Effect of microarc oxidation regimes on corrosion resistance of coatings formed on piston aluminum alloys

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Abstract. The effect of the concentration of a silicate-alkaline electrolyte and electric modes of process micro-arc oxidation on the corrosion resistance of the surfaces formed on aluminum alloys of different chemical composition was investigated. Alloys traditionally used for the manufacture of pistons of internal combustion engines (ICE) were analyzed. The corrosion resistance was investigated in solution, the composition of which to the greatest extent close to the conditions of cylinder-piston group of internal combustion engines. The corrosion resistance of the samples was estimated by the mass rate of corrosion during their exposure in corrosive solution for 144 hours. The regression equations linking the concentration values of the electrolyte and of technological modes of MAO with the corrosion rate was obtained. It is established that the conditions of the process significantly influence the corrosion resistance of the coatings. Surface treatment by the method of MAO increases a corrosion resistance by 2.9...31.9 times, depending on the sample alloy and MAO modes.

1. Introduction

Creation of materials and surface layers with the required properties in accordance with the conditions of functioning of the part or product is an important task for all fields of engineering. Modern trends in mechanical engineering and engine building are associated with increases in the specific indicators that are provided with an increase in power and a decrease in weight reduction while increasing their reliability in exploitation. However, the use of scarce and expensive construction materials for the whole product is not always advisable. For this reason, aluminum alloys are increasingly used and replace steel and titanium alloys.

Aluminum alloys possess a number of advantages: low cost and density, high specific strength and stiffness. However, the surface of aluminum alloy parts are quite often subject to wear, erosion and corrosion [1-3]. Aluminum and its alloys actively interact with oxygen. As a result, a thin oxide films with a thickness of 0.01-0.02 µm are formed on the surface [4-6]. But, such a natural oxide film is not always effective to protect of the metal from corrosion. The corrosion resistance of aluminum alloys can increase the application of special protective coatings or the use of surface modification methods, such as micro-arc oxidation (MAO) [7-9].

MAO is a promising method for the formation corrosion-resistant, wear-resistant and heat-resistant oxide layers on aluminum alloys. MAO coating consists of corundum α-Al₂O₃, γ-Al₂O₃ and other high-temperature oxides [10-13]. This composition makes the surface resistant to corrosion and wear.
2. Statement of the problem
MAO is widely used for hardening of details from aluminium alloys. However, the properties of micro-
arc oxide layers strongly depend on the conditions of the process and the chemical composition of the 
aluminum alloys [14-16]. Aluminum alloys are the most widely distribution in mechanical engineering. In engine of these alloys produced heads, cylinder blocks and pistons [17]. However, the number of 
papers in the area of research of corrosion resistance of the MAO coatings on such alloys is quite small. 
Therefore, the goal of the work was formulated: to study the effect of MAO modes and silicon content 
in the treated aluminium alloys on the corrosion their surfaces.

3. Experimental method

3.1. Sample preparation
All studies were conducted on laboratory samples of high-silicon alloy M244 (Mahle) [18], deformable 
aluminum alloy AK4-1 and eutectic silumin AK12pch GOST4784-97. Chemical composition of alloys 
is given in table 1.

| Elements | Full name      | M244         | AK4-1         | AK12pch        |
|----------|----------------|--------------|---------------|----------------|
|          |                | Mass fraction (%) |
|          |                | Al Aluminium | Si Silicon    | Fe Iron        |
|          |                | 22.00 – 26.00| 0.35          | 0.40           |
|          |                |              | 0.80-1.40     | 0.35           |
|          |                |              | 0.20          | 0.80           |
|          |                |              | 0.08          | 0.80           |
|          |                |              | 0.02          | 0.80           |
|          |                |              | 0.08          | 0.80           |
|          |                |              | 1.20-1.80     | 0.40           |
|          |                |              | 0.75          | 0.24           |
| Other    |                | 0.10         | 0.50          | 0.24           |

The laboratory samples had the form of a plate with a thickness of 4 mm and a surface area of 
1790 mm². The electrolyte was made on the basis of distilled water with the addition of KOH and 
Na₂SiO₃. The MAO process lasted 3 hours, see figure 1 (a). The sample with MAO coating is shown in 
figure 1 (b).

