ISSN 1070-4272, Russian Journal of Applied Chemistry, 2013, Vol. 86, No. 11, pp. 1643−1649. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © L.M. Tyrina, V.S. Rudnev, A.V. Zorin, A.Yu. Ustinov, V.V. Permyakov, I.V. Lukiyanchuk, P.M. Nedozorov, I.V. Chernykh, N.S. Kaminskii, 2013, published in Zhurnal Prikladnoi Khimii, 2013, Vol. 86, No. 11, pp. 1691−1697.

Formation, Composition, and Catalytic Activity of Multicomponent Oxide Structures on Aluminum

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Received May 18, 2013

Abstract—Possibility is considered of obtaining multicomponent oxide systems as afterburning catalysts for automobiles by flame-electrolytic oxidation and impregnation of oxide structures on aluminum.

DOI: 10.1134/S1070427213110037

Together with catalysts on ceramic supports for afterburning of exhaust gases from internal combustion engines, catalysts on various supports, including those of metallic type, are being studied [1, 2]. The advantages of catalysts on metallic supports are in the increased mechanical strength and high heat conductivity. The role of the metal is commonly played by aluminum alloys. A ceramic layer (secondary support) is produced on the surface of aluminum alloys by the conventional anodization in acid solutions, anodization under the action of spark and arc electric discharges (plasma-electrolytic oxidation, PEO), explosive techniques, and gas-thermal spraying [2–6]. Catalytically active compounds or metals are deposited onto the resulting ceramometals (metal + oxide layer).

Of interest for obtaining metal/ceramic layer systems is the PEO method (or anodic-spark electrolysis, microarc or microplasma oxidation) [2, 7–10]. In contrast to the conventional anodization, the PEO method makes it possible to form layers composed of not only oxides of a metal being treated, i.e., multicomponent oxide composites, on aluminum and higher temperature resistant valve metals, e.g., titanium and zirconium [11–13]. For example, the layers can simultaneously contain oxides of a metal being processed and oxides of silicon, or zirconium, cerium, and other metals and nonmetals introduced into an aqueous electrolyte in the form of salts, complex compounds, or solid particles [9, 14, 15]. It is also important in preparation of catalysts that the method is technologically convenient, single-stage, and ecologically acceptable and enables processing of articles of complex geometric shape.

A catalytically active mass is deposited onto the PEO-layer/metal composite by impregnation. As a rule, the mass is composed of transition metal oxides or a mixture of these [2, 14, 16]. The catalyst may also contain platinum metals [14, 17]. Because particles of the active mass undergo aggregation at elevated temperatures, which impairs its activity, oxides of rare-earth metals can be additionally introduced into the composite [2, 3]. In this case, the active component of the catalyst is concentrated on the surface of the ceramic layer.

Preliminary tests of catalysts fabricated by deposition of nickel- and copper-containing coatings on a titanium wire by PEO and impregnation demonstrated their certain activity in conversion of CO on a laboratory installation and a stand-engine [18]. The activity in conversion of CxHy was not determined. To form the starting oxide layers, it is preferable to use a silicate electrolyte because the Si-containing coatings formed in this case have a developed surface and high moistureretention capacity [19].

It was shown in [20] that use of binary oxide composites CuO + M_xO_y, where M = Mn, Fe, Co, Ni on PEO coatings is promising for fabrication of CO oxidation catalyst. Because introduction of second and third components improves the catalyst activity, it was of interest to combine PEO and impregnation methods to form multicomponent catalysts on metallic supports. The goal of our study was to form catalysts containing aluminum and silicon oxides and a mixture of transition and rare-earth metals on aluminum supports by combination of PEO and impregnation methods and to examine these catalysts, including tests on a stand-engine.

EXPERIMENTAL

The oxide layers were formed on AMg5 alloy (4.8–5.8 wt % Mg, 0.3–0.8 Mn, 0.02–0.01 Ti, Al the rest) samples of two types: 22 × 22 × 1 mm planar samples of sheet aluminum, further used to measure the thickness of the deposited oxide layer and determine its elemental and phase composition, and wire samples of the same alloy (diameter 1.67 mm) with a working surface area of 20 cm^2 for catalytic tests under laboratory conditions.

To standardize the surface of the samples prior to deposition of coating, it was chemically polished to mirror shine (8–9th class of finish) with a mixture of concentrated acids: $H_3PO_4 : H_2SO_4 : HNO_3 = 4 : 2 : 1$ (v/v) at 110°C, with the subsequent washing with distilled water and drying at 70°C in air.

