The study of oxide films on the surface of a piston of aluminum alloy after micro-arc oxidation

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Abstract. One of the promising methods of surface hardening of piston aluminum alloys – micro-arc oxidation—is considered in the paper. This type of coating, formed under the influence of micro discharge in the electrolyte solution, is fundamentally different from the base metal. A qualitative analysis of the piston alloy on the energy dispersion x-ray fluorescence spectrometer was carried out for a more accurate assignment of the oxidation parameters, which allowed the most accurate determination of the chemical composition of the alloy. Micro-arc oxidation of the pistons was carried out at the experimental laboratory facility, which allowed to regulate the total density of the ion current II and the quantitative ratio of cathode and anode currents IK/IA in a wide range, which favorably affected the quality of the oxide layers. The mechanism of formation of crystalline inclusions and high-temperature structures depending on the ion current density in time is also described. The conditions of formation of oxide films on the surface of piston alloys based on the physical-geometric Keller model are described and their characteristic features are revealed. The technique of investigation of microstructures of thin films is considered, its characteristic features are described. The obtained microstructures of piston aluminum alloys after micro-arc oxidation are presented. Mechanisms of formation of oxide layers are considered taking into account the influence of alloying elements of piston aluminum alloys. Microphotographs of individual porous cells obtained with the help of an electronic scanning microscope are also shown and analyzed. The basic properties that should have a piston of aluminum alloys: heat resistance, corrosion resistance and abrasive wear. Methods of their research are described. The complex analysis of the received results is carried out. The conclusion about the prospects of these oxide coatings is made.

1. Introduction
Currently, the piston group of modern diesel and gasoline internal combustion engines is experiencing loads close to the maximum permissible. And if alternative fuels are used to power the engine, the temperature and pressure in the combustion chamber increase by 15...20%, which leads to an increase in the thermal strength of the parts of the entire cylinder-piston group [1].

The creation of a fundamentally new generation of parts on the basis of alloys produced by the industry is associated with the application of special hardening and protective coatings on the working surfaces. Such coatings have properties that are radically different from the properties of the main material of the parts. This separation of functional properties promotes re-increase of reliability and operating life of machine parts operating under cyclic, dynamic, alternating loads in conditions of high temperature and pressure [2].
To address the shortcomings of such a plan can create on the surface of the pistons of films composed of aluminum oxide (Al2O3). These films have high heat resistance, hardness, corrosion resistance and low chemical activity. It is these properties that determine the practical significance of the use of these coatings on piston alloys when working in conditions of elevated temperatures and pressures, especially when working on alternative fuels. One of the promising methods for obtaining a similar film on the surface of piston alloys is micro-arc oxidation (MDO). MDO occurs in a certain electrolyte under the action of micro-arc discharges [3]. This type of surface treatment is determined by the presence of electrochemical processes, similar to anodizing. However, the characteristic difference from anodizing is the use of free energy of electric micro-discharges in the electrolyte solution. As a result of this impact on the surface of the piston coatings appear, such as ceramics. The advantage of this process is the possibility of obtaining oxide films on the inner surface of the combustion chamber located in the piston. MDO coating on cylinder-piston parts helps to protect them from high-temperature gas erosion and reduces the temperature of the base metal by about 1.5 times. The chemical composition of these films can be easily adjusted in a very wide range and used as heat, corrosion and wear resistant coatings [3].

Our work is aimed not only at obtaining of the MAO coating, but also in the future to conduct operational research mid-term evaluation of the properties and stability of the obtained films when working in conditions of high temperatures and pressures.