Figure 1. (a) sample in the process of MAO; (b) sample after the process of MAO.
3.2. Description of the experiment plan
All studies were conducted in accordance with the theory of planning a complete factorial experiment of type 2^3 [19]. As independent factors were used: concentration in the electrolyte of potassium hydroxide \( C_{\text{KOH}} \) (g/l), the concentration in the electrolyte liquid glass \( C_{\text{lg}} \) (g/l) and the installation capacity \( C \) (\( \mu F \)). As output parameters were used a corrosion rate \( K \) (mg/(m^2\cdot h)) (table 2).

| Factors                      | Designation | Lower level | Upper level | Interval variations |
|------------------------------|-------------|-------------|-------------|--------------------|
| Concentration of KOH (g/l)   | \( X_1 \)   | 1           | 4           | 1.50               |
| Concentration of Na_2SiO_3 (g/l) | \( X_2 \) | 1           | 4           | 1.50               |
| Installation capacity (\( \mu F \)) | \( X_3 \) | 100         | 400         | 150                |

3.3. Study of corrosion resistance
The surface roughness of the coating were improved to Ra 1.6 \( \mu \)m prior to corrosion tests. Roughness measurement was carried out using the profilograph-profilometer "TR220". Was performed at least 3 measurements in different directions.

Tests on the corrosion resistance of the samples was carried out in accordance with GOST 9.913–90. The samples were exposure in the solution of the following composition: sodium chloride (NaCl) – 225 (g/l), potassium nitrogen (KNO_3) – 50 (g/l), nitric acid (HNO_3) – 5.5 (g/l), base – distilled water. The choice of solution of this composition was based on the fact that it contains nitrogen - and oxygen-containing substance that is largely consistent with a liquid medium formed on the surface of engine parts in the process of their work [20].

Each sample was placed in a separate glass vessel so that the samples did not touch the glass surface. The duration of exposure in the solution was 6 days (144 hours).

The weight of the samples was measured on a laboratory balance VL–120C. The corrosion rate was calculated from the results of measuring the samples weight:

\[
K = \frac{\Delta m}{S \cdot t},
\]

where \( K \) – is the corrosion rate (mg/(m^2\cdot h)); \( \Delta m \) – decrease (increase) weight (mg); \( S \) – the surface area of specimen (m^2), \( t \) – the time of exposure of the sample in solution (h).

The data were processed by methods of statistical analysis in evaluating the adequacy of the coefficients of the regression equations. The dispersion of reproducibility of the experimental data and the adequacy of the regression equation were calculated.

4. Results and discussion
The surfaces on the samples of aluminum alloys with and without the MAO layer before the corrosion tests and after the tests are shown in figure 2.

Visual analysis of the samples after the tests showed that the surface of the samples without a MAO layer was covered with corrosion products; the samples lost its homogeneity and shine. All samples with MAO-layer retained the shape and integrity.

Weight change after testing was recorded on all samples. The results of the experiment are shown in table 3.

The experimental data were processed, see table 3. The linear regression equations with the interaction effect were compiled [19].
Figure 2. Appearance of samples: (a) M244 before the corrosion test, (b) M244 after exposure in the aggressive solution, (c) AK4-1 before the corrosion test, (d) AK4-1 after exposure in the aggressive solution, (e) AK12pch to the corrosion tests, (f) AK12pch after exposure in the aggressive solution.

