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Plasma Electrolytic Oxide Coatings on Silumin for Oxidation CO

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Abstract. Some catalysts of CO oxidation on silumin alloy AK12M2, used for the manufacture of pistons for Russian cars were investigated. The catalysts were prepared by the method of plasma electrolytic oxidation of silumin in electrolytes of various compositions with further activation by the salts Ce, Cu, Co, Ni, Mn and Al. The catalytic tests were carried out in a flow reactor in a mixture of 1% CO and 99% air, with the temperature range of 25-500 °C. The most active catalysts in CO oxidation are those activated with Ce and Cu salts on silumin, treated for 3 hours in an electrolyte containing 4 g/l KOH, 40 g/l $Na_2B_4O_7$ (conversion of CO is 93.7% at a contact time of 0.25 s). However, the catalysts obtained from silumin treated in the electrolyte containing 3 g/l KOH, 30 g/l Na_2SiO_3 are more suitable for practical usage. Because when the treatment time of those catalysts is 10 – 20 minutes it is possible to achieve comparable CO conversion. The morphology and composition of the catalysts were studied by the methods of a scanning electron microscope with energy-dispersive surface analysis and X-ray phase analysis. The surface of the non-activated sample consists of $\gamma\text{-}Al_2O_3$ and SiO_2 particles, due to which the active components get attached to the support. CeO_2 and CuO are present on the surface of the sample with the active component.

INTRODUCTION

Requirements for emissions of harmful substances (HS) with exhaust gases of gasoline and diesel engines are toughened by introducing new standards, at least every five years. Taking into account that a significant proportion of vehicles use internal combustion engines (ICE), designing such engines that would meet the requirements of environmental safety is an urgent task [1] The main components of harmful emissions are carbon monoxide (CO), nitrogen oxide (NO_x) and products of partial oxidation of hydrocarbons (CH). The most dangerous component is carbon monoxide - a toxic gas without colour, taste or smell. Carbon monoxide, by binding the hemoglobin of human and animal blood, forms carboxyhemoglobin which blocks oxygen transport to tissues and organs. This gas causes severe poisoning at concentration of 0.2% by volume, and when it exceeds 1% it becomes lethal. Carbon monoxide (CO) is formed during the combustion of hydrocarbons in a lack of oxygen, during cold-flame reactions in diesel engines or in the dissociation of carbon dioxide (CO_2) in gasoline engines. Reduction of emissions of this component is one of the main tasks in modern engine building. One of the ways to reduce emissions of harmful

substances with exhaust gases is the use of catalytic converters [2]. However, several studies have shown that they are not reliable at low temperatures and at cold-start of ICE. Changing the parameters of the working process of the engine is one of the possible solutions to this problem.

The temperature of the working fluid and the surface of the combustion chamber are the main parameters. The temperature of the piston on the side of the combustion chamber has a significant influence on these parameters; therefore the material for the piston is selected taking into account its influence on the combustion process of the fuel [3]. The temperature must not exceed 400 °C in the engine cylinder, since the destruction of pistons made of various alloys, including bimetallic ones, begins at this temperature. Ceramic-coated pistons can withstand such a temperature [4], but they do not have a catalytic effect on combustion products, neither do corundum-coated pistons.

Catalytic coatings of parts of the combustion chamber of an internal combustion engine are known to be used with preliminary plasma-electrolytic oxidation of their surfaces. In the reference publication [5] it is established that by using such coatings, a fuel economy of 2 to 9 % by weight can be achieved. In [6] it is established that the greatest conversion of carbon monoxide can be achieved by using palladium catalysts on silumin alloys corresponding to the material of the internal combustion engine piston. [7-10].

However, if noble metals are used, the cost of an ICE increases. The use of noble metals also makes this technique difficult to apply to ship and diesel engines. Thus, the solution to the problem of using catalysts that do not contain noble metals in the combustion chamber of an internal combustion engine is an urgent task.

