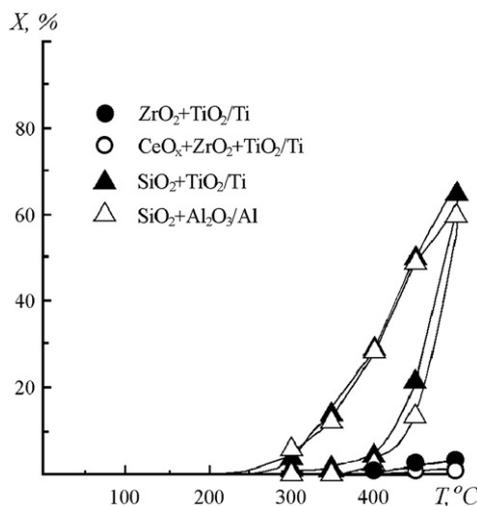
Fig. 2. Temperature dependences of CO conversion (X) for the composites 'PEO-layer/titanium or aluminum alloy'. The composites' formulas are written down based on their elemental and phase compositions (Table 1).

To standardize pre-coating sample surfaces, they were chemically polished to high luster (surface finish class 8–9) in a mixture of concentrated acids. A mixture of H$_3$PO$_4$:H$_2$SO$_4$: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 treating aluminum and titanium, respectively. Then the samples were washed with distilled water and dried by air at 70 °C.

2.2. PEO treatment

PEO solutions were prepared from the distilled water and chemically pure commercial reagents Zr(SO$_4$)$_2$·4H$_2$O, Ce$_2$(SO$_4$)$_3$, NaOH, Na$_2$SiO$_3$·9H$_2$O.

PEO coatings were formed using anodic polarization with the effective current density $i = 0.1$–0.2 A/cm^2 for 10–20 min. The electrolyte compositions and the formation conditions are given in Table 1.

The electrochemical treatment of titanium and aluminum samples was carried out in a thermal glass of 1 l volume. The computer-controlled thyristor unit TER-100/460R-UHL4 (Russia) with unipolar pulse current was used as a power source. The sample under treatment was connected with a positive pole of the power supply while a spiral-shaped stainless steel coil cooled with tap water served as a cathode. The electrolyte in a glass was agitated using a magnetic mixer. The electrolyte temperature was maintained below 35 °C during the process.

Table 2
The impact of PEO-layer/Ti(Al) on phase composition of impregnated composites.

PEO-layer/Ti(Al)	Phase composition			
	Cu–Mn	Cu–Fe	Cu–Co	Cu–Ni
$\frac{ZrO_2+TiO_2}{Ti}$	CuO ZrO$_2$, ZrTiO$_4$ TiO$_2$	CuO, ZrO$_2$ ZrTiO$_4$ TiO$_2$ (r)	CuO, ZrO$_2$ ZrTiO$_4$ TiO$_2$ (r)	CuO, NiO ZrO$_2$, ZrTiO$_4$ TiO$_2$ (r)
$\frac{Ce_2O_3+ZrO_2+TiO_2}{Ti}$	CuO, Mn$_2$O$_3$ Mn$_3$O$_4$ ZrO$_2$. ZrTiO$_4$ Ce$_2$O$_3$, TiO$_2$(r)	CuO, α-Fe$_2$O$_3$ ZrO$_2$, Ce$_2$O$_3$ ZrTiO$_4$ TiO$_2$(r)	CuO, Co$_3$O$_4$ ZrO$_2$, Ce$_2$O$_3$ ZrTiO$_4$ TiO$_2$	CuO, NiO ZrO$_2$ Ce$_2$O$_3$ ZrTiO$_4$ TiO$_2$(r)
$\frac{SiO_2+TiO_2}{Ti}$	CuO(r), Mn$_2$O$_3$ Cu$_{1.5}$Mn$_{1.5}$O$_4$ TiO$_2$(r+a)	CuO, γ-Fe$_2$O$_3$ TiO$_2$(r+a)	CuO, Co$_3$O$_4$ TiO$_2$(r+a)	NiO TiO$_2$(a)
$\frac{SiO_2+Al_2O_3}{Al}$	Cu$_4$O$_3$ γ-Al$_2$O$_3$	CuO γ-Al$_2$O$_3$	CuO, Co$_3$O$_4$ γ-Al$_2$O$_3$	CuO, NiO γ-Al$_2$O$_3$

Table 3
The impact of PEO-layer/Ti(Al) on elemental composition of impregnated coatings (XSA data).

