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Catalytic coatings for improving the environmental safety of internal combustion engines

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Abstract

AK9 silumin samples (Al-Si) were treated by plasma electrolytic oxidation (PEO) in order to obtain surface oxide layer. These samples were not enough active as catalysts in CO oxidation (1% CO vol in air). Palladium activated samples were more active. Thus the temperature of 50% CO conversion for Pd/SiO_2/Al-Si sample is T_{50} = 152 °C and T_{99} is 170 °C. According to IR spectroscopy and Raman spectroscopy as well as scanning electron microscopy data, the active layer of the most active sample Pd/SiO_2/Al-Si presents by noncrystalline SiO_2 with γ-alumina and palladium inclusions. the covering has of 10-20 nm Accordingly to atomic force microscopy data the roughness of surface layer is ~ 10 – 20 nm.

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Keywords: plasma electrolytic oxidation; palladium; CO oxidation; IR spectroscopy; Raman spectroscopy; scanning electron microscope

1. Introduction

Auto exhaust gives the most part of air contamination. The problem is continuously aggravated due to high growth rates of auto park accompanied by a limited throughput performance of cities highways. On the average in

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Russia, motor vehicles contribution to air contamination accounts for 40-45%, and in large cities this part reaches up to 90% [1]. By total volume and total poisoning effect, CO takes the first place among contaminating gases. Carbon oxide content may be over 20 times higher than the threshold limit value (TLV) in large cities (CO TLV is 0.05 mg/m3). The development of CO-to-CO_2 oxidation catalysts represents an important scientific and engineering problem. A traditional approach to such problem solution is to use an exhaust catalytic converter system.

To lower air pollution, exhaust gases are passed through a catalyst converters of various types [3]. The most wide-spread coatings for catalyst converters are the ones containing precious metals (Pt, Pd, Rh), as well as metals oxides (Al_2O_3, SiO_2, CeO_2, ZrO_2, SnO_2, Cr_2O_3, MnO_x, NiO, CuO, Co_3O_4, et ctr.) [4]. Similar coatings can be used in a combustion chamber itself of an internal combustion engine (ICE). For instance, corundum layer on a combustion chamber surface can be applied as a catalyst carrier and as a catalyst itself at elevated temperatures. The results of automotive diesel engine benchmark tests demonstrated that corundum layer application allows lowering the mass of solid particles exhaust by 19-30% [5,6].

The use of catalysts in ICE combustion chamber is of great interest. Indirect injection of diesel fuel was modified in a catalytic engine equipped with a catalytic afterburner (based on Pt-grid). The findings pointed out that substantial diesel fuel economy was registered in this engine resulting in lower exhaust amount in comparison with any petrol or diesel engine [7]. The existing publications contain information that unburned fuel exhausts were reduced by 20% due to catalyst deposition of Pt-coverings on top and side surfaces of the piston [8].

Copper, chromium, manganese and cobalt oxides are known to exhibit catalytic activity during oxidation [9]. These catalysts are effective in hydrocarbons and carbon oxide oxidation. Composite catalysts containing copper, cobalt and vanadium oxides on aluminum oxide support provided good results at engine standstill.

Precious metals (platinum and palladium) on silica and alumina support are highly effective catalysts for hydrocarbons and carbon oxide oxidation. However, to use precious metals as catalysts is not only greatly efficient but expensive as well.

Aluminum alloys, namely silumin, are known to be used in engine cylinders and pistons production. Publications on the subject contain various methods of catalytic coating production based on this material, such as gas-dynamic plasma spraying, and plasma electrolytic oxidation [10,11].

The present work is aimed to perform the synthesis of oxide coverings on silumin by plasma electrolytic treatment, the impregnation of obtained samples with palladium salt solutions and the investigation of the obtained palladium catalysts characteristics. CO oxidation was choosed as the test-reaction.

2. Experimental

Catalysts were prepared in several stages. Cylindrical ribbed samples (original sample in Fig. 1) were produced from AK9 silumin on a turning lathe, following by subsequent milling in order to increase the geometrical surface. Thereupon, plasma electrolytic oxidation (PEO) was undertaken in cooled electrochemical cell in electrolytes with compositions given in Table 1.

Table 1. Electrolytes composition and the resulting coatings on silumin (Al-Si)

№	Sample	Electrolyte composition
1	CeO_2/Al-Si	30 g/l of $Na_2B_4O_7$, 3 g/l of NaOH, 10 g/l of Na_2SiO_3, 10 g/l of CeO_2 powder suspension
2	ZrO_2-CeO_2/Al-Si	30 g/l of $Na_2B_4O_7$, 3 g/l of NaOH, 10 g/l of Na_2SiO_3, 70 g/l of ZrO_2-CeO_2 powder suspension
3	γ-Al_2O_3/Al-Si	30 g/l of $Na_2B_4O_7$, 3 g/l of NaOH, 10 g/l of Na_2SiO_3, 10 g/l of γ-Al_2O_3 powder suspension
4	B_2O_3-SiO_2/Al-Si	30 g/l of $Na_2B_4O_7$, 10 g/l of Na_2SiO_3.
5	SiO_2/Al-Si	3 g/l of NaOH, 10 g/l of Na_2SiO_3
6	SiO_2/Al-Si	3 g/l of KOH, 30 g/l of Na_2SiO_3