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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<sub>2</sub>/Al-Si sample is T<sub>50</sub> = 152 °C and T<sub>99</sub> 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<sub>2</sub>/Al-Si presents by noncrystalline SiO<sub>2</sub> with  $\gamma$ -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/m<sup>3</sup>). The development of CO-to-CO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO<sub>x</sub>, NiO, CuO, Co<sub>3</sub>O<sub>4</sub>, 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 chosen 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)

No	Sample	Electrolyte composition
1	CeO <sub>2</sub> /Al-Si	30 g/l of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , 3 g/l of NaOH, 10 g/l of Na <sub>2</sub> SiO <sub>3</sub> , 10 g/l of CeO <sub>2</sub> powder suspension
2	ZrO <sub>2</sub> -CeO <sub>2</sub> /Al-Si	30 g/l of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , 3 g/l of NaOH, 10 g/l of Na <sub>2</sub> SiO <sub>3</sub> , 70 g/l of ZrO <sub>2</sub> -CeO <sub>2</sub> powder suspension
3	γ-Al <sub>2</sub> O <sub>3</sub> /Al-Si	30 g/l of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , 3 g/l of NaOH, 10 g/l of Na <sub>2</sub> SiO <sub>3</sub> , 10 g/l of γ-Al <sub>2</sub> O <sub>3</sub> powder suspension
4	B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> /Al-Si	30 g/l of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , 10 g/l of Na <sub>2</sub> SiO <sub>3</sub> .
5	SiO <sub>2</sub> /Al-Si	3 g/l of NaOH, 10 g/l of Na <sub>2</sub> SiO <sub>3</sub>
6	SiO <sub>2</sub> /Al-Si	3 g/l of KOH, 30 g/l of Na <sub>2</sub> SiO <sub>3</sub>

Samples 1-5 were treated at the voltage 170 V, current density 3-5 A/dm<sup>2</sup> and treatment time 10 min. Sample 6 was treated at the voltage 220 V, current density 3-5 A/dm<sup>2</sup> and treatment time 120 min, thus greater covering thickness was achieved. The untreated surface of the samples was removed after PEO. Samples 1-5 with oxide coatings were impregnated with [Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> solution, while sample 6 was with Pd(NO<sub>3</sub>)<sub>2</sub> solution. Impregnation with Pd(NO<sub>3</sub>)<sub>2</sub> solution was carried out to determine the effect of palladium precursor nature on the sample catalytic activity. After palladium application, the samples were put for 1 hour in a drying cupboard at the temperature of 120°C, and then they were calcinated in air at 500 °C for 3 hours (Fig. 1, after PEO).



Fig. 1. Original catalyst carrier samples and the catalysts obtained by plasma electrolytic oxidation and palladium activation (after PEO).

The activity of the obtained catalysts in CO oxidation was investigated by using of a flow reactor involving initial gas mixture: 1% of CO + 99% of air. The residence time was around 0.4 s. The inlet and outlet CO concentration was determined by chromatography. The activity was evaluated as the temperature of 50% conversion degree ( $T_{50}$ ). The samples with weight of 3.2-3.4 g were used in catalytic tests.

Sample 5 (Pd/SiO<sub>2</sub>/Al-Si) was further studied by Raman spectroscopy, IR spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

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To investigate the surface composition and morphology, the sample was supported on current conductive carbonic adhesive band, fixed on a portable aluminum-alloy plate on object table with special design. The object table was put in microscope JSM-6610LV (JEOL), equipped with energy dispersive X-ray spectrometer INCAx-act from Oxford Instruments. The samples surface morphology was investigated in secondary electrons at accelerating voltage of 20 kV. Local chemical analysis was undertaken at 500-5000 magnification.

Raman scattering spectra were recorded on dispersion spectrometer DXR Smart Raman from ThermoScientific, equipped with an adaptor for reverse scattered light detection in the range of 50-3500 cm<sup>-1</sup>. The wavelength of exciting laser radiation was 633 nm, and the power amounted to 8 mW. Exposure time and spectrum accumulation number were determined automatically to reach the signal-noise ratio of around 10,000 in 5 min.

