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# Mixed alumina and cobalt containing plasma electrolytic oxide coatings

**G Sh Yar-Mukhamedova<sup>1,3</sup>, M V Ved<sup>2</sup>, A V Karakurkchi<sup>2</sup> and N D Sakhnenko<sup>2</sup>**

<sup>1</sup>Physics Department, Al-Farabi Kazakh National University, IETP, 71 Al-Farabi avenue, Kazakhstan

<sup>2</sup>Physical Chemistry Department, National Technical University “Kharkiv Polytechnic Institute”, 2 Kyrpychova Street, Kharkiv, 61002, Ukraine

E-mail: gulmira-alma-ata@mail.ru

**Abstract.** Principles of plasma electrolytic oxidation of the AL25 aluminum alloy in diphosphate alkali solutions containing cobalt(2+) cations are discussed. It has been established that a variation in the concentration of the electrolyte components provides the formation of mixed-oxide coatings consisting of the basic matrix materials and the cobalt oxides of different content. An increase in the cobalt oxide content in the coating is achieved by the variation in electrolysis current density as well as the treatment time due to both the electrochemical and thermo-chemical reactions at substrate surface and in spark region. Current density intervals that provide micro-globular surface formation and uniform cobalt distribution in the coating are determined. The composition and morphology of the surface causes high catalytic properties of synthesized materials, which confirmed the results of testing in model reaction CO and benzene oxidation as well as fuel combustion for various modes of engine operation.

**Keywords:** AL25 alloy; Cobalt oxides; Plasma electrolytic oxidation; Mixed oxide system; Catalytic activity

## 1. Introduction

Environmental and technical problems accompanying the operation of internal combustion engines (ICE) are associated with the incomplete combustion of fuel and, accordingly, the inevitable formation of toxic components (CO, NO<sub>x</sub>, and soot). One of the perspective ways to improve the performance of ICE can be the use of catalysis in situ in the combustion chamber [1]. Catalytic processes are characterized by lower activation energies and consequently temperatures of the fuel burning start as well as its higher completeness [2]. These lead to a decrease in the maximum pressure in the combustion chamber and, hence, in the severity of engine operation and to the minimization of emissions of hazardous substances with exhaust gases. The first paragraph after a heading is not indented.

The currently available hydrocarbon fuel combustion catalysts are divided into two groups: catalysts based on noble metals (most commonly Pd and Pt) and transition-metal oxides (Mn, Co, Fe, etc.), particularly those with a complex composition. At high temperatures, significant advantages are shown by a family of catalysts based on d-metals in particular cobalt oxides, which exhibit thermal stability and high oxygen affinity [3]. Non stoichiometric cobalt oxides not only provide the thermal stability of the catalysts but also lead to a significant improvement of its reactivity.



In terms of rational designing and effective technology, it seems appropriate to deposit a catalytic layer directly on the surface of ICE pistons manufactured using AL25 alloys with an optimal combination of physic-mechanical and performance properties [4]. The most promising method for the formation of thin layers on aluminum alloys, in particular, silumins, is plasma electrolytic oxidation (PEO). This method provides the incorporation of catalytically active components into an alumina matrix owing to the implementation of both electrochemical and thermo-chemical reactions in high-energy modes [5-6]. However, it should be taken into account that the PEO of silumins is complicated because these materials contain a large number of alloying components and inter-metallic compounds with different chemical properties of oxides. Previously, we have shown PEO expediency of the AL25 alloys in a diphosphate solution with the addition of manganese salts to produce mixed manganese and aluminum oxides of different compositions [7]. On this basis, the aim set in this paper is a study of the electrolyte composition and the PEO modes for the formation of a mixed oxide layer with high cobalt content on the surface of the AL25 alloy.

## 2. Experimental

The studies were conducted using pure aluminum and AL25 alloy samples with a working surface of  $2.0\text{cm}^2$ . The concentration alloying elements in a substrate, mass %: Si – 11.0-13.0, Cu – 1.5-3.0, Ni – 0.8-1.3, Mg – 0.8-1.3, Mn – 0.3-0.6, Fe<0.8, Zn<0.5, Ti<0.2, Cr<0.2, Pb<0.1. The surface preparation included sequential procedures of mechanical grinding, etching in an alkaline solution, thorough washing with distilled water, and drying. Electrolyte solutions for the pretreatment and PEO were prepared from certified reagent-grade reactants and distilled water.