PEO-layer/ Ti(Al)	Elemental composition, at.%			
	Cu–Mn	Cu–Fe	Cu–Co	Cu–Ni
$\frac{ZrO_2 + TiO_2}{Ti}$	1.1 Mn, 3.4 Cu 9.8 Zr 17.5 Ti 68.2 O	1.5 Cu, 3.2 Fe 9.4 Zr 18.4 Ti 67.3 O	1.8 Cu, 1.4 Co 7.3 Zr 18.7 Ti 70.8 O	2.7 Cu, 4.1 Ni 8.4 Zr 17.9 Ti 66.8 O
$\frac{Ce_2O_3 + ZrO_2 + TiO_2}{Ti}$	13.7 Cu, 13.9 Mn 2.1 Zr, 0.7Ce 8.0 Ti 61.6 O	15.9 Cu, 13.9 Fe 0.7 Ce, 1.8 Zr 7.6 Ti 60.1 O	6.4 Cu, 2.4 Co 1.6 Ce, 5.8 Zr 17.2 Ti 66.6 O	6.1 Cu, 12.4 Ni 4.1 Zr, 1.2 Ce 13.7 Ti 62.5 O
$\frac{SiO_2 + TiO_2}{Ti}$	4.1 Mn, 4.0 Cu 9.3 Si, 6.9 C 10.2 Ti 65.5 O	9.1 Fe, 10.6 Cu 13.6 C, 5.8 Si 6.1 TI 54.8 O	3.8 Co, 3.3 Cu 8.6 Si, 20.0 C 8.4 Ti 55.7 O	2.0 Cu, 3.6 Ni 8.2 Si, 15.5 C 11.8 Ti 58.9 O
$\frac{SiO_2 + Al_2O_3}{Al}$	3.2 Cu, 3.4 Mn 7.8 Si, 17.3 C 15.9 Al 52.2 O	14.7 Cu, 12.1 Fe 9.6 C, 0.7 Mg 7.3 Al 54.6 O	6.9 Cu, 6.8 Co 8.1 Si, 11.0 C 14.5 Al, 1.2 Mg 51.5 O	5.0 Cu, 5.5 Ni 11.2 C, 8.9 Si 16.5 Al, 1.3 Mg 51.5 O

After the PEO treatment, the samples were rinsed by the distilled water and air-dried at room temperature.

2.3. Impregnation details

For deposition of transition metal binary oxides, the PEO-coated samples were exposed to an aqueous solution for 1 h containing 1.0 mol/l $Cu(NO_3)_2$ and 1.0 mol/l of one of the nitrates of another transition metal (Mn(II), Fe(III), Co(II) or Ni(II)), with consecutive drying and air annealing in a muffle furnace at 500 °C for 4 h.

2.4. Composite examination

The thickness of coatings was measured using an eddy-current thickness gage VT-201 (Russia). The surface morphology and element composition data (X-ray spectrum analysis, XSA, average readings from areas 50×50 μm², 2–5 μm deep) were obtained by an electron probe micro-analyzer JXA 8100 (Japan) with an INCA energy spectrum analyzer (United Kingdom). To prevent surface charging, a thin layer of chromium or carbon was deposited on the samples prior to measuring. The X-ray diffraction (XRD) patterns were studied with a D8 Advance X-ray diffractometer (Germany) using CuKα radiation. And relevant analysis was done using the EVA retrieval program served by PDF-2 database.

X-ray photoelectron spectroscopy (XPS) was also used to describe the surfaces, e.g. the Specs ultra high-vacuum system with a 150-mm electrostatic hemispherical analyzer. Ionization was implemented using the MgKα radiation. The spectra were calibrated on the C1s line of hydrocarbons, whose energy was assumed to be 285.0 eV, and the surface was etched by argon ions (with 5 keV energy) bombarding.

2.5. Catalytic testing

The catalytic tests in CO oxidation reaction were performed using a BI-CATflow 4.2(A) multipurpose flow system (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Finely cut wire samples with coatings were placed in the active zone of a quartz tube reactor 0.9 cm × 3 cm (diameter and height, respectively). The geometric surface area of the catalyst outer layer supported on the aluminum or titanium alloy was 20 cm². The preliminary tests showed that CO conversion on the metal supports 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, with gas flow rate being 50 ml/min. The outlet concentrations of CO and CO_2 were determined using a PEM-2 IR gas analyzer.

