Developing technology of creating wear-resistant ceramic coating for internal combustion engine cylinder sleeve

Desarrollo de una tecnología de revestimiento cerámico resistente al desgaste para camisas de cilindros de motores de combustión interna

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ABSTRACT

This paper presents the results of testing a wear-resistant ceramic coating on the work surface of an internal combustion engine (ICE) cylinder’s sleeve. A combined coating formation technology is described that consists in applying an aluminum layer to the sleeve’s work face by gas dynamic spraying and then covering this face with a ceramic layer by microarc oxidation (MAO). A tenfold reduction in the reinforced sleeve has been determined by the accelerated comparative wear rig tests of reference (new) sleeve-piston ring coupling specimens and reinforced specimens with a combined coating. The supplementation of nanoparticle admixture to MAO coating reduces the friction factor between the cylinder sleeve face and the piston ring by 25-30%. The proposed technology can be used to reinforce work surfaces of new cylinder sleeves and recover worn out ones.

Keywords: Wear resistance; Friction factor; Gas dynamic spraying; Microarc oxidation; ICE cylinder sleeve.

RESUMEN

El artículo presenta los resultados de la investigación del revestimiento cerámico resistente al desgaste en la superficie de trabajo de la camisa de cilindro del motor de combustión interna. Se describe la tecnología de formación de revestimiento combinado, que consiste en la aplicación sucesiva de la capa de aluminio por el método de gas-térmico en la superficie de trabajo del revestimiento, y luego - de la capa de cerámica por el método de oxidación de micro-arco. Las pruebas comparativas de desgaste acelerado en banco de las muestras de referencia (nuevas) de la conjugación camisa-anillo de pistón y las muestras endurecidas con revestimiento combinado de la superficie de trabajo de la camisa revelaron una reducción del desgaste de la conjugación endurecida en 10 veces. La introducción de nanoaditivos en el recubrimiento de oxidación de microarco conduce a la disminución del coeficiente de fricción entre la superficie de la camisa y el anillo del pistón en un 25-30%. La tecnología desarrollada puede utilizarse para endurecer las superficies de trabajo de las camisas de cilindros nuevas y para restaurar las desgastadas.

Palabras clave: Resistencia al desgaste; Coeficiente de fricción; Aplicación gas-dinámica; Oxidación por microarco; Camisa de motor de combustión interno.
1. INTRODUCTION

Nowadays, the main option for automotive manufacturers at the global market is aluminum engine blocks with cast iron sleeves rigidly mounted by molding or press working or their fully aluminum alloy counterparts with an elevated hypereutectic silicon content. For the detailed description of the flaws and merits of the considered solutions of manufacturers see (Recovering Cylinders with NIKASIL Coating, 2018; Coming back to Nikasil Otherwise Referred to as Alyusil, 2018; Are Aluminum Engines Worth the Cost?, 2015). In both variants, the replacement of the whole block after the damage to the sleeve face (work surface) is necessary.

The application of MAO to creating coatings with certain predefined properties as applied to various metals and alloys is the subject of active debate in the global scientific community.

Papers (Famiyen, and Huang, 2019; Zhang, Fan, Du, et al., 2017; Miao, Wu, Hao, et al., 2013; Xue, Jin, Zhu, et al., 2009; Wang, Wu, Cai, et al., 2010) present the data about using MAO in airspace engineering and other industries and highlight the features of coating properties, observed with the change in the material base composition and MAO modes.

The prospects and areas of using MAO have been identified and the properties of coatings as applied to the region of interest described in a large number of research publications. The long-term benefits and practical value of using MAO in both machine building and healthcare are highlighted in (Kang, Tu, Han, et al., 2019; Peitao, Mingyang, Chaoyang, et al., 2019; Yin, Peng, Liang, et al., 2016; Pezzato, Cerchier, Brunelli, et al., 2019; Yu, and Chen, 2017; Wei, Yan, and Tian, 2005; Matykina, Skeldon, and Thompson, 2013).