The PEO of samples was conducted using a B5-50 stabilized power supply that maintained voltage up to 300V. PEO was implemented in an electrolytic cell under conditions of forced cooling of the electrolyte to a temperature of 20–30 °C at a current density varied in a range of  $i=2-10\text{ A}\cdot\text{dm}^{-2}$  up to final formation voltage 180–235V; duration of oxidation process was to 40–60 minutes. PEO was implemented from working electrolytes composition,  $\text{g}\cdot\text{dm}^{-3}$ :  $\text{K}_4\text{P}_2\text{O}_7$  – 65.0–300.0;  $\text{CoSO}_4$  – 7.5–46.5.

The chemical composition of the coatings was determined by X-ray photoelectron spectroscopy on an INCA Energy 350 energy dispersive spectrometer; X-ray radiation was excited via exposing the samples to a 15-keV electron beam. In addition, X-ray fluorescence analysis was conducted using a SPRUT portable spectrometer with a relative standard deviation of  $10^{-3}-10^{-2}$ ; the error in determining the component content was  $\pm 1$  mass %. The surface morphology of the coatings was studied using a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were recorded by the registration of secondary electrons (BSEs) via scanning with an electron beam; this mode made it possible to study the topography with a high resolution and contrast ratio. The surface roughness was evaluated by the contact method on  $10 \times 10 \times 2$  mm samples with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2 and 0.2 nm, respectively;  $1024 \times 1024$  scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm).

The catalytic properties of the resulting oxide systems were studied in the oxidation of carbon(II) oxide to carbon(IV) oxide and in the flameless oxidation of benzene with air [8].

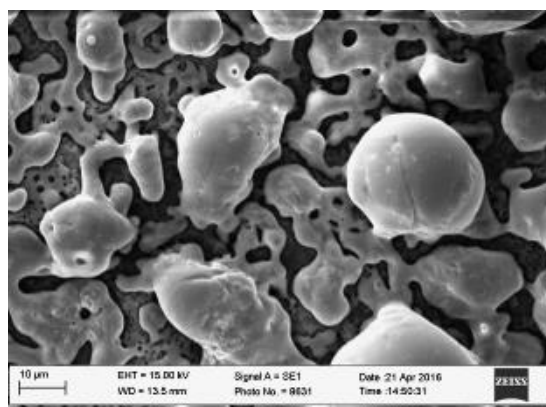
## 3. Results and discussion

The results of experimental studies found that PEO process of alloy AL25 in diphosphate electrolytes containing cobalt(II) is a classic case. It means that the voltage chronograms are divided into four sections: pre-spark, spark, microarc and arc. The pre-spark section is almost linear, which is explained by the growth of barrier alumina film and a corresponding increase in the resistance. In the transition to the sparking section the  $U$ ,  $t$  dependence becomes non linear, and the voltage growth slows down significantly, apparently due to the inclusion of the electrolyte components into the coating. This is particularly evident in the formation of coatings in cobalt-containing solutions when blue freeforms begin to appear in the anode areas, primarily occurring at sharp edges and in defect surface sites. Simultaneous progress of electrochemical oxidation and thermal decomposition of electrolyte components implemented in the mode of PEO contributes high adhesion of an oxide coating to the

substrate and incorporation of catalytic component – cobalt oxides. Composition of multi component oxides depends both on the concentration ratio of the electrolyte components and the oxidation current density. Thus, the oxide system is logically enriched with cobalt by increasing its content in the solution, but the electrolyte stability as well as service time is reduced. At the same time, increasing the diphosphate concentration in the bath is not desirable because it leads to a decrease of PEO efficiency. This is due to the formation of stable complex ions  $[\text{Co}(\text{P}_2\text{O}_7)_2]^{6-}$  in excess of the ligand, which is why the introduction of cobalt into the anode material is difficult.

