Outlooks for the Automobile Application of Oxide Film Catalysts Formed by Means of Plasma Electrolytic Oxidation

N. B. KONDRIKOV[1], V. S. RUDNEV[2], M. S. VASILYEVA[1], L. M. TYRINA[2], T. P. YAROVAYA[2] and A. V. ROZHKOV[1]

[1]*Far-Eastern State University,*
Ul. Oktyabr'skaya 27, Vladivostok 690090 (Russia)

E-mail: kondr@chem.dvgu.ru

[2]*Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,*
Pr. 100-letiya Vladivostoka 159, Vladivostok 690022 (Russia)

E-mail: rudnevvs@ich.dvo.ru

Abstract

In order to solve the problems of fuel combustion in internal-combustion engines and exhaust gas purification, one may use catalytic coatings deposited either on cylinders and pistons or on the surfaces of bulk supports in the systems of catalytic afterburning of exhaust gas. Both problems can be solved by using the manufacturable method of depositing the coatings with catalytic properties – plasma electrolytic oxidation.

Ecological problems arising during the performance of internal combustion engines (ICE) in automobiles are connected, first, with incomplete combustion of fuel in cylinders [1], which causes the formation of toxic components (CO, NO_x, hydrocarbons, aldehydes, carbon black, SO_2 *etc.*); second, with the impossibility of complete purification of exhaust gases with the help of known catalyst converters. The most efficient ones include, as a rule, platinum group metals. In addition, technologies of catalyst supports γ-Al_2O_3 and its modifications, as well as active layers are rather labour-intensive and multistage [2].

Plasma electrolytic deposition (PED) of layers on the surface of valve metals (Ti, Al, Nb, Ta, Zr, Mg *etc.*) is usually used to form protective, wear-resistant and thermally stable coatings [3]. The PED procedure was successfully used to make bulk catalysts based on aluminium, for example, to form aluminium oxide layers as a support for catalytically active compositions on the surface of aluminium foil [4]. However, possibilities to govern the process and to insert the electrolyte components into the oxide layers of substrate metals are of definite interest for the formation of not only the catalysts but also catalytically active layers because oxide systems are thus formed: simple and mixed oxides, spinels, phosphates, borates of di-, tri- and polyvalent metals *etc.* The advantages of the method include the possibility to form a support and a catalytically active layer in one stage; comparative simplicity of technology; control of the phase and chemical composition of the surface layers due to PED regimes and composition of electrolytes; the possibility to deposit coatings onto the parts of complicated shapes and rather simple recovery of the surface oxide layers [3, 5]. Disadvantages of the method include limitations for the set of substrates (at present, only valve metals are used as the latter). It should be noted that aluminium, titanium and zirconium oxides are most widely used as supports in catalysis, though it cannot be excluded that oxide structures can be deposited on other electrically conducting materials.

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TABLE 1

Phase (PC) and elemental (EC) composition of a number of oxide layers formed on titanium and aluminium alloys by means of PED, mass %

Alloy	EC	PC	System type
VT1-0	Ti 61.0	TiO_2 (s.)	Support
AMg-5	Al 38.0	γ-Al_2O_3	«
AMg-5	Ni 22.3, P 19.7,	$NiAl_2O_4$	Catalytically active
	Al 2.83, Mg 0.37	$AlPO_4$	coating + support
AMtsM	Al 69.9, Y 1.3	$Al(OH)_3$	The same
VT1-0	Ti 46.1,	TiO_2 (s.)	
	Y 6.8	TiO_2 (am.)	«
AMtsM	Al 47.0, Ni 1.7, Mn 0.9	$Al(OH)_3$	«
VT1-0	Ti 36.7,	NiO	
	Ni 19.6, Mn 13.1	CuO	«
	Ni 44.0, Ti 10.0	TiO_2 (s.)	
		NiO, Ni	«
	Mn 49.8, Ti 2.3	Mn_2O_3	
		Mn_3O_4	«

State University, oxide structures with potential catalytic properties were formed on the substrates made of aluminium, titanium and their alloys (Table 1). So, both the supports (aluminium and titanium oxides) and oxide compositions of different structures can be manufactured by means of PED by inserting the components of electrolytes. At present, coatings containing individual and mixed oxides were formed, including the compounds of nickel, manganese, rare earths and platinum group metals. High catalytic activity in $CO \rightarrow CO_2$ conversion was demonstrated for the coatings composed of Mn_2O_3, Mn_3O_4 on titanium oxide. Catalytic properties of other oxides and their compositions formed by means of PED are under investigation [6–8].