EXPERIMENTAL PART AND DATA ANALYSIS

The samples used for the research were made from the piston of the VAZ-2108 car. These pistons are known to be made of silumin AK12M2 brand, which was confirmed by atomic emission spectrometry. The analysis was carried out on the Argon-5SF device. The analysis technique is presented in [11, 12].

Table 1 shows the data of the additional spectral analysis of the alloy. The composition of the alloy matches silumin of the brand AK12M2 which complies with the State Standard GOST 1583-93.

TABLE 1. The results of spectral analysis of samples of aluminum alloy

The Material Grade	Elements							
	Si	Cu	Mg	Fe	Ti	Mn	Ni	Al
AK12M2	13.2±0.5	1.77±0.08	0.82±0.05	0.61±0.05	0.01±0.005	0.38±0.02	0.33±0.01	82.9±2.5

The preparation of the catalysts consisted of several stages. The plates were made from silumin of the brand AK12M2 on a milling machine. The pistons of a gasoline engine (ICE) from VAZ-2108 car which are manufactured in a mass production were used as components for this material.
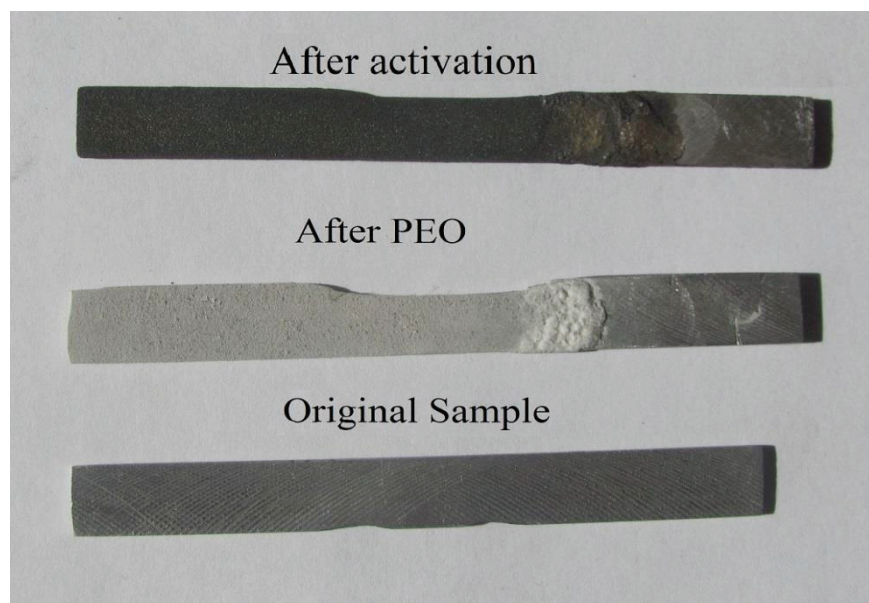
FIGURE 1. Stages of catalyst preparation

The samples of silumin were subjected to plasma electrolytic oxidation (PEO). The samples were then activated with precursors of the active components, dried and calcined at 500 °C for 3 hours. The samples of silumin $80 \times 8 \times 1$ mm were fixed as an anode. The aluminum plate $150 \times 80 \times 1$ mm, folded into a cylinder, served as a cathode. It was placed tightly near the inner side of the electrochemical cell equipped with water cooling. PEO was carried out at a constant current density of 1.1-1.7 A/dm2 in solutions of electrolytes, the composition of those is given in Table 2.

TABLE 2. Electrolytes for PEO coating

Name of Electrolytes	Electrolyte Composition	References
PWB	10.8 g/l Na3PO4, 6.9 g/l Na2B4O7, 1.8 g/l Na2WO4	[13]
PWBF*	10.8 g/l Na3PO4, 6.9 g/l Na2B4O7, 1.8 g/l Na2WO4, 3 g/l NH4F	[13]
PWBNiCu	10.8 g/l Na3PO4, 6.9 g/l Na2B4O7, 1.8 g/l Na2WO4, 20 g/l Ni(CH3COO)2·4H2O и 5 g/l Cu(CH3COO)2·H2O	[13]
KB	4 g/l KOH, 40 g/l Na2B4O7	[14]
KBF*	4 g/l KOH, 40 g/l Na2B4O7, 3 g/l NH4F	[14]
KSi	3 g/l KOH, 30 g/l Na2SiO3	[15]
KSiAl*	3 g/l KOH, 30 g/l Na2SiO3, 1.5 g/l AlF3	[15]