3. Results and discussion

3.1. PEO-coating characterization

The phase and elemental compositions of PEO coatings on titanium and aluminum alloy are shown in Table 1. The coatings formed

Table 4
The elemental composition of surface and sub-surface layers of $CuO + Co_xO_y$/PEO-layer/Ti(Al) composites based on XPS and XSA data.

PEO-layer/Ti(Al)	Elemental composition, at.%														
	Cu		Co		O		C		Ti(Al)		Zr		Si		S	Ce	Mg
$\frac{ZrO_2 + TiO_2}{Ti}$	$\frac{18.9}{22.5}$	(1.8)	$\frac{14.2}{24.8}$	(3.2)	$\frac{48.4}{42.4}$	(67.4)	$\frac{13.8}{6.2}$	–	$\frac{1.0}{1.7}$	(18.7)	$\frac{1.5}{2.4}$	(8.9)			$\frac{2.2}{0}$ –	
$\frac{Ce_2O_3 + ZrO_2 + TiO_2}{Ti}$	$\frac{22.2}{23.5}$	(6.4)	$\frac{15.5}{24.2}$	(2.4)	$\frac{46.0}{39.9}$	(66.7)	$\frac{15.6}{11.5}$	–		(17.2)	$\frac{0.5}{0.9}$	(5.8)			$\frac{2.2}{0}$	(1.6)	
$\frac{SiO_2 + TiO_2}{Ti}$	$\frac{15.1}{16.0}$	(3.9)	$\frac{19.4}{34.8}$	(3.8)	$\frac{46.9}{39.4}$	(55.7)	$\frac{18.5}{9.9}$	(20.0)	–	(8.4)			–	(8.7)		
$\frac{SiO_2 + Al_2O_3}{Al}$	$\frac{13.8}{24.9}$	(6.8)	$\frac{13.7}{25.4}$	(6.8)	$\frac{35.9}{35.0}$	(51.5)	$\frac{18.4}{3.6}$	(11.0)	$\frac{8.2}{11.1}$	(14.5)			$\frac{10.0}{0}$	(8.1)			(1.2)

Notes: numerator and denominator indicate the compositions of surface and subsurface layers, respectively. A subsurface layer depth is ~30 Å. XSA data are given for comparison in brackets.

Table 5
The elemental composition of surface and sub-surface layers of $CuO + NiO$/PEO-layer/Ti(Al) composites based on XPS and XSA data.

PEO-layer/Ti(Al)	Elemental composition, at.%														
	Cu		Ni		O		C		Ti(Al)		Zr		Si		S	Ce	Mg
$\frac{ZrO_2 + TiO_2}{Ti}$	$\frac{18.3}{22.5}$	(2.7)	$\frac{21.8}{31.8}$	(4.1)	$\frac{43.7}{38.1}$	(66.8)	$\frac{13.7}{7.0}$	–	–	(17.8)	$\frac{0.3}{0.6}$	(8.6)			$\frac{2.2}{0}$ –	
$\frac{Ce_2O_3 + ZrO_2 + TiO_2}{Ti}$	$\frac{18.1}{18.8}$	(6.1)	$\frac{21.1}{31.3}$	(12.4)	$\frac{39.3}{34.3}$	(62.4)	$\frac{20.6}{15.4}$	–	–	(13.7)	$\frac{0}{0.2}$	(4.1)			$\frac{1.0}{0}$ –	(1.2)	
$\frac{SiO_2 + TiO_2}{Ti}$	$\frac{18.3}{26.8}$	(2.0)	$\frac{17.0}{24.9}$	(3.6)	$\frac{43.2}{36.1}$	(59.0)	$\frac{19.3}{8.9}$	(15.5)	–	(11.8)			$\frac{2.0}{3.3}$	(8.2)		
$\frac{SiO_2 + Al_2O_3}{Al}$	$\frac{24.9}{27.4}$	(5.0)	$\frac{15.2}{19.3}$	(5.5)	$\frac{39.3}{32.2}$	(51.5)	$\frac{19.9}{3.5}$	(11.2)	$\frac{6.8}{13.0}$	(16.5)			$\frac{3.9}{4.6}$	(9.0)			(1.3)