The expediency of applying MAO in ICE is confirmed in (Malyshev, Gantimirov, Volkhin, et al., 2013; Lesnevskiy, Leznyov, and Lyakhovetskiy, 2015; Kiseleva, Zainullina, Abramova, et al., 2015; Krishtal, Ivashin, Polunin, et al., 2013). The thermal resistance of MAO coatings used in ICE is considered in (Chavdarov, Skoropupov, Milovanov, et al., 2015).

This paper is aimed at developing and testing a wear-resistant ceramic coating on the work surface of an ICE cylinder sleeve. This coating is produced by applying an aluminum layer by gas thermal spraying and then a ceramic layer by MAO.

2. MATERIALS AND METHODS

The objects of research were steel specimens with an aluminum coating applied by gas thermal spraying and a ceramic layer formed on its surface by MAO.

![Figure 1. Specimens with MAO coating](image-url)
The specimens were covered with A20-11 aluminum powder by ultrasonic gas dynamic spraying using a Dimet-403 unit with a special nozzle (Device for Gas Dynamic Coatings of Internal Surfaces of Cylindrical Items, 2020). The mechanical treatment of the specimens was followed by the forty-minute anode-cathode MAO in electrolytes of various composition at a current density of 15 A/Dm². The described modes are recommended for items exposed to thermal dynamic influences in the ICE combustion chamber (Lesnevskiy, Lezhnyov, and Lyakhovetskiy, 2015).

Pieces of an aluminum cylinder block with lined cast iron sleeves were taken as the reference specimens for comparison.

![Reference coupling specimens](image1)

Figure 2. Reference coupling specimens for tribotechnical tests on a frictional machine: a is a specimen cut out from a piece of cylinder sleeve; b is the specimen cut out from a piston ring

A piece of a piston ring in contact with the cylinder sleeve (CSL) face was used as a counterpart specimen. The MAO coating composition was analyzed with the help of a Niton XL3t 900 GOLDD+ X-ray fluorescence spectrometer.

The tribotechnical tests were conducted on a TRB-S-DE frictional machine.

![TRB-S-DE frictional machine](image2)

Figure 3. TRB-S-DE frictional machine for testing tribotechnical properties of materials
The tests were conducted with the counterpart specimen moved back and forth, an oscillation amplitude of 20 mm, an oscillation rate of 0.25 m/s, a standard pressure of 10 N, and the counterpart specimen’s aggregate friction route of 2 000 m. The wear was measured by weighing the specimen and the counterpart specimen on an analytical balance to an accuracy of 1 mg. The compounds added as admixtures to the electrolyte for MAO were copper oxide, vanadium oxide, sodium tungstate, cobalt hydroxide, nickel oxide.

3. RESULTS AND DISCUSSION

The properties of coatings are significantly modified with the supplementation of various admixtures as nanoparticles to electrolyte for MAO. The above-specified admixtures have been chosen proceeding from both, analyzing literary sources (Cobalt Aluminate Production Technique, 2009; Ni-Al Intermetallic Alloy, 2000; Shandrov, Shudrov, and Nuriev, 2016; Aliramezani, Raeissi, Santamaria, et al., 2017; Ihwang, Shin, Lee, et al., 2012).

A popular practical means of significantly reducing the friction factor and facilitating a long service life of friction pairs is to apply a thin copper coating. In particular, this procedure is often used in recovering ICE crankshafts by gas thermal methods. Pure copper is almost unused and does not fit as a nanoparticle admixture to electrolyte. That is why it was decided to use CuO nanopowder instead.

The concentration of admixtures in electrolyte was determined proceeding from previously conducted tests. MAO stops when the preset concentration of admixtures in standard electrolyte is exceeded. A reduction in the concentration sharply decreases an admixture’s fraction in the coating.

Each test was conducted on three specimens. The size verification was carried out in three points along the specimen length before and after MAO as well as after grinding (removal of the temporary loose layer of mullite).