* – NH$_4$F and AlF$_3$ were added to the standard electrolytes for undercutting Al$_2$O$_3$ on the surface of the silumin to develop the surface of the support by the growth of the coating inside the sample. Fluorides also passivate copper contained in silumin, which prevents the destruction of the barrier layer.

The largest gain per time unit was obtained by using the electrolyte KSi due to the deposition of SiO2. PWB, PWBF and PWBCuNi provided smaller gain. In electrolytes KB and KBF the gain was very little or absent, because the coating is formed only from silumin, and not from the electrolyte solution. The names of the catalysts, for example, KSi120CuCe, were given as follows: KSi is the electrolyte, 120 is the PEO time of the sample being treated in the electrolyte solution with the time measured in minutes, CuCe are the active oxide components of the catalysts.

For the studies, 3 series of catalysts were prepared. To determine effects of active oxide properties, a series of samples was prepared: PWB40CuCe, PWB40Co, PWB40Ni, PWB40MnAl and PWB20NiCu (the optimum PEO treatment time in this electrolyte was taken from [14]). To study effects of catalyst support properties, a series of samples was prepared: KSi120CuCe, KSiAl10CuCe, KSiAl40CuCe, KBF40CuCe, KB180CuCe and PWBF40CuCe, PWB40CuCe. To study how the degree of conversion is dependent on the time of PEO in the silicate electrolyte, a series of samples was prepared: KSi10CuCe, KSi20CuCe, KSi30CuCe, and KSi45CuCe.

The application of the active components was carried out by impregnating the prepared supports with solutions of precursors. The following precursors were chosen: Cu(NO3)2·3H2O, (NH4)2Ce(NO3)6, Co(NO3)2·6H2O, Ni(NO3)2·6H2O, Mn(NO3)2·2H2O and Al(NO3)3·9H2O, because when they decompose, dispersed oxides of the corresponding metals are formed, which are active in the oxidation of hydrocarbons and CO. After the application of the precursors of the active components, the samples were placed in an oven for 1 hour at a temperature of 120°C and then calcined in air at 500°C for 3 hours. The temperature of calcination and subsequent catalytic tests is above 400°C, which is essential for determining the maximum activity of the catalyst and choosing the best one for future testing of catalytic coatings in ICE. To obtain catalytic coating of the piston, milder conditions will be used.

The activity of the obtained catalysts in the CO oxidation reaction was studied in a flow reactor using a feed gas mixture of 1% CO + 99% air. The contact time was ~ 0.4 s. The CO concentration before and after the reaction was measured chromatographically. The activity was estimated from the temperatures reaching 50 % of the conversion (T50). For the catalytic tests, samples with a mass of 0.8-1.2 g were used.

The KSi20CuCe sample was further examined by scanning methods of electron microscopy (SEM) and X-ray phase analysis (XRD). To determine the composition and morphology of the surface, the sample was applied to a conductive carbon adhesive tape fixed on a removable aluminum alloy plate with a special design stage that was placed in a "JEOL" microscope including the "INCAx-act" x-ray energy dispersive spectrometer produced by "Oxford Instruments" company. The morphology of the sample surface was examined using secondary electrons at an accelerating voltage of 20 kV. Local chemical analysis was performed at magnifications of 500-5000.

XRD was conducted on a DRON 3M device with a copper anti-cathode. Conditions of the analysis: I = 25 mA, V = 35 kV. A sample of 20 × 8 × 1 mm was fixed in a cuvette and placed in the device.