Notes: numerator and denominator indicate the compositions of surface and subsurface layers, respectively. A subsurface layer depth is ~30 Å. XSA data are given for comparison in brackets.

in $Zr(SO_4)_2$-based electrolytes were found to contain Zr ($ZrTiO_4$ and ZrO_2) crystalline compounds, whereas those formed in alkaline silicate solutions did not contain crystalline silica or silicates. XSA analysis, though showed that Si concentration in the coatings was rather high (13–17 at.%), which could be possibly explained by the coatings containing amorphous silica.
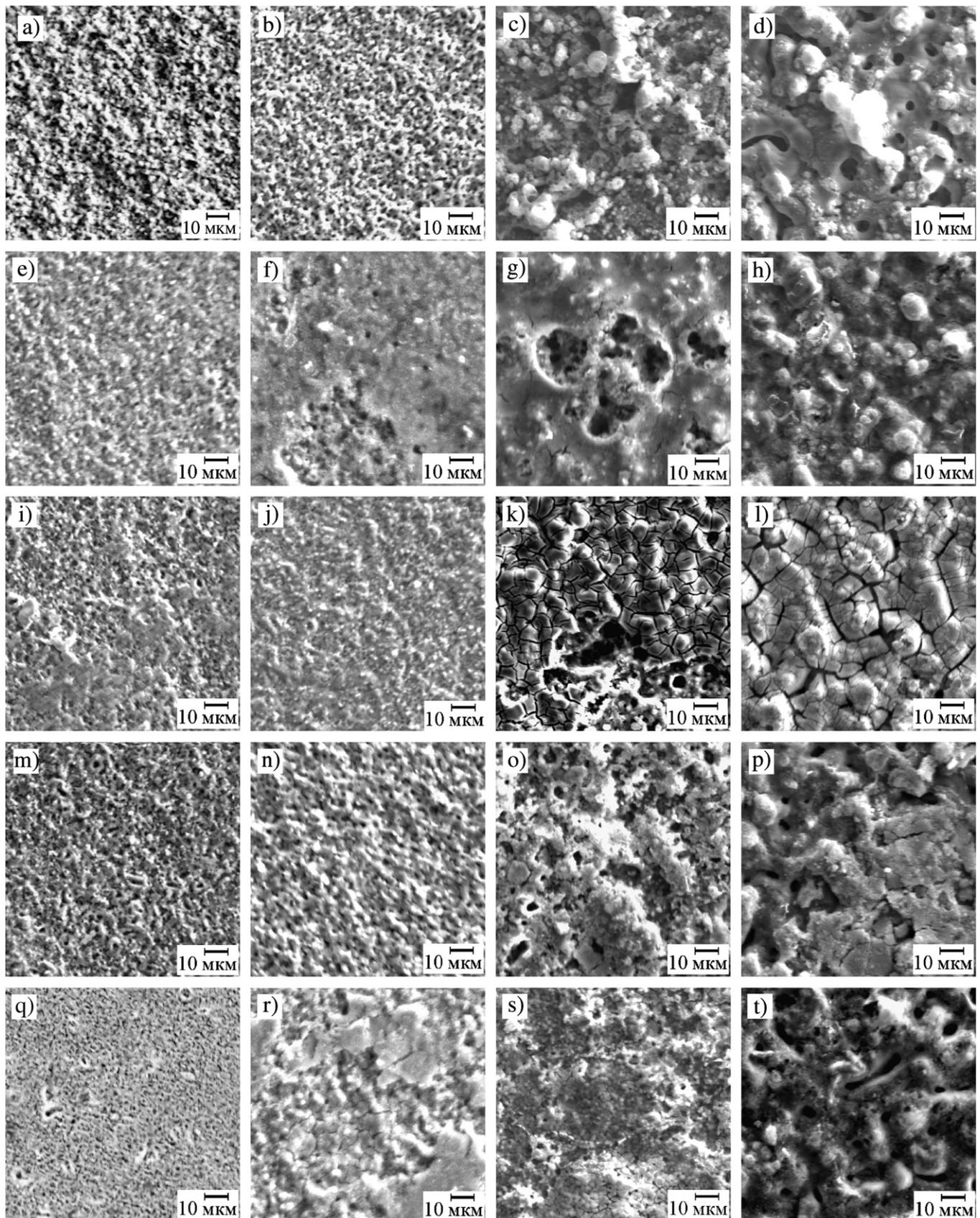
Fig. 3. SEM-images of PEO coatings (a–d) and post-deposition coatings of transition metal oxides: (e–h) $CuO + Mn_xO_y$, (i–l) $CuO + Fe_xO_y$, (m–p) $CuO + CoO_y$, and (q–t) $CuO + NiO$.