PEO coatings were formed with a silicate alkaline electrolyte commonly used for this purpose [7, 19, 21], prepared from distilled water and commercial reagents of chemically pure grade, $Na_2SiO_3{\cdot}9H_2O$ and NaOH. The electrolyte contained (M): 0.05 Na_2SiO_3 and 0.05 NaOH. The coatings were formed in the galvanostatic mode under the action of electric spark and arc discharges. A TEP4-100/460-2 computer-controlled thyristor unit operating in the single-polarity mode served as a current source. The effective current density $i = 0.1$ A cm^{-2}, the formation duration was 30 min. The coatings deposited in this mode had a sufficient thickness at the minimum warming-up of the electrolyte.

The process was performed in a 3-liter stainless steel bath equipped with a water jacket for cooling of the working solution. The electrolyte was agitated with a mechanical stirrer, the solution temperature did not exceed 50°C in the course of the process. After the PEO processing, the samples were washed with distilled water and dried in air.

The catalytically active mass was deposited onto the PEO-coated samples by submerging these samples into a multicomponent aqueous solution contained 0.33 M of each of the following compounds: $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, $Co(NO_3)_2$, $Ce(CH_3COO)_3$, and $La(CH_3COO)_3$ and keeping in this solution for 3 min. Further, the samples were dried at 120°C and annealed in air in a muffle furnace at 500°C for 2 h. These annealing conditions provided a full decomposition of the nitrates and acetates to give the corresponding oxides. The salts of the above metals were chosen because the oxide formed in their annealing are catalytically active in oxidation reactions, including that of CO oxidation [3, 6, 22–24]. The impregnation duration and the salt concentrations were determined experimentally. The aluminum substrate was etched at longer impregnation duration, and the incorporation of the active components decreased at shorter durations. The total concentration of the active components (ions of transition and rare-earth metals was 2 M by analogy with the earlier studies [20].

The mass fraction of the coatings on metal, calculated from sample weights before and after the PEO processing and modification, was 1 to 3%.

The methods used to measure the thicknesses of the coatings, determine their elemental composition by the X-ray fluorescence microbe analysis (XRFA) and the elemental composition of the surface by X-ray photoelectron spectroscopy (XPS), and obtain images of the surface were described in detail in [17].

Laboratory catalytic tests were performed on BI-CATflow4.2(A) universal flow-through installation (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Russia). Samples of PEO-coated AMg5 alloy wire cut into ~0.5-cm pieces were placed in the active zone (0.9 cm in diameter and 3 cm high) of the tubular quartz reactor. The starting reaction mixture contained 5% CO and air. The gas flow rate was 50 mL min^{-1}. The inlet and outlet CO and CO_2 concentrations were measured with a PEM-2 IR gas analyzer (Russia).

The activity of the fabricated ceramic-metallic catalysts in oxidation of CO and hydrocarbons was evaluated on a stand comprising a 4A-FE four-cylinder gasoline engine (piston diameter 81 mm, piston stroke

77 mm, 16 valves, 110 hp at 6000 rpm, torque 145 N m at 4800 rpm, working volume 1587 cm^3) of a Toyota Corolla automobile. Gasoline of AI-92 brand was used. The tests were performed with the engine operating in the idle and working modes.

For engine tests, the oxide catalyst was formed on the surface of a structure made of AMg5 aluminum alloy in the form of successively mounted metallic disks with through apertures (Fig. 1) [25]. The catalyst was placed in a special metallic container fabricated in the form of a cylinder and mounted after the exhaust collector of the engine. Thermocouples were used to monitor the inlet and outlet temperature of the container. After the engine warmed up, the concentrations of carbon monoxide CO and hydrocarbons C_xH_y were determined before and after the catalyst with AVG-4-1 gas analyzers. The apparent surface area of each catalyst disk was 75.4 cm^2, and the total apparent area of the catalyst subjected to tests, 3016 cm^2 (40 disks).

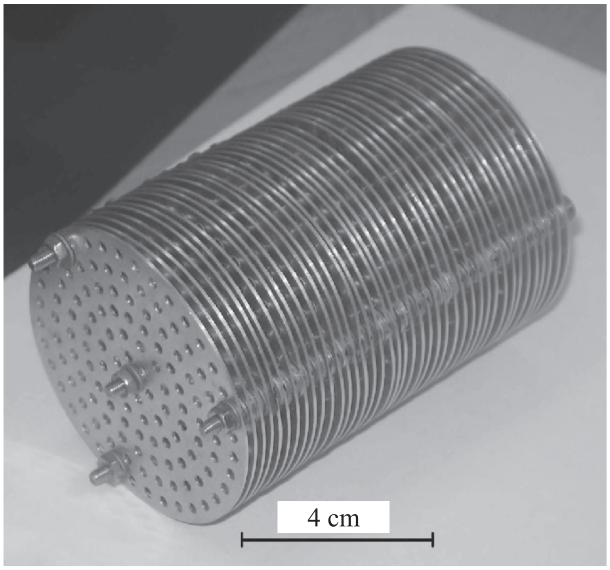

Fig. 1. Outward appearance of the assembled block catalyst.