RESULTS AND DISCUSSION

To determine the comparative activity of the supported oxides, the samples obtained in the electrolyte PWB were used as supports In the course of the study it was found that supports prepared by the plasma-electrolytic oxidation method and pure silumin containing no active component are not very active in the deep CO oxidation. According to the degree of conversion at 500 ° C, oxide catalysts obtained on silumin treated in the PWB electrolyte in the deep CO oxidation form the following series of activities: PWB40CuCe (84.6%)> PWB40MnAl (40.5%)> PWB40Co (21.2%)> PWB20NiCu (10.4%) > PWB40Ni (7.6%).
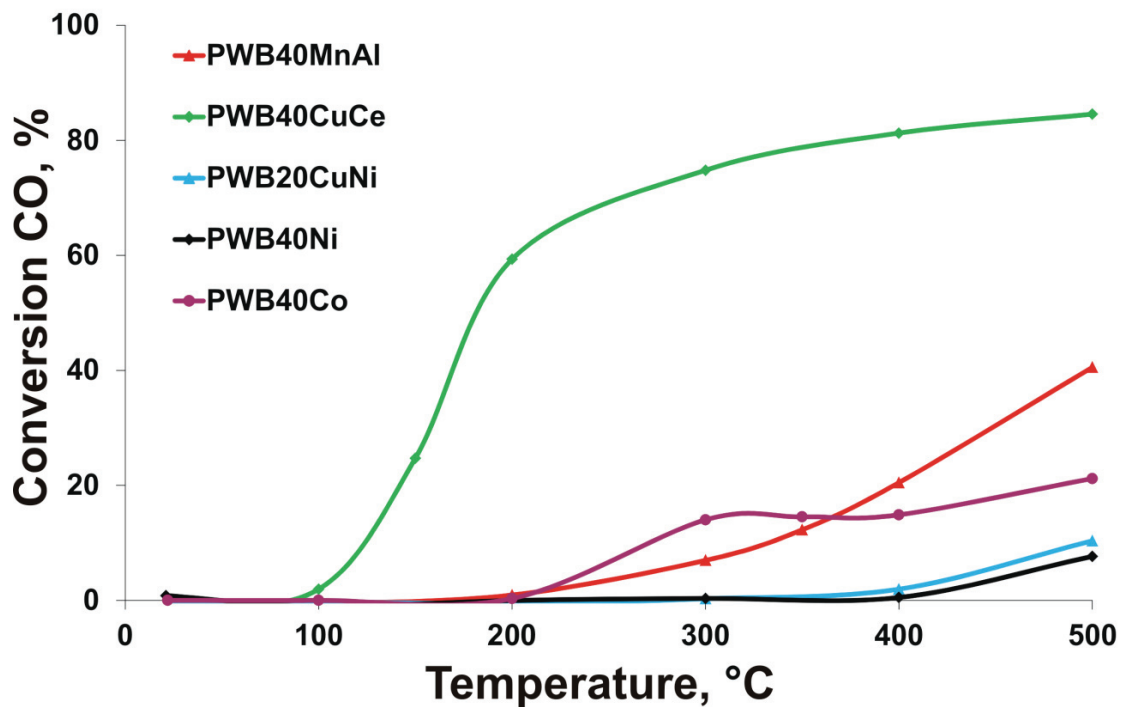
FIGURE 2. The dependence of the catalytic activity on deposited oxide properties

Due to the fact that the KSi120CuCe sample was twice as much more active than the other samples, further studies were carried out on catalysts impregnated with salts of Cu(NO3)2·3H2O and (NH4)2Ce(NO3)6.

