INFLUENCE OF THE PROCESS OF MICROPLASMA TREATMENT IN ELECTROLYTE SOLUTIONS ON THE OXIDE COATING PROPERTIES

Zh. M. Ramazanova
National Center for Space Research and Technology JSC
Aerospace Committee of the Ministry of Defense and the Aerospace Industry of the Republic of Kazakhstan, Almaty, Kazakhstan

K. Zh. Kirgizbayeva, A. U. Akhmedyanov, M. A. Jaxymbetova
Department of Standardization and Certification
Faculty of Transport and Energy
L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

D. Yergaliyev, A. Zhakupova, O. Abdirashev
Department of Space Equipment and Technology
Faculty of physics and technical sciences
L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

ABSTRACT

The development of modern industry requires the development of high-performance methods for producing coatings on the surface of light constructional materials. The use of products and structures made of aluminum and its alloys with high wear resistance, corrosion resistance, prevails in many industries, in particular, in aircraft industry, shipbuilding, transport engineering.

Currently, a more advanced surface treatment method, a microarc oxidation method (MAO) is being used to solve this problem. However, when implementation of a MAO process is carried out using stationary and slowly varying energy effects, there is the problem of limiting widespread use of the method. This is due to high power consumption.

The objective of the study of this work is to study the effect of rapid pulsed effects of the microarc oxidation process on physical and mechanical properties of an oxide coating. This mode allows to obtain coatings with high mechanical properties and reduce power consumption.

Studies were carried out in a pulsed mode with an anodic current pulse duration of 50–200 µs and a polarizing voltage of up to 300 V. An alkaline electrolyte solution
was used as the electrolyte. Results of the study showed that such parameters of coating as roughness, friction rate increase along with an increase of duration of the anodic current pulse from 50 to 200 μs with increasing thickness of the coating. When coating thickness increases, porosity decreases. The micro hardness of the oxide coating with a thickness of 26.5 μm and a roughness of 2.2 μm makes 33 GPa. Oxide coatings formed in the MAO pulsed mode are distinguished by high wear resistance, micro hardness, and different porosity.

Keywords: Microarc oxidation, Oxide coating, Wear resistance, Friction rate.


http://www.iaeme.com/ijmet/issues.asp?JType=IJMET&VType=9&IType=12

1. INTRODUCTION
Currently, aluminum and its alloys are used in many areas of industry and technology due to their properties. Aluminum and its alloys are widely used in aviation, automotive, electrical, chemical and other industries. Aluminum is widely used as a corrosion-resistant coating, it perfectly protects metal surfaces from impact of various chemicals and atmospheric corrosion.

Surface treatment of aluminum and its alloys in order to create wear-resistant, corrosion-resistant, heat-resistant and other coatings by various methods allows to expand the scope of use of aluminum and its alloys significantly.

One of the promising methods for modifying of aluminum and its alloys surface is microplasma treatment in electrolyte solutions, also referred to as microarc oxidation [1–6].

Microarc oxidation (MAO) is an electrochemical process of modifying the surface of valve metals and their alloys in electrolytic plasma in order to produce oxide coatings with different functional properties.

Oxide coatings obtained by microplasma treatment in electrolyte solutions have high adhesion to a substrate [7–9], corrosion resistance [10–19], wear resistance [20–25], and micro hardness [26–29]. Obtained oxide coatings are characterized by different porosity [30–34]. This property of a coating when modifying the surface of titanium, magnesium and their alloys can be used for creating bioactive materials [35–41]. The method allows to treat surfaces of products made by casting and powder metallurgy effectively [42–43]. The coating composition depends on the substrate material and electrolyte composition [44–48].

The method is environmentally friendly compared to the traditional anodizing method.

Implementation of the MAO process can be carried out using stationary and slowly varying energy impacts, which limits the widespread use of the method due to large power consumption [49–50]. Currently, microarc oxidation methods on fast-flowing (pulsed) energy effects, where the voltage change rate reaches 108 V/sec and current density is 600 A/dm², begin to take place [51–54]. This mode allows you to form coatings with much lower energy costs.