The aspects concerning the deposition of catalytically active layers on the surface of cylinders and pistons of ICE, for example, by means of ion implantation, are considered in literature [9]. Approaches to the use of plasma electrolytic oxidation are proposed for the deposition of thermally stable and wear-resistant coatings on ICE cylinders and pistons, that is, on the parts made of aluminium and its alloys [10]. Altogether, as it was demonstrated above, PED procedure allows do deposit on cylinders and pistons not only protective but also catalytically active layers. Due to the low melting point of the carrier metal aluminium, the supports based on titanium – titanium oxide composition are more promising for the catalytic afterburning of ICE exhaust gases. However, these catalytic systems have been investigated insufficiently.

With some compositions, for example Al/Al_2O_3/nickel and copper compounds, $Ti/TiO_2/Mn_2O_3$ and Mn_3O_4, including those modified with silver, rather high catalytic activity for $CO \rightarrow CO_2$ conversion was achieved. The catalytic activity was studied both in the stationary reactors (on the basis of changes in the total pressure of the system [7]) and in flow-type ones Bi-Cat-mr (manufactured at the Boreskov Institute of Catalysis, SB RAS, Novosibirsk) with the chromatographic monitoring of gas concentrations [8]. Multiple cycling within temperature range 20–400 °C had no effect on phase and elemental composition of manganese-containing catalytic active coatings. The catalytic activity of these structures depends on the amount of manganese in the coating, on the morphology of film surface *etc*.

So, two types of catalytic systems have been investigated. The first type includes high-temperature systems intended for more complete combustion of fuel and decrease in the amount of fuel residues and acting similarly

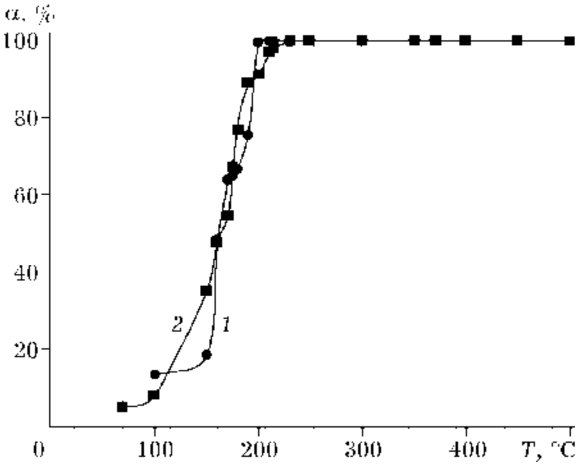

Fig. 1. Degree of conversion of CO as a function of reaction temperature for plasma electrolytic manganese-containing layers on titanium modified with silver compounds. Concentration of Ag, at. %: 71 (*1*) and 4.6 (*2*); experimental conditions: flow set-up Bi-Cat-mr, Ar : O_2 : CO = 75 : 20 : 5, flow rate 50 ml/min, the geometric surface of the samples 40 cm^2.

to gasoline dopes. These systems include coatings containing mixed compositions of nickel and copper compounds on Al_2O_3/Al substrates. Temperature of 50 % CO → CO_2 conversion for these systems in within 400–450 °C.

The second type includes low-temperature systems intended for purification of exhaust gas of ICE; the systems are based on manganese oxides and modified compositions, for example those containing silver. Temperature of 50 % conversion is 160 to 240 °C for these systems (Fig. 1).

Taking into account the fact that for catalyst converters of ICE exhaust gas purification and hybrid automobiles with fuel elements the most interesting catalysts are bulk catalysts on metal supports providing high heat conductivity, development of catalytic systems on the basis of the technology of plasma electrolytic oxidation seems promising for automobile industry.

REFERENCES

1 W. S. Blazowski, D. E. Walsh, *Combustion Sci. Technol.*, 10 (1975) 233.
2 N. M. Popova, S. V. Burmestrov, Primeneniye katalizatorov na metallicheskikh nositelyalh v katalize. Kataliticheskoye gidrirovaniye i okisleniye, Nauka, Alma Ata, 1975.
3 P. S. Gordienko, V. S. Rudnev, Elektrokhimicheskoye formirovaniye pokrytiy na alyuminii i yego splavakh pri potentsialakh iskreniya i proboya, Dal'nauka, Vladivostok, 1999.
4 S. F. Tikhov, G. V. Chernykh, V. A. Sadykov *et al.*, *Catal. Today*, 53 (1999) 639.
5 A. L. Yerokhin, X. Nie, A. Leyland *et al.*, *Surf. Coating Technol.*, 122 (1999)73.
6 Pat. 2241541 RF, 2003.
7 M. S. Vasilyeva, V. S. Rudnev, N. B. Kondrikov *et al.*, *Zh. Prikl. Khim.*, 77 (2004) 222.
8 V. S. Rudnev, M. S. Vasilyeva, N. B. Kondrikov, L. M. Tyrina, *Appl. Surf. Sci.*, 2005, in press.
9 O. V. Klyus, *Probl. Prikl. Mekhaniki*, 17 (2004) 42.
10 Yu. N. Tyurin, M. L. Zharkevich, S. I. Golovenko *et al.*, *Avtom. Svarka*, 2 (2002) 44.