The electrolyte, in which the most active catalyst is obtained, was chosen from those described in the reference literature [13-15].
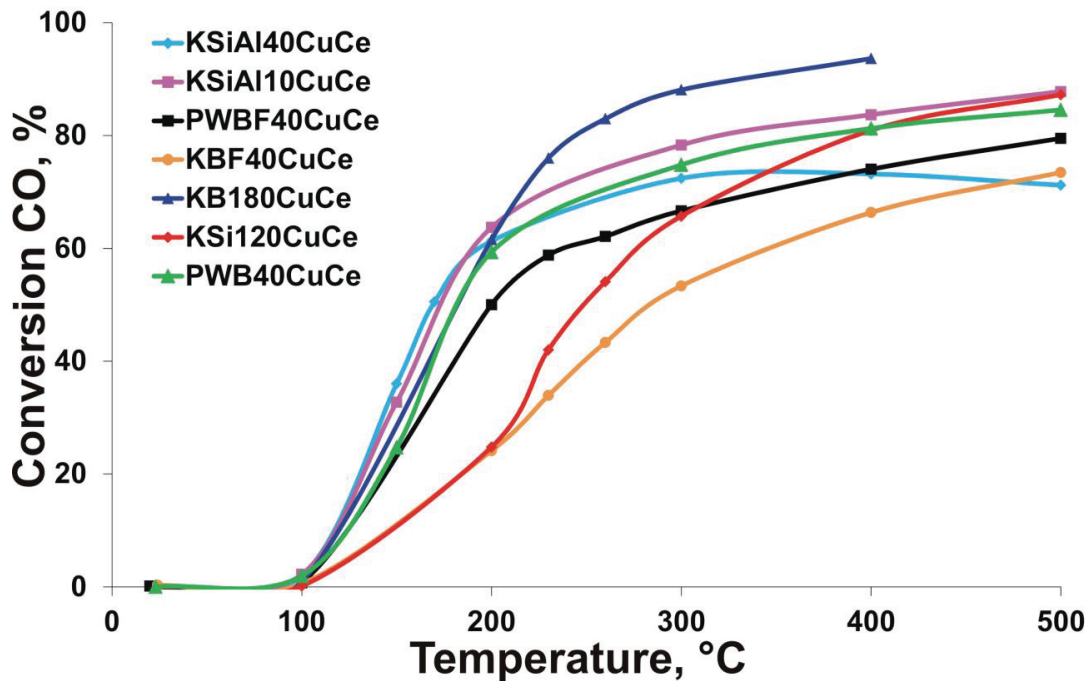
FIGURE 3. The dependence of the sample catalytic activity on electrolyte compounds

According to the degree of conversion at 500°C in deep CO oxidation, the oxide catalysts obtained on silumin which is treated by different electrolytes and activated by copper-cerium compounds the following series is formed: KB180CuCe (93.7 %) > KSiAl10CuCe (87.8 %) > KSi120CuCe (87.2 %) > PWB40CuCe (84.6 %) > PWBF40CuCe (79.5 %) > KBF40CuCe (73.5 %) > KSiAl40CuCe (71.2 %). The sample KB180CuCe shows the maximum activity among the samples activated by copper-cerium compounds, because, according to XRD, it contains γ-Al2O3, which is known to be the best support for the oxide copper-containing catalysts. However, the Al2O3 layer increases very slowly in the KB electrolyte. The fastest growing is the layer of oxides on silumin treated in KSi electrolyte. It can be seen that a much more active catalyst is obtained during a 10-minute-treatment in the KSiAl electrolyte in comparison to a 40-minute-treatment, so it was decided to study the activity of the catalyst depending on the time of treatment in the KSi electrolyte (Fig. 4).
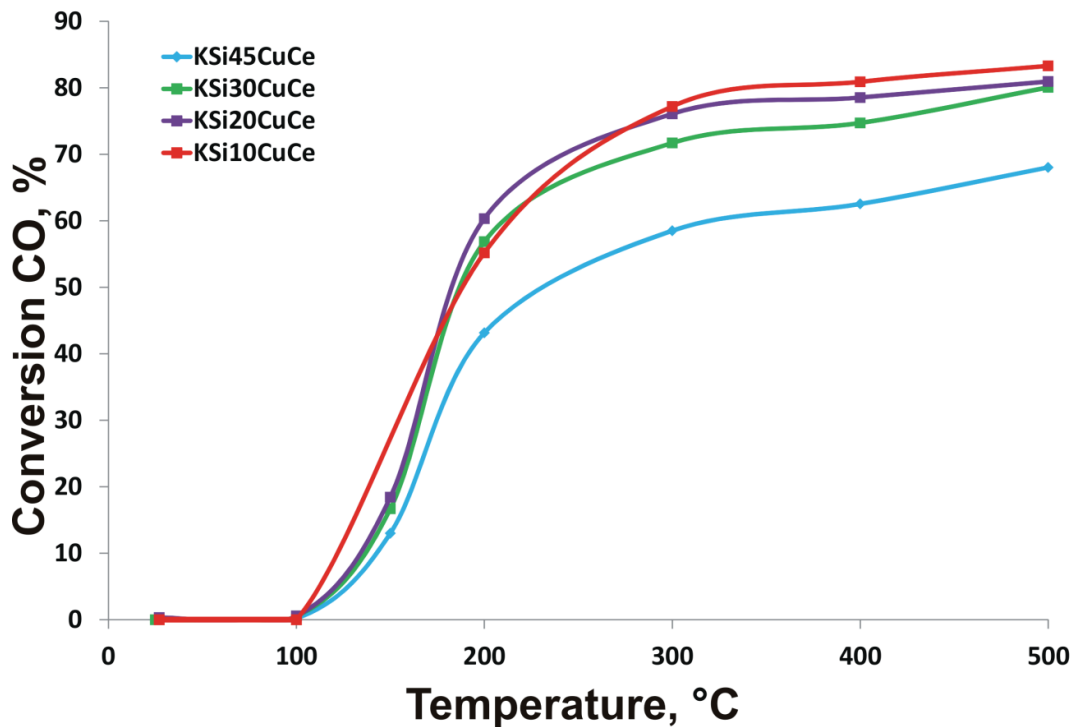
FIGURE 4. The dependence of the catalytic activity of the sample on the time of treatment in the electrolyte KSi