Table 3. Results of the experiment.

| № mode | Corrosion rate K (mg/(m²-h)) |
|--------|-------------------------------|
|        | alloy M244 | alloy AK4-1 | alloy AK12pch |
| 1      | 100±6      | 235±29      | 89±28         |
| 2      | 118±26     | 128±25      | 157±67        |
| 3      | 172±12     | 32±10       | 63±16         |
| 4      | 525±20     | 461±93      | 197±15        |
| 5      | 102±7      | 25±5        | 89±17         |
| 6      | 60±16      | 117±23      | 118±54        |
| 7      | 109±23     | 474±122     | 103±20        |
| 8      | 345±41     | 477±70      | 661±18        |
| Without MAO | 437±34 | 797±7 | 185±11 |
The result has been the derived equations showing the influence of the modes of the MAO process on the corrosion resistance of the surfaces of the samples with MAO coatings formed on aluminum alloys with different fractions of silicon:

\[ K_{(M244)} = 67.0 + 5.9 \cdot C_{KOH} + 23.4 \cdot C_{lg} + 0.24 \cdot C - 17.4 \cdot C_{KOH} \cdot C_{lg} + 0.06 \cdot C_{KOH} \cdot C + 0.11 \cdot C_{KOH} \cdot C_{lg} \cdot C \]  
(2)

\[ K_{(AK4-1)} = -33.1 + 11.9 \cdot C_{KOH} + 59.9 \cdot C_{lg} - 0.70 \cdot C - 15.7 \cdot C_{KOH} \cdot C_{lg} + 0.47 \cdot C_{KOH} \cdot C + 0.35 \cdot C_{lg} \cdot C 
- 0.09 \cdot C_{KOH} \cdot C_{lg} \cdot C, \]  
(3)

\[ K_{(AK12pch)} = 152.3 - 49.1 \cdot C_{KOH} - 17.5 \cdot C_{lg} - 0.89 \cdot C + 12.9 \cdot C_{KOH} \cdot C_{lg} + 0.76 \cdot C_{KOH} \cdot C + 0.22 \cdot C_{lg} \cdot C 
- 0.17 \cdot C_{KOH} \cdot C_{lg} \cdot C. \]  
(4)

Statistical analysis showed that the coefficients of the regression equations (2) – (4) are statistically significant and empirical equations are adequate. Analysis of the experimental data (table 3) showed that the most corrosion-resistant treatment for aluminum alloys is mode number 5.

Analysis of the equations (2)-(4) showed that the corrosion resistance of microarc oxide layers on alloys AK4-1 and AK12pch decreases with increasing concentration of electrolyte components (\( C_{KOH} \) and \( C_{lg} \)) and the installation capacity (\( C \)). This phenomenon is explained by the fact that the increase of these factors increases the voltage and the intensity of the MAO process. An increase in voltage of MAO leads to an increase in the energy of breakdown of gas anode bubbles and the formation of microdefects in the MAO layer. These processes lead to the loosening of the formed coating and decrease its corrosion-protective properties. KOH has a similar effect on the corrosion resistance of coatings on the alloy M244. However, an increase in the concentration of \( C_{lg} \) leads to an increase in the corrosion resistance of the coating for the alloy M244. This is due to the fact that silicon in the aluminum alloy promotes the formation of the MAO-layer of the amorphous phase of SiO₂ [21]. This phase has a sufficiently high corrosion resistance.

5. Conclusions
The corrosion rate of the samples with MAO-layers depends significantly on MAO modes and may differ by 8.8 times on the samples of alloy M244, by 19.1 times on the samples of alloy AK4-1 and by 10.5 times on the samples of alloy AK12pch. The maximum increase in corrosion resistance due to the formation of MAO layer was (in comparison with the samples without MAO): alloy M244 – 7.3 times, alloy AK4-1 – 31.9 times, AK12pch – 2.9 times.

Coatings with high corrosion resistance on alloys AK4-1 and AK12pch are formed at low concentration KOH and Na₂SiO₃ in the electrolyte at installations with small capacity. For the formation of a corrosion-resistant MAO-coatings on the alloy M244 necessary to reduce the concentration of KOH in the electrolyte to increase the concentration of Na₂SiO₃ and reduce the capacity installation.

Acknowledgements
This work was produced during the contract № 14.574.21.0161 from 26.09.2017 sponsored by the Ministry of Education and Science of the Russian Federation (a unique identifier of the work (project) RFMEFI57417X0161).

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