Features of theoretical models of hardening of piston aluminum alloys in aqueous electrolytes

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Abstract. Currently, an effective method of increasing the surface strength and heat resistance of the piston bottom is the method of electrical deposition of chemical coatings based on various compositions. The article deals with the theoretical aspects of the formation of oxide films on piston aluminum alloys during microarc oxidation. Possible schemes of formation of barrier and outer layers of surface coating in aqueous electrolytes are also considered. The mechanism of formation of the interface and possible schemes of deposition of nonmetallic inclusions on the surface are shown. The stepwise formation of oxide layers on the piston surface, which has a fundamental difference from conventional films obtained by anodizing, is described.

1. Introduction

Longer due to the increase in the power density of internal combustion engines, the widespread use of turbocharging and intermediate cooling of the charge air, the load on the engine's piston group increases. In this regard, the question arose about ways to improve the reliability of piston alloys based on the Al-Si system. In addition, when transferring power plants of vehicles to alternative fuels, higher mechanical (inertia forces of reciprocating moving parts, gas pressure forces) and thermal loads act on the piston than when working on regular fuel.

Under the action of a surface of the piston to elevated temperatures, usually reaching more than 350°C, the microhardness of the surface is reduced. Operational factors are determined by a set of thermal, load and speed modes of the engine. During operation of the internal combustion engine, the temperature and pressure in the combustion chamber have a decisive influence on the reliability of the working surface of the piston. In case of unsteady operation, the wear of the piston group is 2 ...3 times higher than in the steady state. The operation of the engine at loads close to critical leads to the formation of microcracks and, ultimately, to the combustion of the piston. After analyzing the promising methods of increasing the strength of piston alloys, it can be noted that microarc oxidation (microarc oxidation - MAO) can significantly improve the heat resistance of the piston and significantly increase the microhardness of the surface [1]. MAO is the most effective and promising method in modern engineering, thanks to the use of thyristor-capacitor plants in galvanostatic mode.

Almost all MAO works are of an applied or research nature only, and there are no theoretical aspects of the formation of oxide films under the influence of a micro-arc. The existing works devoted to the study of MAO influence on mechanical properties of the metal surface of the valve group characterize this method of increasing the mechanical properties of the surface as effective and promising for modern engineering.
2. Materials and methods

To date, there are no unambiguous theories and clear mechanism of formation of oxide films on the metal surface in the MAO process. Analyzing the effect of arc discharges on the surface of metals of valve groups, it is possible to take physical-geometric, colloidal-electrochemical and plasma models [2] for the basic schemes of formation of oxide films on the surface. But taking into account the formation of the barrier layer in the process of microarc impact on the surface of the piston, the main model will be the physical and geometric model of Keller.

This model allows us to generalize the formation of the oxide anode-spark coating in the pre-spark mode of the thyristor-capacitor plant. To understand and generalize the process of formation of anode oxide structures, we consider the structure of thin oxide films on metals of valve groups. Here we will consider the formation of oxide layers under the influence of a micro-arc on an aluminum alloy corresponding to AK4-1 brand.

From the theory of the formation of spark discharges, it follows that the spark discharge at the anode will be only when a coating of a thin dielectric layer is present on the treated surface. Such dielectric properties have a thin oxide film, located on the barrier layer. This layer begins to form in the first stage of MAO. With an increase in the dielectric strength of the barrier-type oxide film, the potential for the beginning of spark formation in the anode region increases. Oxidation of piston aluminum alloy under the influence of a micro-arc in the region of the positive electrode in electrolytes, dissolving the resulting anode oxide, completely determines the kinetic aspects of the formation of special films formed during MAO.

Formation of the barrier layer at the initial time occurs in separate active centers with the maximum potential on the surface of the base metal. After that, in the active centers, there is a growth of hemispherical lenticular microcells, which later coalesce into a homogeneous and monotonous barrier layer. According to the theory of closed infinite sets, a monotonous mosaic is formed on the surface, with touching cells that represent a hexagonal prism. Due to the influence of local and widespread effects of ions in the surface barrier layer, the pore base located in the geometric center of the cell is born. The number of pores formed will be proportional to the reduction of the potential on the surface of the base metal. At the same time, in the center of the cell, there is a decrease in the barrier layer, which leads to an increase in the electric field strength. It is at this point that the ion flux density increases and the oxidation rate increases. The increase in temperature in the channel leads to a decrease in its nominal diameter, so an equilibrium system is formed on the surface, which holds the thickness of the barrier layer within certain boundaries.