The study of the conversion degree dependence on the time of PEO was carried out to determine the optimum treatment time in order to reduce the treatment time and reduce the costs of electricity and reagents when moving to larger scale production in the future. Despite small differences in the degree of conversion at 500°C, it can be concluded that with an increase of the treatment time of silumin, the activity in the CO oxidation deposited on the oxidized silumin of copper-cerium catalysts decreases. In accordance with the degree of conversion at 500°C, the oxide catalysts obtained on silumin treated in the KSi electrolyte and activated by Cu(NO3)2·3H2O and (NH4)2Ce(NO3)6 in the deep CO oxidation form the following series: KSi10CuCe (83.3 %) > KSi20CuCe (80.9 %) > KSi30CuCe (80.1 %) > KSi45CuCe (68.0 %). The activity of samples treated only for 10-30 minutes is higher than the activity of samples treated for 45 minutes, which is connected with the development of the surface at the starting time, due to the formation of craters from breakdown and the formation of a highly dispersed phase of oxides, mainly γ-Al2O3. With the increase of treatment time, the dispersion of the oxide phase begins to fall due to reflow and coarsening of the primary oxide particles. Moreover, the contribution to the reduction of the SiO2 phase, which is less suitable for the deposition of oxides, increases. If the treatment time is increased, the oxide layer grows, which can have a negative effect on the functioning of the internal combustion engine due to the damage of the cylinder-piston parts during the process of separation of the coating. Therefore, it can be recommended to use the minimum treatment time for silumin elements from 10 to 20 minutes. The catalytic coating must fulfill the requirements not only for testing it on a laboratory equipment, but also for testing the piston in the ICE.
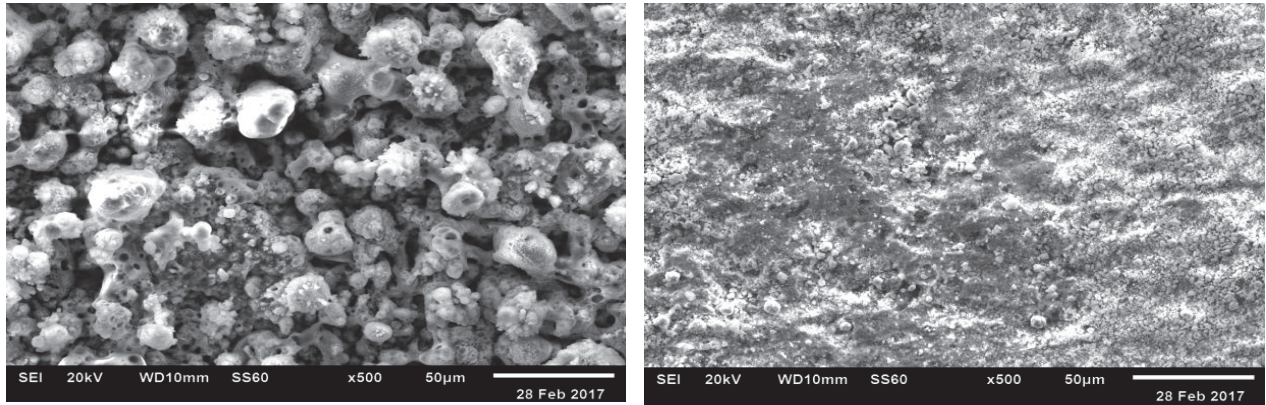
<center>(a)</center>
<center>(b)</center>

