THE FORMATION OF A SURFACE LAYER DURING MICROARC OXIDATION OF ALUMINUM ALLOYS*

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Abstract. The formation of a surface layer during microarc oxidation has been investigated. The results of experimental studies aimed at determining the structure and composition of oxide coatings on aluminum alloys are presented. The studies found out that, in contrast to existing ideas about the initial stages of micro-arc oxidation, a "barrier layer" grows unevenly over the sample area and there is no clear boundary between a pre-spark and a spark mode of the process. Uneven growth of a "barrier layer" is connected with different distribution of electric field on the surface of a sample and different concentration of electrolyte components. Depending on the electrolytes used the inside coating layers consist mainly of aluminium oxide, and the outer layers contain components formed as a result of thermochemical transformation of the electrolyte.

Microarc oxidation (MAO) is a promising method of surface hardening of parts made of valve metals (Al, Ti, Mg, etc.), which allows one to receive ceramics-like coatings with high mechanical, electrical and thermal characteristics [1-5]. MAO coating formation process has a complex mechanism and consists of several stages proceeding sequentially. They are pre-spark, spark, arc and microarc periods. The formation of coatings occurs as a result of simultaneous effects of several factors such as plasma-chemical, thermal, hydrodynamic ones [1].

All these three factors act simultaneously, although the degree of their impact varies depending on the treatment conditions. Despite a large number of papers devoted to the study of the formation of MAO-coatings nowadays there is no unified theory of the mechanism of formation and growth of the coatings. Practically all scholars agree that the process of coating formation starts during the pre-spark treatment period (1-20 seconds after the beginning of treatment depending on current density). According to the most common version it is believed that during this period there occurs a formation of a thin oxide layer similarly to traditional anodizing. Some researchers believe that this layer is amorphous and pore-free [1,2,6], while others, on the contrary, argue that this layer has high porosity [7-9]. Later on (in a spark period) according to the authors [1,2] there occurs electric breakdown of a dense anodic film in the birthplace of electron avalanches. Some part of the energy of electrons is transformed into heat, which greatly increases the temperature in the breakdown path. The interaction

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between the molten film substance and electrolyte components takes place at the points of contact of the breakdown path with the solution. As a result of such processes a high temperature modification of aluminum oxide $\alpha - \text{Al}_2\text{O}_3$ is formed in MAO layer.

According to another theory [7-9] bubbles of a gas-vapor phase appear in the pores of the anodic coating as a result of electrolysis. Electrical discharges that are a potent heat source and a cause of ionization of gas and shock waves occur in these bubbles. Discharges result in decomposition of the oxygen molecules in a gas bubble into atoms that acquire considerable kinetic energy under the action of the shock wave and due to this energy they penetrate into the metal.

Thus, many theories explaining the formation a coating can be divided into two main groups [10]: ion breakdown caused by the introduction of electrolyte ions into the oxide and accordingly the local growth of its ionic conductivity, and electronic breakdown the reason of which is supposed to be the "injecting" of electrons into the oxide conductivity zone and electron avalanche that occurs due to impact ionization.

Further growth of the coating occurs due to two simultaneous processes [7-9]:
- exothermic interaction between oxidants and juvenile surface of the bottom of microdischarges channels followed by the oxidation of evaporating atoms of alloy metal components;
- deposition of oxides on the surface of the coating or drawing them into the microdischarges channels after plasma-chemical and thermochemical conversion composing an electrolyte.

Correct understanding of the mechanism of MAO in aluminum alloys will allow one to manage this process and produce coatings with the desired structure and properties.

To find out the mechanism of formation of MAO coating the definition of the structure and composition of the coating at all stages of the process has been performed in the work.

The first step of research was to determine the dynamics of formation of MAO coatings in the initial stages. AlMg-6 alloy plate of dimensions 16x20 mm and thickness of 3 mm was used as a sample. To obtain a qualitative picture of the structure on an optical microscope the sample was preliminarily polished. Microstructure of the sample without treatment is shown in Figure 1a. Coating was performed by set IAT -T in the alkaline electrolyte containing NaOH (5 g / l) and Na$_2$SiO$_3$ (10 g / l). Set IAT - T allows independent adjustment of the anodic and cathodic current components.