RESULTS AND DISCUCSSION

The elemental composition of PEO layers before (no. 1) and after (no. 2) modification is presented in Table 1. In addition to the alloy components (aluminum, magnesium, and oxygen) the as-deposited PEO coatings (no. 1) contain silicon and sodium, elements from the electrolyte. Upon the impregnation in a multicomponent solution and annealing at 500°C (sample no. 2), the surface layers of the catalyst contain up to 1 at % nickel, copper, manganese, cobalt, cerium, and lanthanum, i.e., the transition and rare-earth metals are incorporated in proportion to their content in the impregnating solution. Of crystalline phases, the coatings contain only γ-Al_2O_3. Because the content of silicon in the coatings is rather high (14–15 at %), it can be assumed that amorphous silica is present. No crystalline phases of transition and rare-earth metal oxides were found. Possibly, the active component of the catalyst (sample no. 2) contains amorphous or finely crystalline oxides of nickel, copper, manganese, cobalt, cerium, and lanthanum.

Figure 2 shows scanning electron microscopic (SEM) surface images of the samples under study after the PEO and modification, obtained in the phase contrast mode. In this mode, different phases on the surface are differently colored: those containing heavier

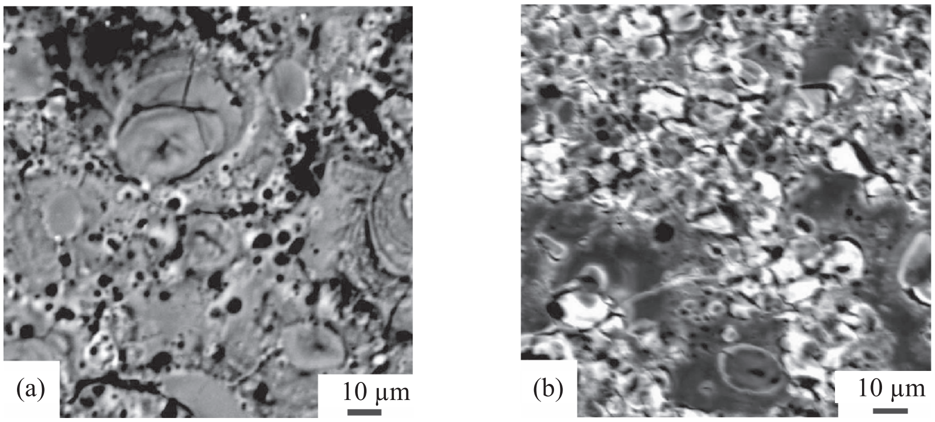

Fig. 2. SEM images of the surface of PEO coatings (a) before and (b) after the modification with transition and rare-earth metal oxides. The images were obtained in the phase-contrast mode. Sample (Table 1): (a) no. 1 and (b) no. 2.

Table 1. Elemental composition of coating according to XRFA and XPS data

Method of analysis	Sample no.	Elemental composition, at %												
		O	Na	Mg	Al	Si	C	Mn	Co	Ni	Cu	La	Ce	Pt
XRFA	1	60.7	0.8	1.6	22.4	15.2	–	–	–	–	–	–	–	
	2	59.8	–	1.4	19.4	–	–	–	1.0	1.0	0.9	0.9	0.9	
XPS	2	39.3[a]	–	–	9.3	4.9	36.8	1.4	2.7	1.1	2.1	1.3	1.1	–
		53.5			9.9	9.1	9.2	2.1	4.6	0.9	3.6	3.6	3.5	
	M1	48.7	–	–	4.7	1.2	36.8	0.9	2.2	1.4	2.1	0.9	1.1	–
		46.9			8.9	2.8	21.0	2.7	5.6	1.5	3.7	3.4	3.5	
	3	54.7	–	–	5.8	4.2	21.7	2.0	2.4	1.0	3.3	1.8	2.1	1.0
		59.0			5.1	10.5	8.3	2.5	3.2	0.9	2.2	3.3	4.2	0.8
	M(Pt)	52.8	–	–	3.5	1.7	24.0	2.6	4.8	1.3	5.2	1.6	1.6	0.9
		51.0			7.1	–	13.1	4.4	8.0	2.0	5.9	3.9	4.0	0.6