Table 6
The impact of PEO-layer/Ti(Al) on the temperature of 50% CO conversion (T_{50}).

PEO-layer/Ti(Al)	T_{50}, ºC			
	Cu–Mn	Cu–Fe	Cu–Co	Cu–Ni
$\dfrac{ZrO_2 + TiO_2}{Ti}$	237	286	212	323
	235	290	217	335
$\dfrac{Ce_2O_3 + ZrO_2 + TiO_2}{Ti}$	231	270	243	345
	196	259	241	354
$\dfrac{SiO_2 + TiO_2}{Ti}$	220	283	201	259
	219	279	200	262
$\dfrac{SiO_2 + Al_2O_3}{Al}$	274	265	223	250
	242	273	243	251

Notes: numerator and denominator indicate T_{50} at heating and cooling, respectively.

The catalytic tests of PEO-layer/Ti(Al) composites have shown that only Si-containing coatings on titanium and aluminum alloy display a certain activity in CO oxidation (Fig. 2).

3.2. Coatings impregnated by CuO and other transition metal oxides

The PEO coatings on valve metals can serve as secondary carriers for deposition of catalytically active compounds. In this case a metal substrate, a PEO layer and a catalytically active composition may influence the catalytic properties of final composites.

3.2.1. Phase and elemental composition

Tables 2 and 3 illustrate phase and elemental compositions of impregnated coatings, respectively. The general composite formula may be presented as $CuO + M_xO_y$/PEO-layer/Ti(Al), where M_xO_y is transition metal oxide (Mn, Fe, Co, Ni). However, in some cases oxides are not found in the crystalline form. For example, crystalline copper oxide is not found out in $CuO + NiO/SiO_2 + TiO_2$/Ti composites. Crystalline manganese and iron oxides are not present in the composites deposited on $ZrO_2 + TiO_2$/Ti and $SiO_2 + Al_2O_3$/Al, while crystalline cobalt oxides cannot be detected in $ZrO_2 + TiO_2$/Ti-based composites. No changes of support phase compositions were observed.

Crystallization of Cu_4O_3 indicates a partial reduction of $Cu^{2+} + e \rightarrow Cu^+$, which may occur as a result of a copper nitrate interaction with a metal aluminum or at a thermal decomposition of CuO under annealing conditions. Earlier Cu^{2+} and Cu^+ presence was confirmed by XPS data [10].

According to XSA data (Table 3), highest and smallest summary concentrations of transition metals are commonly observed in impregnated $Ce_2O_3 + ZrO_2 + TiO_2$/Ti-based and $ZrO_2 + TiO_2$/Ti-based composites, respectively. Such incorporation of activity components is not related to a PEO coating surface roughness (Table 1), though it may be explained by their morphology features and a surface layer composition.

