Effect of electrolyte composition on electrochemical formation and properties of ceramic-like coatings on aluminum alloys

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Abstract. The electrochemical formation of ceramic-like coatings on D16 aluminum alloy was carried out using microarc oxidation method in phosphate (1.5 g/L NaOH + 9 g/L Na2SiO3 + 3 g/L Na3PO4) and molybdate (5 g/L NaOH + 30 g/L Na2SiO3 + 5 g/L (NH4)6Mo7O24) electrolytes. White and black ceramic-like coatings with thickness of 200–300 microns were obtained in phosphate and molybdate electrolytes, respectively.

1. Introduction

Improvement of technical characteristics (hardness, wear resistance, heat resistance, corrosion-protective, physic-mechanical, electrical insulating properties etc.) of parts made of valve metals is associated with development of the technology for formation on their surface the protective coatings obtained by microarc oxidation (MAO) method [1]. These coatings are ceramic-like layers, the main components of which are high-temperature oxides. MAO consists in the electrochemical treatment of metals and alloys in the mode of burning on their surface of randomly moving microdischarges. It’s possible to obtain the thick (up to 400 μm) coatings, characterized by high parameters of the above mentioned properties, as well as high adhesive strength and adjustable porosity.

Currently, extensive information has been accumulated on the morphology, elemental and phase compositions of coatings formed by the MAO method in various electrolytes on valve metals and their alloys, see for example [1–4]. At the same time there remain open questions related to changes in the composition, structure and properties of coatings during their formation, as well as with complex dependencies of coatings characteristics on such technological parameters of process as electrolyte composition and duration of MAO treatment.

2. Experimental

Cylinders of D16 aluminum alloy with a diameter of 10 mm and a thickness of 6 mm served as samples for research. They were oxidized in the anode-cathode mode at a current density of 10 A/dm² in two different electrolytes: phosphate (1.5 g/L NaOH + 9 g/L Na2SiO3 + 3 g/L Na3PO4) and molybdate (5 g/L NaOH + 30 g/L Na2SiO3 + 5 g/L (NH4)6Mo7O24). The duration of the MAO treatment ranged from 5 to 320 minutes. MAO coatings formed in the phosphate electrolyte were
white in color, and those obtained in the molybdate electrolyte were black. Such a difference in the optical properties makes the MAO method promising for the production of thermal control coatings for aerospace engineering elements [4]. The study of the samples included: analysis of the elemental composition and distribution of elements in depth using the method of nuclear backscattering (NBS) spectrometry, measurement of geometric thickness, through porosity, microhardness of MAO coatings before and after abrasive removal of the coating outer technological layer.

The NBS spectrometry of protons with an initial energy of 7.7 MeV was carried out at the Institute of Nuclear Physics of Moscow State University [5]. The coating thickness was measured with an Ultramer V-60 thickness gauge. The through porosity was measured by the express method described in [1]. To measure the microhardness Vickers method is used.

3. Result and discussion
Figure 1 show typical NBS spectra for MAO coatings obtained in the phosphate electrolyte with the duration of their formation of 5, 30, 60, and 90 minutes. It can be seen that with an increase in the duration of oxidation, the amount of oxygen in MAO coatings increases. According to the results of the analysis of NBS spectra, concentration profiles of oxygen distribution over the thickness of MAO coatings were obtained (figure 2). In all the cases studied the thickness of the oxide layer is more than two times less than the geometric thickness measured by the eddy current thickness gauge. This discrepancy between the thicknesses indicates the presence of developed porosity in MAO coatings which grows with the increase of treatment duration.

![Figure 1. Spectra of NBS of protons for coatings obtained in phosphate electrolyte with different MAO treatment duration \( \tau \) (5, 30, 60 and 90').](image1)

![Figure 2. Oxygen concentration profiles over the thickness of MAO coatings obtained from NBS spectra in figure 1.](image2)

Analysis of the dependences of coating thickness on the duration of MAO treatment (figure 3) showed that the coatings formed in molybdate electrolyte are thicker than the layers obtained in phosphate electrolyte. The dependences of the through porosity of MAO coatings on treatment duration (figure 4) showed qualitative differences for molybdate and phosphate electrolytes. For samples obtained in molybdate electrolyte (filled circles) at the beginning of the oxidation process, a dense almost non-porous coating is formed and then the formation of through pores begins in the range of MAO coating thickness from 4 to 26 \( \mu \)m. By 30 minutes of the oxidation process the through porosity reaches \(~30\%\), and then slightly changes during the next five hours of MAO treatment. In coatings obtained in a phosphate electrolyte the dependence of the through porosity on the thickness (empty circles) is non-monotonic. Firstly the thin island coating with high through porosity is formed. In the future the growth of islands is observed, they gradually grow together, due to which sharp decrease in through-porosity occurs and the dense, almost nonporous coating is formed. This behavior is observed for MAO coatings with a thickness of about 50 microns at treatment duration from 90 to 120 min.
Then (120–180 min) the coating is etched, and etching occurs both on the outer layer and on the through pores themselves, which is observed for thickness range of 50–150 μm.

A joint analysis of the concentration profiles (figure 2) and the characteristics of MAO coatings allows us to conclude that in coatings obtained in a phosphate electrolyte, a large through porosity takes place first, and then closed porosity begins to develop. MAO coatings have a complex structure, which is manifested in a gradual decrease in the amount of oxide and, accordingly, in an increase in the substrate material.

The microhardness of the working layer, which is formed after abrasive removal of the outer technological layer of the coatings, for both electrolytes gradually increases with the treatment duration and is up to two times higher than the microhardness measured before removal of the outer technological layer (figure 5). It can be seen that the microhardness of MAO coatings obtained in the phosphate electrolyte significantly exceeds the microhardness of coatings formed in the molybdate electrolyte.

4. Conclusion
White and black ceramic-like coatings with thickness of 200–300 microns were obtained by microarc oxidation in phosphate and molybdate electrolytes, respectively. The oxidation in the molybdate electrolyte makes it possible to obtain thicker oxide layers with lower microhardness and high through
porosity, which can be used as thermal control coatings. The coatings obtained in the phosphate electrolyte are less thick, but more hard. The through porosity of coatings obtained in the phosphate electrolyte has the complex dependence on duration of the MAO treatment. The differences in data on the thickness of MAO coatings obtained using NBS proton spectrometry and an eddy current thickness gauge indicate the presence of developed porosity in coatings.

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