Analyzing the physical-geometric model of Keller we can distinguish the following positions:

- oxide structured cells are formed normally to the surface of the base metal at MAO;
- in general, the oxide film is characterized by the presence of polytypical isolated cells, which are a prism with a hexagonal base;
- in the center of each cell, there is a separate pore, which has the shape of an elongated channel. The linear dimensions of the formed channel directly depend on the electrolyte, the chemical composition of the alloy and the electrical characteristics of the MAO process;
- the base of the unit oxide cell is a barrier layer on which there are no pores. The thickness of such a layer varies from 5 to 150 microns. It is characterized by a cellular structure with matching sizes of conjugate cells;
- in microarc oxidation at the initial stage, a barrier layer is formed, where the selection of individual polytypical cells occurs. After a certain time, it passes into a porous layer. In the future, there is an increase in the linear dimensions of the pores, due to the fact that the bottom of the pores, which is the surface of the barrier layer, all the time interacts with the electrolyte.

The second theory considers the oxide films obtained on the surface as colloidal formations [4]. In this theory, the porosity of oxide films is determined by the rate of their linear growth, and the oxide
prenka is a gel, which under the influence of a magnetic field is normally oriented to the surface of the base metal. It is formed on the basis of beetnik and hydrargillite chains (Al(OH)₃-AlOOH).

As a result of chemical reactions near the active centers of the positive electrode, a large number of monons (fine particles) are formed, which are the initial nuclei of micelles. Over time, the monons begin to grow and eventually form separate polyons. They are certain micelles of fibrous structures having a rod-like shape. These particles form the base of the gel used for further production of oxide films. This also includes anions of electrolytic solution, which contribute to the partial destruction of the hydrate shell [3]. The parameters of Keller elementary cells correspond to the linear dimensions of micelles formed as a result of chemical reactions of Al(OH)₃ gel.

Intermicellar spaces are formed as a result of a certain arrangement of individual micropores and submicropores. Micelles under the influence of the potential difference are twisted so that the formed porous layer corresponds to sheaf-like formations. Individual sub-fibers with a diameter of 10...65 nm are formed by chain-like arranged monohydrates of aluminum oxide and have an amorphous structure. Here are introduced some elementary particles of the electrolyte, which are involved in the process of obtaining an oxide film and having some properties of anode oxides. Considering and generalizing the colloidal-micellar theory, it is worth noting that the anode oxide film on the surface of the aluminum alloy is formed by particles of aluminum hydroxides of a certain degree of dispersion. These particles create an inorganic polymer on the piston surface [2].

The theory of obtaining oxide films on aluminum alloys with the formation of a plasma zone on the surface (plasma theory) generalizes the questions arising in connection with a certain glow on the surface at MAO. According to the plasma theory, there is no permanent barrier layer on the surface. In the absence of electric current there is a phenomenon of polymerization of the elementary plasma layer touching the anode and ionized gas, the amount of which during this period is maximum. The continuous flow of gas is constantly in a raging state and is constantly updated.

Features of the theory of plasma formation are shown in figure 1.

Figure 1. Plasma model of formation of surface oxide layers.

According to the theory of plasma, formation should be allocated 3 stages of formation of intermediate elements.

Ionization and polymerization stage:

- ionization of the aluminum alloy at the anode: \( \text{Al} \rightarrow \text{Al}^{3+aq} + 3\text{e}^- \);
- formation of the core oxide film: \( 2\text{Al}^{3+aq} + 6\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \);
- polymerization of the formed oxide: \( n\text{Al}_2\text{O}_3 \rightarrow [\text{Al}_2\text{O}_3]^n \).

Stage of hydrotation:
• hydrotation of part of oxide: \( \text{Al}^3+ + 3\text{OH}^- \rightarrow \text{Al(OH)}_3; \text{Al}_2\text{O}_3 + \text{Al(OH)}_3 \rightarrow 3\text{HAlO}_2 \).