In this regard, it is relevant to study the effect of rapid energy impacts on properties of formed coatings.
Influence of The Process of Microplasma Treatment In Electrolyte Solutions On The Oxide Coating Properties

2. MATERIALS & EXPERIMENTAL PROCEDURES

The coating was formed on flat aluminum samples of A0 grade (Aluminum 1100, ENAW-1100). Samples were made of rectangular shape with a size of 2x2x0.3 cm.

Preliminary sample preparation included mechanical polishing up to Ra = 0.09 µm. For formation via microarc oxidation method, a solution of the composition was used as the electrolyte, g/dm$^3$: Na$_2$HPO$_4$·12H$_2$O — 40; Na$_2$B$_4$O$_7$·10H$_2$O — 30; H$_3$BO$_3$ — 20, NaF — 10. The electrolyte was prepared on distilled water from "a. r. g.", "c. p." reagents type.

A 1000 ml stainless steel bath with water cooling system served as an electrochemical cell. In this case, the bath body served as a cathode, the sample being processed – as an anode. To modify the surface of the aluminum sample, a pulsating voltage source was used to generate rectangular shape pulses. The anode pulse repetition rate was 50 Hz. Coatings were formed under anodic polarization of aluminum samples. In this case, two batches of samples with oxide coating were obtained. The first batch of samples with oxide coating was obtained under different durations of anode current pulse, conditions of the MAO process are given in Table 1.

<table>
<thead>
<tr>
<th>Polarizing voltage, V</th>
<th>Duration of anodic current pulse, ms</th>
<th>Electrolyte temperature, °C</th>
<th>MAO process time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>50</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>150</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>200</td>
<td>25-27</td>
<td>20</td>
</tr>
</tbody>
</table>

The second batch of samples was obtained at different values of polarizing voltage, process conditions are given in Table 2.

<table>
<thead>
<tr>
<th>Polarizing voltage, V</th>
<th>Duration of anodic current pulse, ms</th>
<th>Electrolyte temperature, °C</th>
<th>MAO process time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>200</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>200</td>
<td>25-27</td>
<td>20</td>
</tr>
<tr>
<td>400</td>
<td>200</td>
<td>25-27</td>
<td>20</td>
</tr>
</tbody>
</table>

Since during the MAO process a voltage source was used, the current rate in accordance with Ohm's law was determined by the load resistance, which depends on composition of the electrolyte, material of electrodes, etc. Under such conditions of conducting the process, the current density was 114-120 A/dm$^2$.

Microhardness of the oxide coating was determined on a nanohardness tester “Nano Hardness Tester” manufactured by the CSEM by indentation of an indenter with a diamond tip with a load of 20 mN upon it. Processing of experimental data was carried out according to measurement results of at least 3 prints.

Wear resistance of oxide coating was determined on a high-temperature TNT-S-AX0000 tribometer. The principle of operation of this device is based on friction of the indenter against the surface. A ball indenter from a tungsten-cobalt hard alloy was used at this. The load during the test for wear resistance was 1N, the linear velocity was 2.5 cm/s, measurements were carried out at a temperature of 25°C, air humidity of 50%. The value of wear resistance was determined by the area of the track measured on a three-dimensional
surface meter using the Mountains Map Universal PC software and obtaining three-dimensional images of surface of samples with the track. For each sample, an odd value of area measurements of tracks greater than 7 was obtained, and the arithmetic average was found. Roughness of oxide coating was also determined on a Micro Measure 3D station profilograph.

Coating thickness was measured on a QuaNix-1500 thickness gauge. Porosity and pore distribution were estimated using micrographs taken on a Quanta 200i 3D scanning electron microscope using the methods of planimetry, intersecting lines and points as the ratio of the area of the pore image to the total area of the observation area [39]. At the same time, the arithmetic mean value of results of calculating porosity and distribution of pores obtained in at least three photographs was taken as the test result.