IR spectra were recorded with IR Fourier spectrometer IRPrestige-21 (Shimadzu) in spectral range 400-7800 cm<sup>-1</sup> with resolution 4 cm<sup>-1</sup> and spectrum accumulation number equal to 50. IR spectra of the coverings from the top of the ribs and between the ribs were recorded with the same parameters. For IR investigation the tablet of 1 mg of the sample mixed with 100 mg of KBr powder was pressed.

Atomic force microscopy investigation was carried out with Asylum Research AFM MFP-3D Stand Alone.

### 3. Results and discussion

The research demonstrated that palladium-free carriers and pure silumin, obtained by plasma electrolytic oxidation, are slightly active in deep CO oxidation. In deep CO oxidation, the oxide catalysts form the following sequence according to the conversion degree at 500 °C: Al-Si (4.5 %) > SiO<sub>2</sub>/Al-Si (2 %) > B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/Al-Si (1 %) > ZrO<sub>2</sub>-CeO<sub>2</sub>/Al-Si (0.5%) ≈ γ-Al<sub>2</sub>O<sub>3</sub>/Al-Si (0.5 %) > CeO<sub>2</sub>/Al-Si (0 %).

Table 2 contains the results of determining catalytic activity in CO oxidation. Sample Pd/SiO<sub>2</sub>/Al-Si reaches 99% CO conversion, and its weight is 25% higher than that of the other samples. Consequently, it has a larger covering with catalytically-active component. Therefore, its T<sub>50</sub> = 152 °C, i.e. 12 °C lower than the temperature of the other samples (save for samples Pd/B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/Al-Si and Pd/SiO<sub>2</sub>/Al-Si). Samples Pd/γ-Al<sub>2</sub>O<sub>3</sub>/Al-Si and Pd/CeO<sub>2</sub>/Al-Si proved to have similar activity at T<sub>50</sub>, both having 99% and 100% conversion degree at the temperatures of 165 °C and 220 °C, respectively. For sample Pd/B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/Al-Si T<sub>50</sub> = 152 °C, but at 220 °C CO conversion reaches 87 %. The highest T<sub>50</sub> = 166 °C was registered for sample Pd/ZrO<sub>2</sub>-CeO<sub>2</sub>/Al-Si, i.e. it is almost equal to that of samples Pd/γ-Al<sub>2</sub>O<sub>3</sub>/Al-Si and Pd/CeO<sub>2</sub>/Al-Si, while at 220 °C its CO conversion amounts to 82 % (Fig. 2). Sample Pd\*/SiO<sub>2</sub>/Al-Si, obtained with palladium nitrate, is slightly less active than the catalysts from ammonia complex of palladium nitrate. Therefore, samples 1-3 (Table 2), prepared from ammonia complex, have similar T<sub>50</sub>. Samples with SiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> as a support for palladium are more active. Palladium ammonia complex is adsorbed considerably stronger on acid carriers indicating higher dispersion ability of palladium particles in final catalyst and, consequently, higher activity. At higher temperature (220°) the samples with lower T<sub>50</sub> may be inferior in CO conversion degree resulting from different CO oxidation activation energy E<sub>a</sub> for various samples and overlapping of mass and heat transfer effects on catalytic reaction kinetics at temperature increase.

Table 2. Catalytic characteristics of oxide catalysts activated with palladium, Pd concentration 0.25 wt. %.

№	Catalyst	Temperature of X = 50%, T <sub>50</sub> , °C	Conversion degree at 220 °C, %
1	Pd/CeO <sub>2</sub> /Al-Si	165	100
2	Pd/ZrO <sub>2</sub> -CeO <sub>2</sub> /Al-Si	166	82
3	Pd/γ-Al <sub>2</sub> O <sub>3</sub> /Al-Si	165	99
4	Pd/B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> /Al-Si	152	87
5	Pd/SiO <sub>2</sub> /Al-Si	152	99
6	Pd*/SiO <sub>2</sub> /Al-Si	169	96