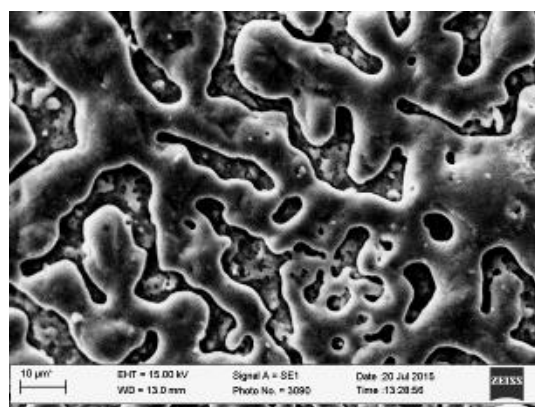
It was also established that the cobalt content in mixed oxide coatings increases when PEO is performed in the incident power mode. Starting current density  $i_1$  is higher for forming barrier aluminum oxide film on the AL25 substrate, which is accompanied by oxidation of the alloying components and particularly silicon with soluble substances forming and promotes homogenization of the alloy surface [9]. After the process enters a mode of stable arcing current density for the second stage  $i_2$  is reduced to ensure a formation of the mixed oxide layer. The current density for the first PEO stage in cobalt-diphosphate solution does not exceed the interval  $8\text{--}10 \text{ A}\cdot\text{dm}^{-2}$ , while the second stage is advisable to hold at current density of  $2.5\text{--}3.0 \text{ A}\cdot\text{dm}^{-2}$ . Arcing voltage  $U_i$  of PEO process in electrolyte  $200 \text{ g}\cdot\text{dm}^{-3} \text{ K}_4\text{P}_2\text{O}_7$  and  $30 \text{ g}\cdot\text{dm}^{-3} \text{ CoSO}_4$  is  $115\text{--}120 \text{ V}$ , and the resulting formation voltage  $U_f$  is  $140\text{--}160 \text{ V}$ . It should be noted that all voltage parameters grow with the electrolyte dilution and with increasing current density. The cobalt content in the mixed oxides increases with the current density and uniformity of its distribution on the surface is improved [10].

Surface morphology and composition of PEO coatings doped with cobalt oxides both depends on the concentration of electrolyte and oxidation conditions – current density, voltage and time of formation (Figure 1). The incorporation of the cobalt in oxide systems affects the formation of separate spheroid islets of characteristic blue-purple color. During the treatment the number of islet structures significantly increases, some the islets grow together, agglomerated and form a ceramic like mosaic patterns. The higher content of cobalt the more developed but at the same time the less uniform is the surface of coating (Figure 1 a, b). Formed oxide systems with cobalt content  $8\text{--}30 \text{ at.}\%$  and low concentration of impurities have high developed micro globular surface, which is essential for the high catalytic properties of the material [5]. Analysis of the composition of oxide systems indicates non stoichiometric ratio of cobalt and oxygen which is favorable for the implementation of catalytic processes involving oxygen.