3. RESULTS & DISCUSSION

At present, use of the microarc oxidation method based on a rapidly changing (pulsed) energy effect, makes it possible to form an oxide coating with much lower energy costs [55–59]. The value of duration of anode current pulse has a significant impact on quality of coating. Implementation of the process with anode pulse durations from 50 to 200 μs with a repetition rate of 50 Hz leads to the fact that microarc discharges occur within a short period of time. Since anodic pulses are generated at a frequency of 50 Hz, there is no strong overheating of both the near-electrode layer of the electrolyte and the aluminum base itself. During this period of time, heat has time to be discharged deep into the solution. This allows to obtain high-quality coatings.

Figure 1 shows dependences of thickness and roughness of oxide coating on duration of anode current pulse according to conditions of the microarc oxidation mode 1 (Table 1).

![Figure 1](image1.png)

**Figure 8.** a – Dependence of thickness of oxide coating on duration of anode current pulse; b – dependence of coating roughness on duration of anode current pulse.

The duration of microplasma discharges depends on duration of anode current pulse. With an increase in duration of anode current pulse, which leads to intensity of microarc discharges, productivity of formation of coating increases. According to experimental data, an increase in coating thickness is observed. The latter leads to an increase in roughness of oxide layer.

Micrographs of surface of oxide coatings obtained at different durations of anodic current pulse are shown in Fig. 2. The study of morphology of surface of oxide coatings showed that
with an anodic current pulse duration of 50 μs, formation of coating occurs via islands. The average pore diameter is smaller compared to coatings obtained for larger values of anode pulse duration (Table 3). With an increase in duration of anodic current pulse with an increase in thickness of oxide layer in micrographs, formation of a uniform coating is observed. Formation of coating occurs not only due to transformation of substrate at bottom of pores, but also due to reactions with hydroxide ions and metal ions inside and around pores, where under influence of high temperature metal hydroxides become oxides. Formation of an oxide coating also occurs from components of electrolyte solution. As a result of these processes, existing pass-through pores are filled. A pore transits from a pass-through one into a closed one, and other pores are also formed. An increase in coating thickness, which is observed with an increase in duration of anode current pulse, leads to formation of pores of a larger diameter, but the number of pores per unit area decreases at the same time.

![Morphology of surface of oxide coating](image)

**Figure 2.** Morphology of surface of oxide coating is:

- a – with an anode current pulse duration of 50 μs;
- b – with an anode current pulse duration of 100 μs;
- c – with duration of anode current pulse 150 μs;
- d – with anode current pulse duration of 200μs

During studying of physicomechanical properties of formed coatings, wear resistance was determined from track area measured on a three-dimensional profilometer using Mountains Map Universal PC software and obtaining three-dimensional images of surface of samples with a track.
Table 3. Surface Porosity of Oxide Coating

<table>
<thead>
<tr>
<th>Polarizing voltage, V</th>
<th>Duration of anodic current pulse, ms</th>
<th>Time, min</th>
<th>Coating thickness, microns</th>
<th>Porosity ΔS, %</th>
<th>Number of pores per cm$^2$ of coating</th>
<th>Average pore diameter, microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>50</td>
<td>20</td>
<td>7.8</td>
<td>16.6</td>
<td>6.6·10$^5$</td>
<td>3.3</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>20</td>
<td>11.1</td>
<td>21.9</td>
<td>4.4·10$^5$</td>
<td>4.9</td>
</tr>
<tr>
<td>300</td>
<td>150</td>
<td>20</td>
<td>19.7</td>
<td>15.1</td>
<td>2.2·10$^5$</td>
<td>5.1</td>
</tr>
<tr>
<td>300</td>
<td>200</td>
<td>20</td>
<td>26.5</td>
<td>14.6</td>
<td>2.0·10$^5$</td>
<td>5.4</td>
</tr>
</tbody>
</table>

From three-dimensional images of surfaces of samples with a track (Fig. 3), it is clear that width of the track of original sample without coating exceeds width of tracks of samples with an oxide coating obtained for different durations of anodic current pulse.

Figure 3. Three-dimensional images of sample surfaces with a track:

a – for a sample without coating;
b – for a sample with a coating obtained with a current pulse duration of 50 μs;
c – for a sample with a coating obtained with a current pulse duration of 100 μs;
d — for a coated sample obtained with an anode current pulse duration of 150 μs;
e – for a coated sample obtained with an anode current pulse duration of 200 μs

Physical and mechanical properties and area of tracks are given in Table 4 for uncoated and oxide coated samples obtained at various pulse durations.