\* - Pd, obtained by impregnation from Pd(NO<sub>3</sub>)<sub>2</sub> solution

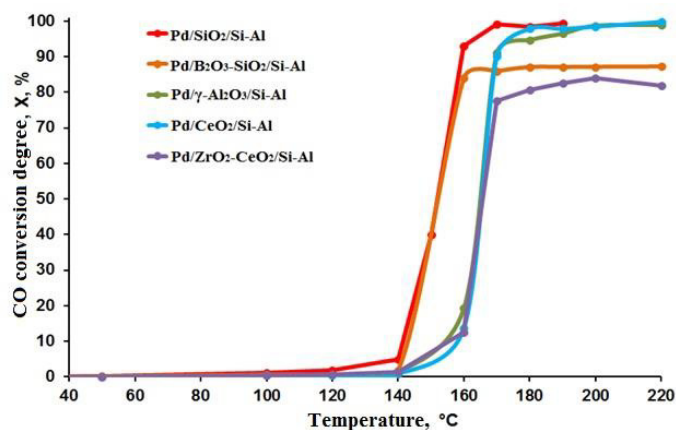


Fig. 2. Catalytic activity of sample palladium catalysts

#### 4. Investigation of sample Pd/SiO<sub>2</sub>/Al-Si with physical methods

Fig. 3 shows IR spectra of the coatings removed from silumin samples. Strong absorption bands are registered in IR spectra at 461, 794 and 1089 cm<sup>-1</sup>, indicating the Si-O bond stretching and bending vibration in amorphous silicon oxide (SiO<sub>2</sub>).

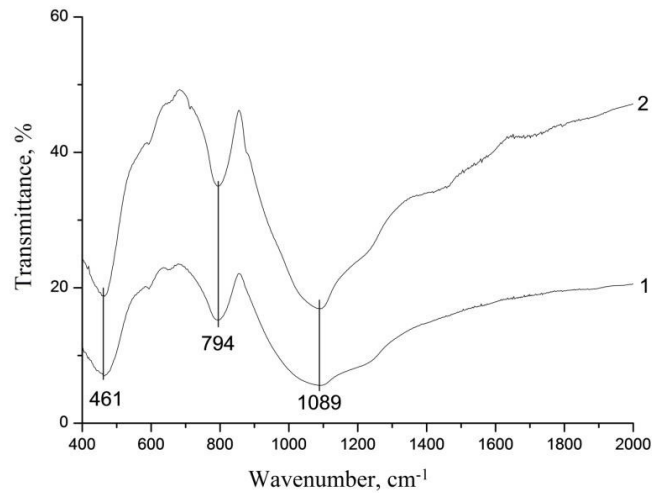


Fig. 3. IR spectra of the silumin parts surfaces: 1 - rib, 2 - concave

Fig. 4 shows Raman scattering spectra of the coating on SiO<sub>2</sub>/Al-Si sample. Scattering band is registered in Raman scattering spectra at 648 cm<sup>-1</sup>, corresponding to stretching vibrations of Si-O bond.

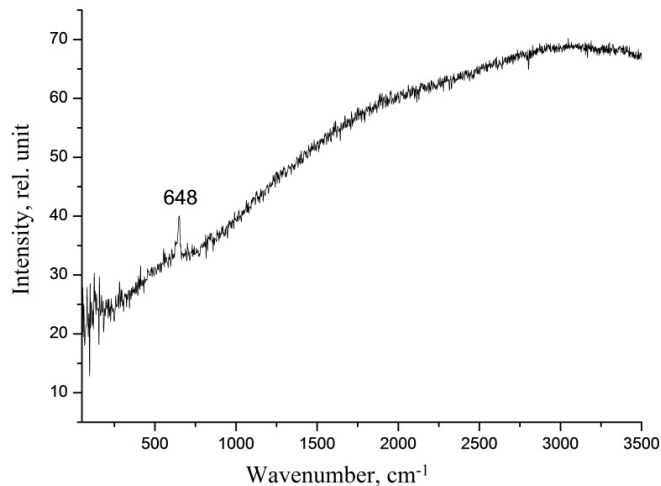


Fig. 4. Raman scattering spectra of the coating on silumin (sample 5)

The results of SEM study for active catalyst Pd/SiO<sub>2</sub>/Al-Si are given in Fig. 5-7. One may conclude that the applied layer has areas with differing degree of particles dispersion and morphology.