XPS data for composites containing copper, cobalt or nickel oxides were obtained (Tables 4 and 5). In both cases transition metals are
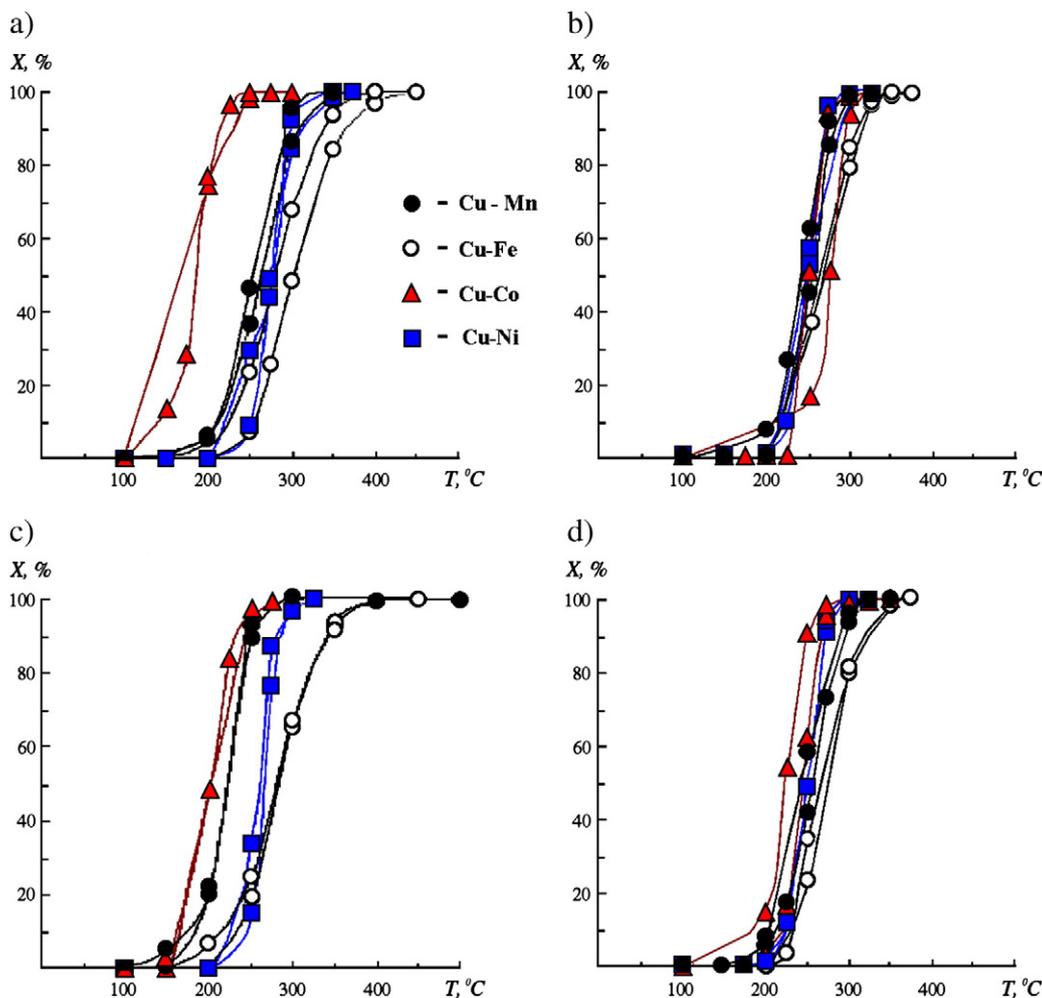
Fig. 4. Temperature dependences of CO conversion for the PEO coatings modified by binary oxides of transition metals (see the legend). The PEO coatings were formed as follows: a) on VT1-0 titanium in Zr-containing electrolyte, b) on VT1-0 titanium in Ce-, Zr-containing electrolyte, c) on VT1-0 titanium in alkaline silicate electrolyte, and d) on AMg5 aluminum alloy in alkaline silicate electrolyte.

concentrated in sub-surface layer, whereas surface layer is contaminated by carbon. Titanium is noted to be absent in surface layers, though an aluminum concentration is rather high. The content of PEO-layer elements in surface layers is lower than in bulk modified coatings.

Table 4 shows the sum of cobalt and copper concentration to fluctuate within the range of 27.5 to 37.7 at.% in surface layer and to be 47.3 to 50.8 at.% in sub-surface layer. The sum of nickel and copper concentration could be $35.5 \div 40.1$ and 46.7 to 54.3 at.% in surface and sub-surface layers, respectively (Table 5).

Thus while concentration of transition metals in various composites could be different (Table 3), their content in surface and sub-surface layers can be close (Tables 4 and 5). The main difference between modified coatings supported on aluminum alloy and those based on titanium consists in aluminum presence in surface layers.

3.2.2. Surface morphology

Fig. 3 demonstrates scanning electron microscopy images of the PEO coatings on titanium and aluminum before and after their impregnation. The PEO treatment of titanium in Zr- or Ce-, Zr-containing electrolytes results in forming dense oxide layers with pores of about ~1 μm on its surface, see Fig. 3(a,b). The silicate PEO coatings on aluminum alloy and titanium have a more developed relief: larger pores and protuberances — Fig. 3(c,d).

All impregnated composites usually duplicate the relief of initial supports. Both the finely porous structure of Zr- and Ce-, Zr-containing PEO coatings as well as developed relief of silicate PEO coatings remain after impregnating and the following annealing. In some cases, Fig. 3(f, g, o, p, r), concentrated solution application of transition metal nitrates brings about deposition of the metal oxides which looks like precipitate islets giving a relatively heterogeneous coating to the surface. The structures of aluminum and titanium silicate coatings are known to differ from other ones after deposition of copper and iron oxides. They look as if they were cracked crusts Fig. 3(k, l).