2. Experimental
For MDO was chosen piston group diesel engine D-245.7. The chemical composition of the piston group was determined to determine the compliance of the GOST alloy and the correct electrolyte selection. It was determined by energy dispersive x-ray fluorescence spectrometer EDX-720P/800P designed for rapid non-destructive determination of qualitative and quantitative elemental composition of solid and liquid samples, powders, granules, wafers, films. Its principle of operation is based on excitation of fluorescence radiation of atoms of the studied substance by radiation of low-power x-ray tube. Fluorescent radiation from the sample is selected by a semiconductor detector SDD-type, where the quanta of different energies are converted into electrical pulses, the amplitude of which is proportional to the energy absorbed by the quanta. The pulse repetition rate of a certain amplitude is proportional to the concentration of the chemical element in the sample. The use of this equipment made it possible to determine the content of components up to thousandths of a percent, and to conduct a comprehensive analysis of the phase composition of the alloy.

Obtained by the chemical analysis showed (figure 1) that the pistons are made of AK4-1 alloy. High-temperature alloys AK4-1 system Al – Si – Fe – Ni the chemical and phase compositions very close to duraluminum, but instead of manganese as alloying elements contain iron and Nickel.

Micro-arc oxidation of pistons was carried out on an experimental laboratory installation of thyristor-condenser type in the treatment of electrolytes with Koh concentration ranges – from 1.5 to 2.0 kg/m³ and NaAlO2 – from 14 to 16 kg/m³ (this concentration is optimal for the studied piston aluminum alloys). The bath was used as a base bath for electroplating with a power source changed to a thyristor-capacitor one. This setting allows you to adjust the total density of the ion current II and the quantitative ratio of cathode and anode currents IK / IA in a wide range. At a certain voltage value, separate micro-arc discharges appear on the piston surface. The power of these discharges ensures the appearance of a powerful ion stream in their channels, which has a high reactivity. At this point, chemical reactions begin to occur, which lead to the formation of aluminum oxide Al2O3. In addition, the components of the electrolyte can be included in the resulting aluminum oxide. Parallel to the plasma in the vicinity of the craters we are seeing the disintegration and melting of the products of intermediate reactions. The consequence of micro-arc discharges is an increase in the rate of formation of Al2O3 and changes in the chemical and physical properties of the resulting films. Instead of oxides having an amorphous structure, crystalline inclusions are formed and high-temperature structures appear [4, 5].

The phase composition of the piston head after MDO carried out on the spectrometer EDX-
720P/800P, did not reveal the same amount of Mg and Cu on the surface. This is due to their low concentration and the fact that the bulk of these alloying elements dissolved in an aluminum matrix.

At constant voltage, the thickness of the oxide layer increases. The discharges are relocated to the nearest areas, where the thickness and, accordingly, the breakdown voltage is lower. The oxide layer grows as long as the density of the ion current reaches a level. Then the oxidation process is terminated. Oxide layers formed on piston alloys, due to the clear multi-phase structure, have high thermal, abrasion resistance, corrosion resistance.

The structure of the porous oxide film obtained at MDO fully corresponds to the representations of the physical and geometric Keller model [6] (figure 2).

Considering this model, it is possible to distinguish the following main provisions [4, 6]:

- porous oxide film is a tightly packed oxide cells having the shape of a prism, which is based on a hexagon (hexagonal prism);
- oxide cells have a normal orientation to the metal surface;
- in the center of the cell there is one time, which is a channel, the size of which is determined by the electrolyte composition, the chemical composition of the base metal and the electrical parameters of the oxidation process (figure 2 at 35 nm);
- the basis of the oxide cell is a barrier layer of non-porous type (Figure 3 at 0.145 mm). This layer has a cellular structure. The dimensions of the paired cells are the same;
- in the process of micro-arc oxidation, the beginning of the formation of cells occurs with the formation of a barrier layer, turning into a porous one. In the process of MDO, the pores are
3. Results and discussion

Microstructural study of the surface of a piston of aluminum alloy after MAO was carried out using scanning electron microscope SEM-103-01. This microscope has the ability to increase from 12 to 55,000 times. You can also consider the topology of a surface with considerable roughness. The peculiarity of this microscope is the difficulty of studying the oxide layers with dielectric properties. This is due to the ingress of an electric charge on the oxide film and the accumulation of absorbed electrons on it (the film obtained with MDO has dielectric properties). As a result, there is no drain on the grounding circuit. Areas charged with electrons appear on the film, which leads to image distortion and significantly changes the emission of electron flux. To ensure the clarity of the bitmap image, a single-frame exposure was used. Figure 3 shows the micro-images of the surface layer of the piston aluminum alloy after MDO are presented.