Table 4. Properties of oxide coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Track area, $\mu$m$^2$</th>
<th>Microhardness, MPa</th>
<th>$K_{tr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated sample</td>
<td>13592.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A sample with an oxide coating obtained under anode current pulse duration of 50 μs</td>
<td>3127.22</td>
<td>1522.7</td>
<td>0.85</td>
</tr>
<tr>
<td>A sample with an oxide coating obtained under anode current pulse duration of 100 μs</td>
<td>241.55</td>
<td>1888.2</td>
<td>1.12</td>
</tr>
<tr>
<td>A sample with an oxide coating obtained under anode current pulse duration of 150 μs</td>
<td>178.52</td>
<td>3775.7</td>
<td>2.16</td>
</tr>
<tr>
<td>A sample with an oxide coating obtained under anode current pulse duration of 200 μs</td>
<td>113.3</td>
<td>33543.9</td>
<td>3.6</td>
</tr>
</tbody>
</table>
As can be seen from the table 4, areas of sample tracks with an oxide coating are significantly less than the area of the track of the original sample, which indicates a high wear resistance of the coating. The highest wear resistance and micro hardness are observed for the oxide coating obtained under anodic current pulse duration of 200 μs.

When implementing any technological process, an important criterion for performance of a process is the time or rate of formation of the coating. From results of the study it can be seen that the rate of formation of the coating is about 0.4; 0.6; 0.9 microns per minute at the values of the duration of the anode current pulse 50 μs, 100 μs, 150 μs, respectively (Fig. 1 a). When duration of anodic current pulse makes 200 μm, the rate of formation of the oxide layer is about 1.3 μm per minute, what is more acceptable.

Thus, based on studies of morphology and physicomechanical properties of the coating and processability, it can be said that the main functional layer with high wear resistance [14; 20–25], microhardness and roughness is 2.2 μm and forms under anode current pulse duration of 200 μs. This value of duration of anode pulse is selected for further research.

Studies on the effect of polarizing voltage onto properties of the coating according to conditions of the MAO-2 mode (Table 2) showed that with polarizing voltages of 100 V, 200 V under anode current pulse duration of 200 μs, thin coatings of up to 3 μm are formed (Fig. 4 but).

Figure 4. a – Dependence of thickness of oxide coating on duration of anode current pulse;

b – Dependence of coating roughness on duration of anode current pulse

With an increase in polarizing voltage, thickness and roughness of the coating increase (Fig. 4 a, b). Photomicrographs of the oxide coating surface at different polarizing voltages are shown in Fig. 5. At a voltage of 100 V, a non-porous thin coating (Fig. 5a) with a low roughness is formed. In the process of oxidation, spark processes are observed rarely. Carrying out the process at a voltage of 200 V, arising microarc discharges lead to formation of small pores, the coating thickness remains negligible (Fig. 5 b). At a voltage of 300 V, microarc discharges occur almost from first seconds of the process. The rate of formation of the coating increases. In places of occurrence of microplasma discharges, pores are formed. As the coating thickness increases, pores overgrow alongside with appearance of other pores. At this voltage, the coating formed is denser (Fig. 5 c). At a voltage of 400 V, sizes of microarc discharges increase. The intensity of microplasma discharges leads to a strong heating of electrolyte up to 40°C. High electrolyte temperature affects the quality of the coating. The functional outer layer is formed rougher and more friable. Porosity of the coating
increases, its microhardness decreases (Fig. 5 e, Table 5). Implementation of MAO at 400 V to obtain a better coating requires additional electrolyte cooling systems.