Stage of oxidation:

• after the current is supplied by the thyristor-capacitor unit, the anions create an obstacle to the flow merging into one whole [3].

The plasma model of the formation of oxide films is characterized by the following factors:

• the formation of plasma on the metal surface explains the partial polymerization of aluminum oxide and the heterogeneity of the linear dimensions of the oxide films (in the area of local contact occurs aluminum alloy compaction);
• the presence of luminescence at the point of contact occurs after the absorption of a significant amount of energy. This luminescence is characterized by the dependence of "voltage – brightness". Such a spectrum corresponds to a stable flow of fully ionized gas at a glow discharge observed at high pressure;
• the particles present in the electrolyte solution give the oxide an opaque shade and the appearing glow at MAO is almost imperceptible. In this regard, there is a distinct impression that a bright glow occurs directly under the oxide film.

Generalizing the proposed theory of formation of the surface layer in the MAO process, and comparing these theories with the results of scientific experiments, it is impossible to accurately determine a clear and unambiguous scheme of formation of surface oxide films. The mechanisms of microarc discharges and the mechanisms of oxide film growth in the border regions are quite complex and are characterized by complex theories that take into account the physical-geometric, colloidal-electrochemical and plasma models [3].

The chemical composition and internal structure of the surface oxide layers are determined by the local conditions of their formation. The most important role is played by the composition and structure of the electrolyte. The elementary particles of the electrolyte are included in the separate structure of the film, the predicted composition of which is given by the electrolyte, the power source and the mode of action of electric arc micro-discharges on the surface of the piston aluminum alloy.

The dependence of the anode voltage \( U_a \) on the exposure time \( t \) at a constant current density is shown in figure 2.

![Figure 2](image)

**Figure 2.** The dependence of the formation of the anode potential from the time when MAO piston aluminum alloy in 3% aqueous solution of \( \text{H}_2\text{SO}_4 \) (density of ion current of 30 mA/sm²).
Considering the main areas of dependence, and conducting their analysis, it is necessary to distinguish four stages of growth of porous oxide films formed on the surface of the base metal. Stage 1 is characterized by a direct proportional dependence of the potential growth on the surface of the positive electrode. It is here that the solid oxide film begins to form \([4]\). The linear dimensions of the barrier layer depend on the parameters of the thyristor-capacitor installation. By the end of this stage, it is noted the presence of small formations to a depth of 14 nm in the outer regions of the barrier layer. At stage 2, the rate of potential growth at the anode slows down. It is at this stage that micropores begin to emerge and form in the oxide film on the surface of the base metal. Also here the "spreading" continues of the outer region of the formed film on the surface of the base metal. In addition, local areas are deepening and branching of various sections of the oxide film. Sometimes there are gaps that lead to changes in the structure. The most often described effects are formed at the interface of the "film – electrolyte" phases.

At stage 3, the potential begins to decline due to the transverse expansion of the local electrolyte pathways. In this case, there is a decrease in the resistance of the total barrier layer, leading to a temporary decrease in the voltage at the anode.

At stage 4, the voltage on the anode is equalized and its value remains constant, since the linear dimensions of the barrier layer do not change.

Some semblance of the equilibrium state is formed due to partial dissolution of aluminum oxide. This state is observed at the bottom of the pores and at the "base metal – oxide" boundary and is explained by the movement of O\(^2\)/OH\(^-\) ions behind the barrier layer to the base of the pores. It is here that regular pores of the main oxide film on aluminum alloy are formed. It is worth noting that the partial dissolution of the oxide film is one of the main conditions for the growth of the porous oxide layer. The higher the concentration and temperature of the electrolytic solution, the lower the anode voltage values correspond to the maximum ordinate dependence of the anode potential formation \([5]\).

The formation of a porous oxide film during oxidation can be carried out at a constant potential on the electrodes. Features of this process will be to change the \(I_U\) ion current density in time \(t\).

At the initial stage, there is a decrease in the \(I_U\) ion current density, which then increases to a constant value. This character of the ion current change is rather isolated and is typical only for the formation of an anode porous film \([6]\). This dependence of the current density on time is shown in figure 3.