To research the initial stages of MAO coatings formation the following parameters were used: the ratio $I_k/I_a= 1$, the current density of 10 A/dm$^2$. Treatment time: 5, 15, 25, 40, 55, 300 seconds. After each treatment the sample was washed, dried, and its surface microstructure was studied by the optical microscope NEOPHOT 32 at magnifications x250-x800. Then the sample was placed in an electrolytic bath and treatment was continued until the next time interval.

Experimental studies revealed that the first spark discharges occur on the surface of the sample in 15 seconds after the beginning of treatment. The voltage was 250 V. Before this coating is formed on the sample surface by the electrochemical method, and areas of coating growth (barrier layer) are located over the sample unevenly.

Thus, the coating grows unevenly on the sample area and it is impossible to discern a clear transition from a spark stage to a pre-spark one on the surface of the entire sample. The transition occurs in places where the barrier layer of sufficient thickness (1-2 microns according to our measurements) is formed. This observation is not consistent with the existing
notion of staging of MAO coatings application. Uneven growth of a "barrier layer" with the subsequent spark stage on it, according to our understanding, is associated with uneven distribution of electric field intensity over the sample surface and uneven concentration of active ingredients of the electrolyte.

In the second stage of the study the effect of treatment parameters on the formation of microstructure in the growth stage was determined.

Plates of the alloy AlMg-6 of dimensions 100x100mm and thickness of 3 mm without pretreatment were used as a sample. Coating was carried out by set IAT-T in two types of electrolytes:

1) NaOH (5 g/l) + Na₂SiO₃ (10 g/l);
2) Na₂HPO₄*12H₂O (40 g/l), Na₂B₄O₇*10H₂O (30 g/l), NaF (10 g/l), H₃BO₃ (20 g/l)

During treatment the following parameters were changed:

For electrolyte № 1: current density (from 10 to 20 A/dm²), treatment time from 30 to 60 minutes.

For electrolyte № 2: current density (from 30 to 60 A/dm²), treatment time from 5 to 30 minutes.

Electron microscopic studies were performed on a scanning electron microscope JSM-7001F at magnifications from x500 to x10000. A transverse section was prepared by mechanical thinning.

The results show that the dynamics of coating growth changes depending on treatment time. Increase of the coating into the sample with large and pronounced breakdown paths was observed. With time and increase of current density the breakdown paths are clogged because oxides are deposited and drawn into them. Oxides are formed as a result of thermochemical transformations of electrolyte components (in this study they are silicon and phosphorus oxides).

Research results show differences in the structure of the coatings formed according to the electrolyte used. But differences concern an outer layer formed as a result of the thermochemical transformation of the electrolyte. The internal structure of the coating distinguishable in breakdown paths remains practically unchanged since it is formed by the oxidation of the sample surface and consists of Al₂O₃.

The internal pores of "particles" can be seen on the electron microscopic images. The pores diameter is about 0.1-0.2 microns. The macropores diameter is about 5-10 microns.

Also there were conducted microscopic studies of the cross layer of coatings obtained. The coating consists of two layers having no clear boundary.

At the final stage of the research the analysis of the formed coatings chemical composition was conducted.

AlMg-6 alloy plates of dimensions 100x100mm and thickness of 3 mm without pretreatment were used as samples. Coating was performed in electrolyte number 1. Current density was 20 A/dm², the treatment time was from 5 to 120 minutes.

Microanalysis of the chemical composition was carried out on a scanning electron microscope GEOL GSM6380 allowing to measure surface-chemical composition with the depth of probe radiation penetration from 1 to 3 microns and identify elements with the atomic mass more than 3 a.m.u.

Microanalysis of coatings of various thicknesses shows that the composition of the coatings obtained depends on the processing time. The percentage of compounds obtained as a result of electrolyte thermochemical transformations increases towards aluminum oxide (Al₂O₃) with the increase of the treatment time duration.
Conclusions:
1) The studies found out that, in contrast to existing ideas about the initial stages of the micro-arc oxidation, a "barrier layer" grows unevenly over the sample area and there is no clear boundary between pre-spark and spark modes of the process. Uneven growth of a "barrier layer" is connected with the different distribution of electric field on the sample surface and uneven concentration of electrolyte components.

2) Depending on the electrolyte used the inside coating layers consist mainly of aluminium oxide, and the outer layers contain compounds formed as a result of the thermochemical transformation of electrolyte.

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