![Figure 5. Morphology of surface of oxide coating is:](image)

a – at polarizing voltage of 100 V;
b – at polarizing voltage of 200 V;
c – at polarizing voltage of 300 V;
d – at polarizing voltage of 400 V

In the study of mechanical characteristics, the sample obtained at a polarizing voltage of 100 V was not tested, since it had a thin coating and it was obvious that wear resistance was not high. Physical and mechanical characteristics of the oxide coating are given in table 5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Track area, µm²</th>
<th>Microhardness, MPa</th>
<th>Ktr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated sample</td>
<td>13592.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sample with oxide coating obtained at a polarizing voltage of 200 V</td>
<td>12002.6</td>
<td>563.2</td>
<td>1.48</td>
</tr>
<tr>
<td>Sample with oxide coating obtained at a polarizing voltage of 300 V</td>
<td>113.3</td>
<td>33543.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Sample with oxide coating obtained at a polarizing voltage of 400 V</td>
<td>110.9</td>
<td>2605.0</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Comparing values of wear resistance of the coating over the area of the track obtained at 300 V and 400 V of polarizing voltages, it can be noted that values do not differ from each other very much. Taking into account the combination of mechanical properties for wear resistance and surface micro hardness, it is most preferable to form a coating at a polarizing voltage of 300 V with anode current pulse duration of 200 µs and a process time of 20 minutes.

A chemical analysis of the formed coating under anode current pulse duration of 200 µs and polarizing voltage 300 V, a process time of 20 minutes showed that the coating is based on aluminum oxide (Fig. 6). The oxide coating also includes compounds of elements of the electrolyte composition, which can form oxide and other compounds with the aluminum base.
Influence of The Process of Microplasma Treatment In Electrolyte Solutions On The Oxide Coating Properties

Figure 6. Chemical composition of the oxide coating

Weight and atomic percentages of corresponding elements of the coating are given in Table 6.

Table 6. Weight and atomic percentages of the coating composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percent, Wt%</th>
<th>Atomic percentage, At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3.26</td>
<td>5.89</td>
</tr>
<tr>
<td>C</td>
<td>4.08</td>
<td>6.65</td>
</tr>
<tr>
<td>O</td>
<td>30.49</td>
<td>37.27</td>
</tr>
<tr>
<td>F</td>
<td>12.81</td>
<td>13.18</td>
</tr>
<tr>
<td>Na</td>
<td>11.74</td>
<td>9.99</td>
</tr>
<tr>
<td>Al</td>
<td>35.13</td>
<td>25.46</td>
</tr>
<tr>
<td>P</td>
<td>2.49</td>
<td>1.57</td>
</tr>
</tbody>
</table>

5. CONCLUSION

The influence of rapidly changing energy effects of MAO on properties of the coating was investigated. It is shown that the coating roughness increases under increase in duration of anode current pulse and increase in thickness of the oxide layer.

Increase of the coating thickness leads to overgrowth of pass-through pores and formation of closed ones. An increase in duration of anodic current pulse leads to decrease in porosity of the coating, but the average pore diameter increases.

Increase in the value of polarizing voltage leads to increase in the rate of formation and coating roughness.

With anode pulse duration of 200 µs and polarizing voltage of 300 V, a coating with high wear resistance, surface microhardness of 33.5 GPa, and roughness of 2.2 µm is formed.

Implementation of the process at small values of duration of current pulses allows you to avoid formation of friable outer layer of the coating. At the same time, there is no need for subsequent technological process – mechanical treatment of the outer layer (grinding). The outer layer is formed as a dense one and may be functional. It is known that under stationary and slowly varying energy impacts, the formed outer layer is characterized by high roughness, low wear resistance. This layer is not functional and is removed by machining operation. In this regard, use of rapidly changing energy impact mode on the material being processed is energetically beneficial and allows to obtain coatings with a relatively low roughness of 2.2 µm, which does not require further mechanical processing – grinding – in many cases of application.

REFERENCES


Influence of The Process of Microplasma Treatment In Electrolyte Solutions On The Oxide Coating Properties


[28] Li, H. and Zhang, J. Preparation of a Modified Micro-arc Oxidation Coating Using Al2O3 Particles on Ti6Al4V. J Material Sci Eng, 6(6), 2017, 400. DOI: 10.4172/2169-0022.1000400.


Influence of The Process of Microplasma Treatment In Electrolyte Solutions On The Oxide Coating Properties