![Figure 3. Morphological features of a piston aluminum alloy after MDO at increases of × 190 (a) and × 560 (b).](image)

The figure 3 shows that the surface of the coating is heterogeneous, has a developed relief and has a significant roughness. On it there are small particles, and pores. The study of cross-sections showed that there is no through porosity in the resulting coating, which may indicate high protective properties of the coating. Such a developed surface of the oxide coating can indicate its high thermal insulation ability, which generally leads to a decrease in the heat stress of the piston groups of diesel engines [7].

Studies have shown that the oxide films on the surface of aluminum alloys, which are formed in water electrolytes dissolving aluminum oxide, consist of two main layers. These layers have a distinct interface. The first layer – barrier-adjacent directly to the base metal. It has a sufficiently high density and is characterized by almost complete absence of pores. The second layer is an outer layer with a large porosity formed from a set of micro-arc discharges. The majority of researchers also identifies two similar layers obtained by oxidation [8].

The electron scanning microscope MIRA – 3 was used for a more detailed study of the resulting coating porosity. The picture shows that the pore sizes vary directly in the range from 0.1 to 8 microns (figure 4). Structure of branched pores with a variety of complex branches and closed cavities. Coatings that do not contain pores can not be obtained. This is due to the nature of the flow of micro-arc discharges. In certain cases, the presence of pores is a positive development. When the coating under conditions of oil starvation, the lubricant enters the pores of the coating and ensures a permanent oil film. In diesel pistons, the influence of porosity on the bottom of the piston on the performance properties is minimal, due to the characteristics of soot formation as a result of combustion of hydrocarbon fuels.
A special feature of MDO is that in the near-cathode layer in the interval between the liquid electrolyte and the piston micro-arcs occur, the local temperature rises and the electrolyte boils, begins to evaporate, forming an ion electron flux having a very high density. At the same time, there is an intensive electrolysis process, in which free oxygen is formed. Conditions are created for high-temperature oxidation of the piston surface. The surface of the piston bottom comes into direct contact with the active medium having a high concentration of oxygen. The surface of the bottom of the piston begins to oxidize hard. The phase composition of the surface will depend on the number of alloying elements and the composition of the electrolyte liquid phase [6–8].

As a result of oxidation, a protective coating is obtained, which consists of oxides of alloying elements distributed in a plastic matrix of aluminum. The coating formed under MDO has good adhesion, and also has a non-uniform, developed surface. This circumstance, in the absence of through pores, is a prerequisite for high heat resistance and reduce the heat stress of the piston group. The study of the chemical composition of the surface after MDO proves intensive mass transfer to the oxide layer of electrolyte elements and subsequent diffusion deep into the base metal. Formed on the surface of the coating is quite uniform, no liquors on the content of chemical elements. Obtained on the surface of the MDO process special nanoporous structure of anodic aluminium oxide (figure 5), was described by Keller in the mid-50-ies of the last century, but the generalized model of the formation of such nanoporous structures in the MLD is still not fully described.

![Figure 4. Micrograph of the surface of the coating after MDO.](image)

![Figure 5. A longitudinal section of the surface of a piston of aluminum alloy, obtained by electron scanning microscope.](image)

Currently nanoporous oxide layers are obtained on other metals (Zr, Ta, Ti, Pb, etc.). It is shown that MDO of many metals leads to obtaining ordered structures of two types: porous and tubular with different morphology. Due to this structure, the resulting oxide layers have a wide range of applications. The reason for the formation of such structures is the synergetics of chemical processes of formation and dissolution of the oxide film, as a result of the influence of a powerful electric field. However, the completed theory explaining the mechanism of self-organized growth of oxide films in MDO has not yet been created [9–11].