FIGURE 5. Microphotograph of coating on silumin (a) after PEO (sample KSi20), (b) after activation with copper and cerium compounds (sample KSi20CuCe)

The source silumin of the brand AK12M2 has a smooth homogeneous structure. According to energy-dispersive analysis, the signals from Al and Si were predominantly recorded in the spectra. After PEO (Fig. 5a) on electron microscopic images, it is seen that the surface of the sample is represented by conglomerates of particles of round shape up to 30 μm in size. According to energy-dispersive analysis, large particles are mainly amorphous SiO_2, while aluminum oxide forms an even coating. Also, in the thinnest parts of the coating some metallic aluminum is found According to the total spectrum, aluminum and silicon, as well as some impurities of sodium and potassium from the electrolyte are contained in the coating in the form of oxides. Impregnation of the samples with PEO coating with a solution of precursors of active components and subsequent calcination results in the formation of a less rough layer, as evidenced by a decrease in the size of the conglomerates of the particles down to 10 μm (Fig. 5b). According to the total spectrum, the support elements – aluminum and silicon – are mostly covered with the deposited oxides of copper and cerium Thus, the silicon content in the surface layer is reduced from 36% to 9%, and the aluminum content is reduced from 7.9% to 1.6%. That is a decrease by 4 - 5 times. This result also indicates that the oxides of copper and cerium cover the support with a continuous layer.
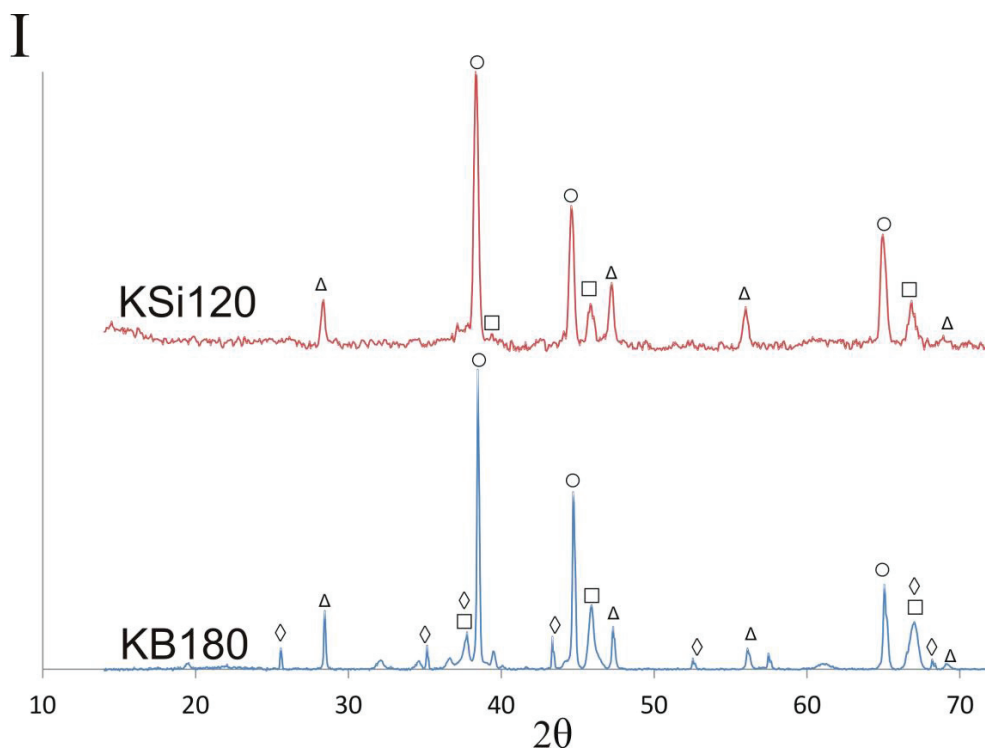
FIGURE 6. X-ray diffractograms of samples KSi20 and KB180: $\square - \gamma\text{-}Al_2O_3$, $\Delta - \alpha\text{-}Al_2O_3$, $\circ - Al$, $\lozenge - Si$