The results of all of the measurements were processed and recorded in the respective summary Table 1.

| Solution, g/l | Extr. no. | Size pre-MAO | post-MAO | post-grinding |
|--------------|-----------|--------------|----------|---------------|
| KOH – 1.5; Na2SiO3 - 6 | 1 | 10.36 | 10.56 | 10.37 |
| + CuO - 5 | 2 | 10.37 | 10.56 | 10.36 |
| + V2O5 - 1 | 3 | 10.34 | 10.54 | 10.34 |
| + Na2WO4 - 1 | 4 | 10.38 | 10.53 | 10.37 |
| + Co(OH)2 - 5 | 5 | 10.35 | 10.52 | 10.34 |
| + NiO - 5 | 6 | 10.36 | 10.53 | 10.35 |

As shown by analyzing the exposed data, the supplementation of nanoparticle admixtures to electrolyte had little effect on the specimens’ sizes after both, MAO and grinding. The results exposed in Table 1 allow making the following conclusions:

- the supplementation of nanoparticle admixtures has almost no effect on the coating’s growth kinetics;
- the sleeve’s recovered surface should be processed to nominal size. Geometrically, MAO has almost no effect on the sleeve’s internal diameter.
For the processed results of analyzing the specimens on a Niton XL3t 900 GOLDD+ X-ray fluorescence spectrometer, see Table 2.

Table 2. Results of X-raying MAO coatings

| No. | % additive | Time, mins | Thickness, μm | Mg  | Al  | Si  | additive | Mn  | Fe  | Cu  |
|-----|------------|------------|---------------|-----|-----|-----|----------|-----|-----|-----|
| 1   | -          | 60         | 55-60         | 0.5 | 36.3| 51.62| -        | 0.9 | 0.6 | 1.1 |
| 2   | 5 CuO      | 60         | 76-85         | 0.8 | 39  | 41   | Cu 10.1  | 0.7 | 0.5 | 10.1|
| 3   | 1 V₂O₅     | 60         | 70-75         | 1.1 | 45.3| 35.3 | V 8.03   | 0.9 | 0.47| 1.4 |
| 4   | 1 NaWO₄    | 60         | 75-80         | 0.9 | 40.7| 36.8 | W 8.8    | 0.7 | 0.6 | 1.2 |
| 5   | 5 Co(OH)₂  | 60         | 70-75         | 0.2 | 41  | 43   | Co 5.4   | 0.9 | 0.4 | 1.5 |
| 6   | 5 NiO      | 60         | 73-75         | -   | 39  | 52   | Ni 6.5   | 0.66| 0.5 | 1.1 |

The coating thicknesses from Table 2 are given for the cases with the loose upper mullite layer removed. As shown by analyzing the exposed data, the elements used as admixtures in electrolyte, even the ones almost insoluble in water, remain in the coating due to electrophoretic processes.

To compare the behavior of the MAO coating with the actual tribotechnical pair in the ICE, a piece of a cylinder block (reference) was mounted on the frictional machine and several tests were conducted with the above-described parameters. For the results of measuring the relation of the friction factor to the test duration, see Figure 4.

![Figure 4. Time relation of friction ratio for the running pair of a cast iron CSL piece and a piston ring piece](image)

The readings’ stability reveals that the friction pair is well run-in. The average friction factor was 0.061, the cylinder sleeve’s piece and the piston ring’s piece got worn by 0.012 and 0.022 g, respectively.

Three specimens were prepared for the test for each electrolytic composition. Only averaged data for each batch of specimens is provided below.

The difference in wear among the specimens with the addition of CuO to electrolyte was insignificant Figure 5. The specimen running-in took about 90 seconds on average. The average friction factor was 0.049. The ring wear was 0.023 g.
The run-in of the specimens with the addition of vanadium oxide to electrolyte took about 80 seconds on average Figure 6. The average friction factor was 0.046. No wear of the specimens was registered. The ring wear was 0.003 g.

The run-in of the specimens with the addition of sodium tungstate to electrolyte took about 80 seconds on average Figure 7. The average friction factor was 0.049. No wear of the specimens was registered. The ring wear was 0.003 g.
Figure 7. Time relation of the friction ratio for the running coupling of a sleeve piece with MAO coating with sodium tungstate and a piston ring piece.