The study derived nanoporous (nanotrubkami) structures on aluminum piston alloys is important from fundamental and applied points of view. The existing technologies for obtaining such oxide structures involve the use of special electrolytes, large time and electrical energy, the use of expensive control equipment. Therefore, new approaches to the creation of such porous anodic oxides on aluminum alloys are very important. A comprehensive approach to this issue has allowed to create an environmentally friendly method of forming a porous anodic oxide film on a piston aluminum alloy. The application of the proposed method of MDO makes it possible for a short time to form porous films of aluminium oxide of polycrystalline mesostructure with pore sizes from 15 to 160 nm, thickness from 10 to 100 µm on the surface of the piston aluminum alloy [12, 13].
For piston aluminum alloys, the main characteristics determining their basic properties are thermal, corrosion and abrasive wear. These characteristics were determined in accordance with GOST R 9.318-2013.

Control of the thermal stability of coatings was investigated by cyclic method. Each of the 100 cycles included exposure of samples in the muffle furnace PM-10 at a temperature (280±5)°C for 60 minutes. After that, the heated samples were immersed in distilled water with a temperature of 20°C and aged for 20 minutes until completely cooled down. On the MDO coating after the study of heat resistance, no visible damage of the coating in the form of flakes, blisters, cracking, peeling or changing the color of the coating was visually detected, which fully meets the requirements of the current state standard.

Determination of abrasive wear was carried out on the basis of FGBOU in Vyatka GU. Wear was determined using Taber using abrasimeter. This device provided a measurement of the load with a relative error of ±5%. The absolute error of the frequency of rotation was ±4 vol./min Each sample was weighed on an analytical balance, with an absolute error no more than ±3 mg Sample was fixed under the abrasive wheels with the rotational speed of the disc is about 60./min, under a load of 9.8 N. Removal of wear products from the field of abrasive action was carried out using compressed air and amounted to 100% with the total number of cycles – 7000. The results of studies of abrasive wear was 55 mg per 1000 cycles, which meets GOST R 9.318-2013.

Formed on the surface of the piston oxide coatings have high temperature resistance, resistant to abrasive wear, chemically inert to almost all aggressive media. In General, studies of the surface film proved the absence of through porosity on the alloy surface, which corresponds to the formation of the oxide layer according to the physical and geometric Keller model.

4. Conclusion
Considering the results of previous and presented studies, we can generalize the idea of the technological ensuring the corrosion resistance of thin MDO coatings: these coatings provide the highest possible corrosion resistance of alloys on aluminium basis, even in conditions of high temperatures and pressures. In the future, it is planned to establish the relationship between the quality parameters of thin MDO coatings and the fundamental laws of corrosion destruction, depending on the electrolytes used and the thickness of the oxide layer.

Looking at and summarizing the topic of the MLM, it can be noted that most of the work on this issue is of a research or applied nature, and the set of theoretical developments on the mechanism of the MLM is based on the aspects proposed by Keller and does not take into account many factors. If we consider the work on the MLD in the aspect of GOST R 9.318-2013, we can note the almost complete absence of any data on the MLD, especially in relation to the chemical composition of the hardened alloy. In General, the number of works devoted to MDO-effects on the surface of metal materials is constantly growing, which characterizes the process of hardening as a promising and far-reaching.

The obtained results allow us to recommend the use of oxide films obtained as a result of MDO to protect the pistons of thermal engines and reduce the heat stress of piston groups. The hardened alloys obtained in the MDO process are currently undergoing operational tests at elevated temperatures and pressures. A comprehensive analysis of microstructures after operational tests will be described in detail in the relevant scientific publications.

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