Impregnation and annealing conditions being similar, the relationship between the transition metal incorporation and the surface roughness or relief of the secondary carriers PEO layer/Ti(Al) was not established.

3.2.3. Catalytic properties in CO oxidation

All composites were tested in CO oxidation reaction. Table 6 shows the temperatures of 50% CO conversion. The silicate coatings on titanium as the data in Table 6 indicate are more promising for depositing $CuO + Mn_xO_y$ or $CuO + Co_xO_y$ oxide compositions. Silicate coatings on aluminum and Ce-, Zr-containing coatings on titanium are available for obtaining $CuO + Fe_xO_y$ oxide composites. These coatings on titanium and aluminum alloy can be used for deposition of copper and nickel oxides. The $CuO + Co_xO_y/SiO_2 + TiO_2/Ti$ and $CuO + NiO/Ce_2O_3 + ZrO_2 + TiO_2/Ti$ composites show the highest and the lowest activities in CO oxidation, respectively.

Fig. 4 shows the temperature dependences of CO conversion for binary oxide compositions supported on different PEO-layers. Under a catalytic activity decreasing, the binary oxide compositions on base of Zr- and Ce-, Zr-containing PEO coatings ranged as follows: Cu-Mn > Cu-Co > Cu-Fe > Cu-Ni (Fig. 4a,b). The activity pattern for modified silicate coatings on aluminum and titanium differs from the above: Cu-Co > Cu-Mn > Cu-Ni > Cu-Fe. In both cases, however, binary oxide Cu-Co and Cu-Mn composites show higher activity in CO oxidation, thus agreeing with ref. [11]. Note that all modified PEO coatings on aluminum alloy display similar activity in the reaction of CO oxidation. The similar activity may be related to the effect of γ-Al₂O₃ which is widely used as a support in heterogeneous catalysis. As mentioned above, (Tables 4 and 5), aluminum concentration in surface layers is rather high.

The difference between the active line obtained for modified PEO coatings on aluminum alloy and that for coatings formed by one-stage PEO technique (Cu-Ni > Cu-Co > Cu-Fe > Cu-Mn, Fig. 1 [9]) may be explained by the presence of different compounds in the final coating composition. The outer layers of modified coatings mainly consist of transition metal oxides, whereas outer layers of PEO coatings formed in electrolytes of PBWMCu-series consist of smaller concentrations of transition metals and additionally contain other components of electrolytes P, B, and W [10]. The concentration of PEO electrolyte components in outer layer of modified coatings is far less than that of modified ones. This fact is confirmed by XPS data presented for Co–Cu and Ni–Cu oxide composites on various supports (Tables 4 and 5).

4. Conclusion

The composites $ZrO_2 + TiO_2/Ti$, $Ce_2O_3 + ZrO_2 + TiO_2/Ti$, $SiO_2 + TiO_2/Ti$, and $SiO_2 + Al_2O_3/Al$ were obtained using the method of plasma electrolytic oxidation (PEO) on aluminum alloy and titanium. The above composites are very promising in application as carriers in heterogeneous catalysis. Copper, manganese, iron, cobalt, and nickel oxides were incorporated into the systems by using the impregnation and followed by annealing to obtain supported catalysts. All the composites containing binary transition metal oxides have been demonstrated to be active in CO oxidation into CO_2 at temperatures above 150–250 °C. The lines of catalytic activity drop were the same for Zr- and Ce-, Zr-containing modified PEO coatings on titanium: Cu-Mn > Cu-Co > Cu-Fe > Cu-Ni and differed from the lines for Si-containing ones on aluminum and titanium: Cu-Co > Cu-Mn > Ni-Cu > Cu-Fe. The difference between the active line obtained for modified PEO coatings on aluminum alloy and that for the coatings formed by one-stage PEO technique (Cu-Ni > Cu-Co > Cu-Fe > Cu-Mn) was supposed to be possibly explained by the presence of different compounds in the final coating composition. The comparative analysis of the resulting composites showed, that copper and cobalt binary oxides deposited on silicate PEO coatings on titanium $CuO + Co_xO_y/SiO_2 + TiO_2/Ti$ are more promising catalytic systems for further studies.

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