The run-in of the specimens with the addition of cobalt hydroxide to electrolyte took about 80 seconds on average Figure 8. The average friction factor was 0.058. No wear of the specimens was registered. The ring wear was 0.003 g.

Figure 8. Time relation of the friction ratio for the running coupling of a sleeve piece with MAO coating with cobalt hydroxide and a piston ring piece.

The run-in of the specimens with the addition of nickel oxide to electrolyte took about 80 seconds on average Figure 9. The average friction factor was 0.048. The specimen wear reached 0.001 g. The ring wear was 0.008 g.
The summary table of the test results for analyzing the findings is presented below.

Table 3. Collective wear test results

| no. | % additive  | Specimen wear, g | Ring wear, g | Wear-in time, sec | Friction factor |
|-----|-------------|------------------|--------------|------------------|----------------|
| reference | - | 0.012 | 0.022 | 30 | 0.061 |
| 1 | grinding-in | 0.428 | 0.332 | 200 | 0.332 |
| 2 | 5 CuO | 0 | 0.022 | 90 | 0.049 |
| 3 | 1 V₂O₃ | 0 | 0.003 | 80 | 0.046 |
| 4 | 1 NaWO₄ | 0.001 | 0.003 | 80 | 0.049 |
| 5 | 5 Co(OH)₂ | 0 | 0.003 | 80 | 0.058 |
| 6 | 5 NiO | 0.001 | 0.008 | 80 | 0.048 |

In the reference pair the cylinder sleeve got worn almost twice as little as the piston ring, which corresponds to the test results from (Dudareva, Kalschikov, Musin, et al., 2013). In all of the considered variants the specimens with MAO coating showed almost no wear, which means that all of the coatings are highly wear-resistant.

In terms of ring wear, the results delivered by the four remaining coatings were roughly the same. In addition, the friction factor of these specimens was by 25-30% lower than in the reference one, except for the coatings with cobalt hydroxide.

It should be noted that the supplementation of nanoparticle admixtures to electrolytes yields the same results of reducing the friction factor as the permeation of the MAO layer with an ultrahigh molecular polyethylene (Malyshev, Gantimirov, Volkhin, et al., 2013).

The influence of the dispersibility of nanoparticle admixtures on the wear resistance and friction coefficient of the test couplings was analyzed. The admixtures to electrolyte that are considered in this
article have different water solubility. In this respect, the most preferable admixture is sodium tungstate fully soluble in water and found in electrolyte as ions. The rest of the analyzed admixtures are insoluble in water and found in electrolyte as suspended solids. As shown by the analysis, the size of suspended particles ranges from 10 to 50 μm, depending on the admixture. Despite the highest molecular weight of vanadium oxide and a minor fraction of vanadium of about 8% in MAO coating, the tests showed the minimal ring wear in the presence of vanadium, which confirms the efficiency of the global practice of using vanadium for wear reduction and reducing the friction coefficient.

The test data analysis allows us to state that the wear resistance and friction factor of the MAO coating-piston ring pair are unaffected by the dispersibility of the admixtures to electrolyte.

4. CONCLUSIONS

The addition of nanoparticle admixtures to MAO coating reduces the coefficient of friction between the cylinder sleeve face and the piston by 25-30%.

Nanoparticle admixtures allow achieving a tenfold reduction in the wear of piston rings and cylinder faces.

The wear resistance and friction factor of the MAO coating-piston ring pair are unaffected by the dispersibility of the admixtures to electrolyte.

The compounds recommended for use as nanoparticle admixtures in standard alkaline electrolytes are vanadium oxide and sodium tungstate in an amount of 1g/l.

In terms of wear and friction factor, the proposed technology of creating a ceramic coating on the ICE cylinder face is very viable and practically valuable in both, manufacturing new and repairing used ICE.

The investigation results from (Sabri, and El Mansori, 2009) are recommended for use in processing the MAO coatings formed on the item of interest.

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