![Figure 3. Change in the ion current density depending on the time of microarc oxidation (3% aqueous solution H\(_2\)SO\(_4\) at \(t=45^\circ\mathrm{C}, U=30\mathrm{V}\)).](image)

The area of current density reduction (a) is characterized by the formation of an oxide film of the barrier layer. In the region (b), the local surface of the formed film has a greater waviness. It is here that the formation of individual cells begins. In the region (c), separate local pores are formed, the diameter of which varies within 3...5 nm. Isolated pores can have a nominal diameter of up to 20 nm.

At a constant ion current density (region d), the original structure is preserved, but the linear dimensions of the resulting porous film increase. By analyzing the growth kinetics of separate cells...
and the structure of film oxide coatings, we can offer a qualitative model of the formation and flow of the processes of formation, growth, and dissolution of surface oxide films.

At a constant potential at stage (a) at the initial time, the rate of formation of the oxide film is sufficiently large. This can be explained by the small linear dimensions of the film and the increased current density. Due to the high values of the magnetic field, the decomposition of H₂SO₄ aqueous solution is accelerated to obtain the isolated SO₄²⁻ anions. They, in turn, react with freely moving Al³⁺ cations. Here and formed a comprehensive ionoi Al(SO₄²⁻)₃, then easily passing into the solution. Here their dissolution is very easy. Therefore, SO₄²⁻ ions cannot get into the oxide layers in the form of the original components. Approaching the stage (b) the transition barrier layer increases in size, the electric field strength decreases and the ion current density decreases. This ensures that individual SO₄²⁻ ions get into the oxide film. At stage (C) there is a maximum decrease in the magnetic field strength and, together with SO₄²⁻ hydrogen ions H⁺ enter the surface layer of the anode oxide film. Here dissolution occurs at the base of the pores, where the electric field strength retains its value. In stage (c), the increase in current density is due to the formation of hemispherical pore bottoms and to the change in the larger side of the surface area. Because of this, the thickness of the main barrier layer is reduced compared to the previous stage (b). Similar kinetic dependence of the current density is maintained in all of the pore-forming electrolytes. There is almost always a decline in the anode current, which subsequently leads to its rise to certain constant values.

Having carried out a complex kinetic analysis, it can be noted that in the process of increasing the thickness of the porous anode oxide film, after the formation of pores, the thickness of the barrier layer becomes relatively stable, and microarc oxidation is reduced to an increase in the linear dimensions of the porous part of the oxide. The dimensions of the porous part first increase linearly, but later, its saturation occurs and the dimensions stabilize. This is due to the fact that over time there is stretching of the pores, and the partitions between the pores are thinned due to the dissolution of the oxide. If the temperature of the aqueous electrolyte solution is high, and the duration of the MAO process is significant, then due to chemical reactions of dissolution at the end of the MAO process, the walls of the obtained pores begin to crumble. By reducing the aggressiveness of the aqueous electrolyte solution, it is possible to increase the thickness of the porous layer formed [7].

3. Conclusion
Analyzing the MAO kinetics by the type of graphical dependence of the ion current density and the anode potential, it is possible to comprehensively assess all the separate morphological features of the anode oxide film. Despite the unambiguous conclusions, a complete analysis of the theoretical results is difficult, since a number of chemical and physical processes occur simultaneously in the MAO process: oxidation of the base metal, formation, growth and partial dissolution of oxides, changes in pore length and diameter. It can be noted that most of the studies of porous oxide films are devoted to their study only at the stage of stationary pore growth [8].

Many researchers are engaged in the subject of microarc oxidation, but the problems and prospects of the technology of obtaining such coatings are still relevant and attract the attention of many scientists. In the light of the development of modern technologies, it became possible to very accurate, fast non-destructive determination of the qualitative and quantitative elemental composition of various alloys, and at the same time a comprehensive analysis of the coatings [9-10]. Our work is aimed not only at obtaining MAO coatings, but also in the future to conduct operational studies with an intermediate assessment of the properties and stability of the films obtained during the operation of the piston group at elevated temperatures and high pressures in the combustion chamber of diesel.

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