[a] Numerator, data for the surface layer; denominator, data for the near-surface layer at a depth of about 3 nm.

elements look light. It can be seen that the surface of the as-deposited coatings is rater uniform in phase composition (Fig. 2a). Light areas appear on the surface after the modification, which indicates that elements heavier than aluminum, silicon, and oxygen are present, i.e., elements from the impregnating solution are built in the surface layer (Fig. 2b). The thicknesses of the as-grown (20.5 μm) and modified layers (19.9 μm) nearly coincide. This means that compounds (oxides) of the modifying elements mostly fill pores and defective parts of the coatings.

According to the XPS data, the concentrations of manganese, nickel, lanthanum, and cerium in the 3-nm-thick surface layer of the coatings almost coincide with those found by the microprobe analysis (Table 1), whereas the concentrations of copper and cobalt are approximately two times higher. In addition, the surface layers contain a substantial amount of carbon. After a layer with a thickness of about 3 nm is removed, the concentration of carbon decreases and, accordingly, the quantitative content of other elements grows. The XPS spectra obtained before and after the etching demonstrate the presence of carbon in two forms: as aliphatic carbon bound to hydrogen or another carbon and as oxidized carbon bound to oxygen. The maximum amount of aliphatic carbon is contained in as-grown samples. Analysis of these data suggests that, upon modification, the active components from the impregnating solution are concentrated in the near-surface layer of the thus formed catalyst.

According to the XPS data, the surface layer of the samples under study contains Cu^{2+}, Ni^{3+}, MN^{4+}, Co^{3+}, Ce^{4+}, La^{3+}, Si^{4+}, and Al^{3+}. After a layer with a thickness of about 3 nm is removed, copper in the near-surface layer is in the Cu^{+} and, possibly, Cu^{0} states, the contribution of Ce^{3+} to the spectra becomes more pronounced, and the states of Ni, Mn, Co, and La are not changed to any noticeable extent.

In laboratory studies, the activity of the composites obtained was judged from the temperature dependence of the CO conversion (Fig. 3). The catalytic process starts at temperatures above 300°C. The 50%-conversion temperature T_{50} falls within the range 320–325°C, and the complete-conversion temperature T_{100} is 400–425°C. The same activity was observed for (Ni,Cu)-containing oxide catalysts on an aluminum support [16], previously fabricated by combination of PEO and impregnation method. For these catalysts with coatings containing 10 at % Ni and 5.5 at % Cu, T_{50} was 310–320°C. The existence of a “counter clockwise” hysteresis and the increase in CO conversion in subsequent heating-cooling cycles in catalytic tests indicate that the samples are activated in a high-temperature interaction with the gaseous reaction mixture in which CO can serve as activating agent.

The results of stand tests of block catalysts (of design shown in Fig. 1) are presented in Table 2. In contrast to the laboratory conditions, the gas flow velocities in stand tests are higher and exhaust gases contain, in addition to CO and C_xH_y, also CO_2, NO_x, and other components. Nevertheless, the tendencies remain the same: the conversion of both CO and C_xH_y grows as the temperature is raised from 300 to 470°C. For block catalysts containing transition and rare-earth metal oxides, the conversion of CO and C_xH_y at increased engine rpm (X_{CO} = 14.4% and X_{CH} = 21.9%) exceeds that in the idle mode (Table 2 run nos. 1 and 2) because a higher temperature is reached in the former case. The comparatively low catalytic activities toward CO and CxHy are due to the small specific surface area of the catalysts. . According to [9], the specific surface area of PEO layers is 0.2–0.7 m^2 g^{-1} and increases by approximately an order of magnitude upon impregnation [18]. Calculations show that the surface area of the catalysts being tested should be raised to 6 m^2 to obtain a high conversion.

On being subjected to stand tests, the block catalyst was examined under laboratory conditions. For this purpose, it was disassembled into the constituent disks, one of which was analyzed by the XPS method (Table 1, sample M1). According to XPS, the content of transition and rare-earth metals in the surface and near-surface layers of M1 sample and laboratory sample no. 2 nearly coincide.