Thus, Fig. 5 shows the conglomerate on the rib of silicon particle at 1000 magnification. Mosaic amorphous mass, primarily composed of silicon and aluminum oxides, is seen. The large number of fractures is caused by a

high current density used at the coating preparation. The coating has chaotically arranged pores, this being a favourable factor for the coating application as a catalyst carrier. Whereas, taking the number of fractures on the coating surface into account, and consequently, an increased detachment chance, one can conclude that to obtain the best possible coating the current density should be lowered during deposition of the most important components.

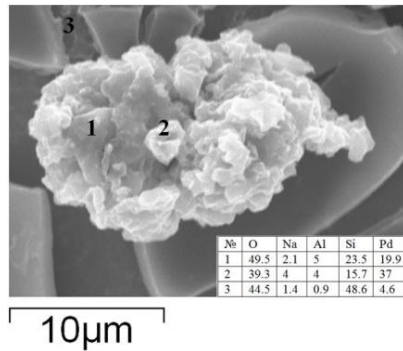


Fig. 5. Micrograph of the coating on silumin on the rib and ED-analysis at 1000 magnification.

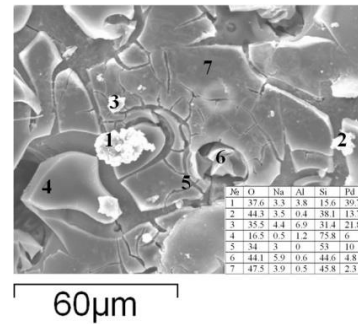


Fig. 6. Micrograph of the coating on silumin on the rib and ED-analysis at 5000 magnification.

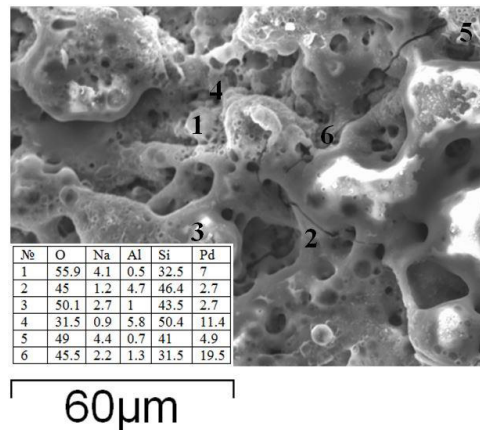


Fig. 7. Micrograph of the coating on silumin in the concave with ED-analysis at 1000 magnification and ED-analysis.

ED-analysis with mapping demonstrated that palladium is spread more uniformly in the coating on the rib tops compared to the concaves. Stabilization of its particles also takes place mainly on aluminum oxide particles having more porous structure in contrast with amorphous silicon dioxide phase. ED-analysis of the surface reveals the presence of sodium in the surface layer caused by its occurrence in the electrolyte. Palladium aggregation (Fig. 5) occurs in the areas with the highest aluminum concentration. This is likely to happen due to stronger stabilization of PdO (Pd) on aluminum oxide having acid Lewis sites unlike silicon oxide, whereon the primary attachment of the palladium ammonia complexes takes place. Sites 2 and 3 indicate that (Fig. 6). The area mapping also illustrated that palladium arrangement on the coating is non-uniformly.

The surface of the concaves in silumin parts (Fig. 7) appeared to have more uniformly arranged pores and almost no fractures. Moreover, the surface curvature is lower compared to the ribs surface, thus promoting more durable coating. This also indicates that too high current density should be avoided in the coating application. Palladium distribution in the concaves is more uniform in contrast to the ribs due to better arranged porosity. As reflected by the analyses, Pd and Al occur together nearly at all sites. This means that aluminum inclusions in the surface layer

may be the centers of palladium particles attachment stabilizing its dispersion. In general, the conclusion can be made that the samples activity is determined by the palladium presence and its dispersion.