Al – 48.7; Co – 23.6; O – 25.9; Si – 1.8

a

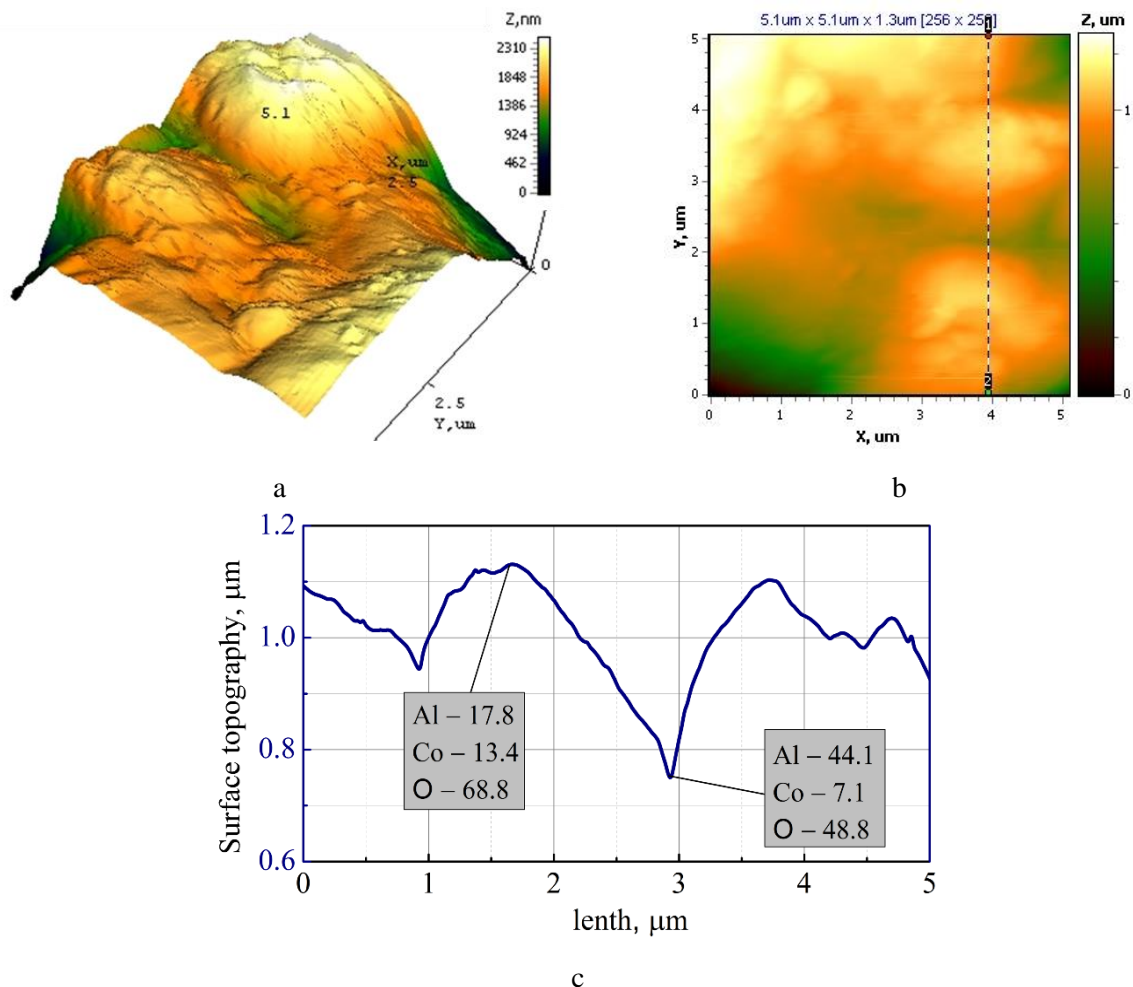


Al – 33.3; Co – 8.7; O – 55.2; Si – 2.8

b

**Figure 1.** Surface morphology and composition (at.%) of mixed oxide systems  $\text{Al}|\text{Al}_2\text{O}_3\cdot\text{CoO}_x$  obtained in PEO two stage mode ( $i_1=8 \text{ A}\cdot\text{dm}^{-2}$ ,  $i_2=2.5 \text{ A}\cdot\text{dm}^{-2}$ ) in diphosphate electrolytes ( $200 \text{ g}\cdot\text{dm}^{-3} \text{ K}_4\text{P}_2\text{O}_7$ ) with  $\text{CoSO}_4$  concentration,  $\text{g}\cdot\text{dm}^{-3}$ : a – 30; b – 10. Magnification 2000.

It was established by AFM analysis that the surface topography of Al | Al<sub>2</sub>O<sub>3</sub>·CoO<sub>x</sub> system with cobalt content of 8–12at.% (Figure 2) is characterized by the high roughness and large grain size. Mixed oxide coatings are composed from the set of spheroid grains with an average size of 1-2μm which gather and form the parts of smooth surface with the spherical grain agglomerates of 6-8μm (Figure 2a). The surface roughness may be characterized with the spread of grain size on the cross section between markers 1-2 (Figure 2b). In addition, the surface topography of oxides is characterized by rather large difference between hills and valleys of 0.3μm up to 1.2μm and alternating the spheroid and torus-shaped structures (Figure 2c).



**Figure 2.** 3D- (a) and 2D (b) maps of the surface and cross section profile (c) between markers 1 and 2 for mixed oxide system Al | Al<sub>2</sub>O<sub>3</sub>·CoO<sub>x</sub> with cobalt content 8.7 at.%. Scanning area 5 x 5 μm.