It was of interest to find out how addition of a noble metal will affect the activity of a multicomponent oxide catalyst tested in a stand-engine. For this purpose, disks of the disassembled catalyst were impregnated for 3 min with an aqueous solution containing 2.9 × 10^{-3} M H_2PtCl_6. We used the same concentration of chloroplatinic acid as that in obtaining Pt-containing layers by the single-stage PEO method [26]. Then the disks were dried at 120°C and annealed at 450°C in a muffle furnace in air for 2 h. The impregnation and annealing were repeated twice.

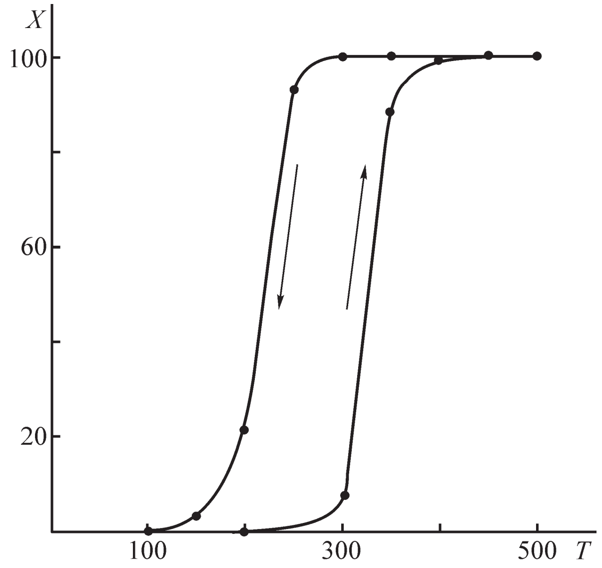

Fig. 3. CO conversion X vs. temperature T for a laboratory sample with a PEO coating modified with transition and rare-earth metal oxides. The arrows show the temperature variation direction (raising and lowering).

According to XPS data, the content of platinum in the surface layers was about 1 at % [Table 1, laboratory sample no. 3, block catalyst disk M(Pt)]. According to the found binding energies, platinum is in the Pt^{4+} state on the surface (74.4 eV for the Pt $4f_{7/2}$ level. Its state upon etching is close to the atomic Pt^0 (71.7 eV), which does not contradict published data [27, 28]. The presence of platinum in various oxidation states: Pt^{4+}, Pt^{2+}, $(PtO_2)_s$ upon its deposition onto the Al_2O_3 surface from an aqueous solution of H_2PtCl_6 and annealing was confirmed by the method of temperature-programmed reduction and IR spectroscopy [27]. In addition, the presence of metallic platinum and platinum dioxide on the surface of the aluminosilicate support upon impregnation with an H_2PtCl solution and subsequent annealing at temperatures $T \geq 550$°C was confirmed by

Table 2. Conversion of CO and C_xH_y on a stand-engine λ = 1.00–1.14, total disk surface area 3016 cm^2

Run no.	n, rpm	T, °C	χ_{CO}	χ_{CH}
			%	
1	2500	470	14.4	21.9
2	822	300	9.2	5.7
3(Pt)	2600	495	11.3	43.6

an X-ray fluorescence analysis with a VRA-20 analyzer with a W-cathode of the X-ray tube [28].

The platinum-modified disks were again assembled into the structure shown in Fig. 1 and tested on a stand-engine. As a result, the conversion of CO remained nearly unchanged (11.3%) and that of hydrocarbons increased by more than a factor of 2 (43.6%) (Table 2, run no. 3). Thus, introduction of platinum affects only the conversion of hydrocarbons. Meanwhile, the catalyst rather efficiently works in the absence of platinum and is promising for practical applications.

CONCLUSIONS

(1) Catalysts containing oxides of transition metals (Ni, Cu, Mn, Co) and rare-earth elements (Ce and La) were produced on aluminum supports by a combination of plasma-electrolytic oxidation and impregnation, followed by annealing. It was found that the composites formed on an aluminum alloy catalyze the reaction of CO oxidation at temperatures higher than 300°C.

(2) Tests of block catalysts containing oxide of transition and rare-earth metals on a stand based on the engine of a Toyota Corolla automobile exhibited a certain activity in deep oxidation of CO and hydrocarbons. Additional modification of block catalysts with platinum improves the activity of the samples.

(3) The data obtained demonstrate that a combination of the plasma-electrochemical oxidation in silicate electrolyte and impregnation is promising for production of industrial catalysts.

ACKNOWLEDGMENTS

The authors are grateful to T.A. Kaidalova (Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences) for assistance in X-ray phase analyses.

The study was supported in part by grants from the Presidium of the Far-Eastern Branch, Russian Academy of Sciences.

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