As seen (Fig. 8) the profile diagram obtained with AFM allows to conclude that the coating surface structures in the concaves differ in surface formations morphology, i.e. in the height of the hillocks, their thickness and mutual arrangement. The surface between the ribs has more sharp structure of the hillocks. This is associated with the lower current density used in samples preparation resulting in a less intensive and chaotic growth of the coating. The maximum difference between the peak of hillocks and concaves bottom is 9.6 nm in the first diagram. This results from the higher current density causing the melting of a part coating during the plasma electrolytic oxidation. The coating in the concave turned out to have more rounded crests due to lower current density. More porous and coarser coating form between the sample ribs resulting from the more smaller surface melting owing to the lower current density.

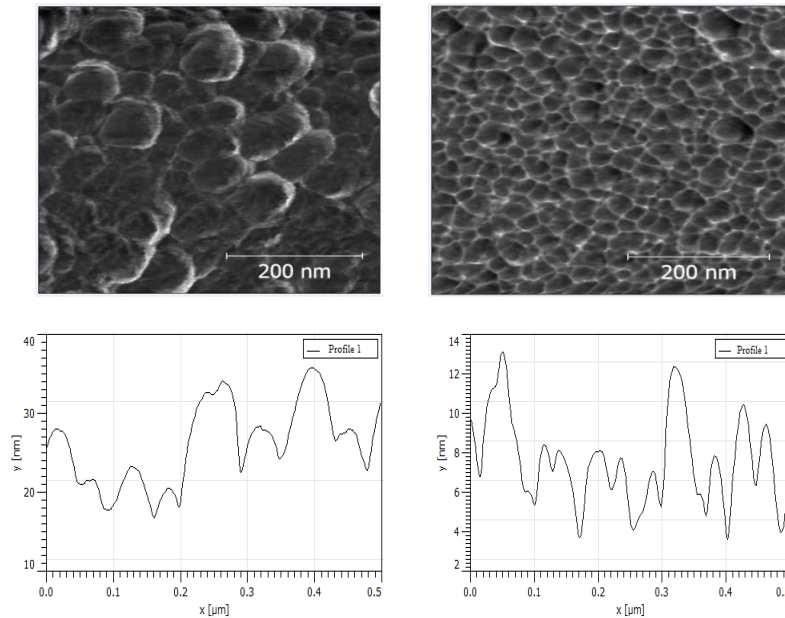


Fig. 8. Atomic force microscopy: a concave is on the left, a rib is on the right

The conducted study allows making the following conclusions:

1. Catalysts non-activated with palladium are low-active. They can be arranged in the following sequence by CO conversion degree at 500 °C, %: Al-Si (4.5 %) > SiO<sub>2</sub>/Al-Si (2 %) > B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/Al-Si (1 %) > ZrO<sub>2</sub>-CeO<sub>2</sub>/Al-Si (0.5%) ≈ γ-Al<sub>2</sub>O<sub>3</sub>/Al-Si (0.5 %) > CeO<sub>2</sub>/Al-Si (0 %).
2. Palladium activated samples are active. Activity sequence by T<sub>50</sub> is as follows: Pd/SiO<sub>2</sub>/Al-Si = Pd/B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>/Al-Si > Pd/CeO<sub>2</sub>/Al-Si = Pd/γ-Al<sub>2</sub>O<sub>3</sub>/Al-Si = Pd/ZrO<sub>2</sub>-CeO<sub>2</sub>/Al-Si. At 220 °C the activity sequence based on CO conversion degree changes due to higher influence of mass and heat transfer on the process kinetics.
3. According to IR and Raman spectroscopy, the base of the catalytic coating surface in active sample Pd/SiO<sub>2</sub>/Al-Si is amorphous silicon oxide.
4. By SEM data, the coating surface between the item ribs is more porous and better arranged. To obtain catalytic coating, lower current density is more preferable since it provides better arranged and more porous coating. According to AFM, the inter-ribs coating is coarser. AFM results correspond well to SEM ones.
5. The investigation in the chosen field may further evolve into obtaining the coating with the thickness of 70-150 μm having a thermo-barrier effect. Cheaper catalysts should be found, as well.



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