X-ray diffractograms (XRD) showed that the surface of the catalyst KSi20 is formed by the phases $\gamma\text{-}Al2O3$, Al and Si-elements of the base. The phase of silicon dioxide is not detected, probably due to its location on the surface of the sample in the X-ray amorphous state. For comparison, XRD of the best support KB180 was performed - the surface of the sample was based on the phases - $\gamma\text{-}Al2O3$, $\alpha\text{-}Al2O3$, Al and Si.

CONCLUSION

The catalysts based on silumin alloy AK12M2 were prepared with the PEO method with the subsequent activation by Ce, Cu, Co, Ni, Mn and Al salts and investigated in CO oxidation. It was established that the oxide catalysts obtained on the silumin treated in the PWB electrolyte with the deep CO oxidation and with the degree of transformation at 500°C form the following series: PWB40CuCe (84.6%) > PWB40MnAl (40.5%) > PWB40Co (21.2%) > PWB20NiCu (10.4%) > PWB40Ni (7.6%).

The oxide catalysts obtained on silumin treated in other electrolytes and activated by Cu(NO3)2·3H2O and (NH4)2Ce(NO3)6 in the deep CO oxidation and with the degree of conversion at 500°C form the following series: KB180CuCe (93.7%) > KSiAl10CuCe (87.8%) > KSi120CuCe (87.2%) > PWB40CuCe (84.6%) > PWBF40CuCe (79.5%) > KBF40CuCe (73.5%) > KSiAl40CuCe (71.2%).

The oxide catalysts obtained on silumin treated in the KSi electrolyte and activated by Cu(NO3)2·3H2O and (NH4)2Ce(NO3)6 in the deep CO oxidation and with the degree of conversion at 500°C form the following series: KSi10CuCe (83.3%) > KSi20CuCe 80.9%) > KSi30CuCe (80.1%) > KSi45CuCe (68.0%).

According to SEM after PEO it can be seen that the surface of the sample KSi20 is comprised of conglomerates of round-shaped particles with a size up to 30 μm, which after activation, with further formation of the active catalytic component, are reduced to conglomerates of particles with sizes up to 10 μm.

Aluminum and silicon - the support elements are largely covered by oxides of copper and cerium. XRD showed that the surface of the sample KSi20 based on phases $\gamma\text{-}Al2O3$, and Al and Si – the base elements. It is more

efficient to use catalysts obtained on samples of silumin treated in an electrolyte containing 3 g/l of KOH, 30 g/l of Na2SiO3.

Thus, the optimum conditions are found for obtaining the catalytic coating based on silumin alloy AK12M2, and a possibility is presented in this research how to improve the internal combustion engine's environmental characteristics with the use of catalytic coatings not containing platinum metals.

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