Testing of the synthesized oxide systems in the model reaction of carbon(II) oxide oxidation to CO<sub>2</sub> showed that the ignition temperature is 230 °C and the complete conversion is achieved at 305 °C which is comparable with the indicators of platinum catalysts 217 °C and 297 °C respectively [7]. Completeness of model reaction of flameless oxidation of benzene at Al | Al<sub>2</sub>O<sub>3</sub>·CoO<sub>x</sub> catalyst is also higher than at palladium-containing ones. For instance the degree of benzene oxidation, which is determined by the amount of resulting CO<sub>2</sub>, for example, at a temperature of 300 °C, is 5.0 times higher than on contacts SiO<sub>2</sub> Pd (with Pd content about 5 wt.%). Tests of materials based on mixed oxide systems in model reactions of CO and benzene oxidation have shown that their catalytic activity is not inferior to the contacts that contain noble metals. This can be attributed to several factors: firstly due to a high affinity of non-stoichiometric cobalt oxides to oxygen and the corresponding decrease in

the activation energy of destruction double bonds O=O [11-12]. Secondly, the developed micro globular surface of oxide systems is characterized by a large number of catalytic centers and provides an increase in the number of elementary collisions and interactions in multicomponent systems.

Pilot tests of mixed oxides deposited on the surface of combustion chambers piston of ICE confirm the change in fuel consumption and NO<sub>x</sub> emissions at forced diesel engine operating modes (Table 1). Analysis of data shows that the use of a catalytic coating based on manganese oxide compared to serial piston coated with Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> virtually unchanges hour fuel consumption (Table 1). However, the catalytic coating based on cobalt oxide can reduce diesel fuel consumption within 1–3%. Catalytic coating based on manganese oxide has almost no effect at NO<sub>x</sub> emissions (Table 1), but cobalt oxide system can reduce NO<sub>x</sub> emissions by 4–5% at loads when the emission of nitrogen oxide is most significant namely at crankshaft torque 40–70 N·m or loads level at 50–100 %. This is due to lower ignition temperature of the air-fuel mixture on Al<sub>2</sub>O<sub>3</sub>·CoO<sub>x</sub> catalyst composed of non-stoichiometric oxides and their more developed surface comparing with Al<sub>2</sub>O<sub>3</sub>·MnO<sub>x</sub> system.

**Table 1.** Indicators for fuel combustion in the chamber of ICE.

Composition of catalytic layer	NO <sub>x</sub> emission (ppm)					Fuel consumption (kg h <sup>-1</sup> )				
	Crankshaft torque (N m)									
	15	30	40	55	70	15	30	40	55	70
Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	600	1,200	1,750	2,200	2,400	1.25	1.60	2.00	2.4	3.00
Al <sub>2</sub> O <sub>3</sub> MnO <sub>x</sub>	590	1,200	1,730	2,160	2,370	1.25	1.61	1.99	2.38	2.98
Al <sub>2</sub> O <sub>3</sub> CoO <sub>x</sub>	575	1,150	1,660	2,090	2,280	1.23	1.57	1.96	2.34	2.90

Thus we can conclude that the varying conditions of the PEO process allows formation of oxide coatings of different composition and morphology that are expected to affect their functional properties including catalytic activity in the process of burning fuel in internal combustion engines, and reduce the toxicity of emissions improving fuel efficiency and environmental performance of engines.

#### 4. Conclusions

(i) Mixed oxide systems Al<sub>2</sub>O<sub>3</sub>·CoO<sub>x</sub> were obtained on Aluminum alloy AL25 by plasma-electrolytic oxidation in a diphosphate electrolyte added with cobalt(II) sulfate. It was shown the composition and surface morphology of oxides strongly depends on the bath concentration and PEO regimes. It was established non stoichiometric ratio of cobalt and oxygen in deposits as well as that the cobalt content in mixed oxide increases when PEO is performed in the incident power mode.

(ii) Obtained mixed oxide systems have developed micro globular surface containing torus-shaped structures which roughness is caused by cobalt content. Such morphology is characterized by a large number of catalytic centers.

(iii) Synthesized oxides exhibit catalytic properties not inferior to the contacts that contain noble metals and can be recommended for use in the neutralization of gas emissions systems, as coatings for ICE combustion chamber for the removal of toxins of various natures.

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