Electrochemical studies of ceramic-like MAO-coatings on the E110 alloy

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Abstract. Ceramic-like coatings with the thickness up to 35 μm were formed on E110 zirconium alloy by microarc oxidation in electrolyte with the addition of yttrium oxide powder with average particle size 0.28 μm. The electrochemical behavior in 0.2M LiOH, structure, and phase composition of the obtained coatings have been studied. Polarization study in 0.2MLiOH at room temperature showed the anode currents on the coating up to 4 times less than on the uncoated alloy. Increasing the electrolyte temperature to 100 °C leads to growth in the anode currents on the coated samples, but current density values still correspond to the passive state.

1. Introduction

Microarc oxidation (MAO) is a promising method for the formation of protective coatings on zirconium and its alloys. Due to their properties, MAO coatings are of great interest for nuclear fuel elements structural materials protecting from corrosion, accelerated oxidation at high temperatures, embrittlement, and absorption of oxygen and hydrogen [1–3]. In recent years the implementation of the method of electrophoretic deposition in MAO process by incorporating fine particles from electrolyte suspensions into the structure of oxide coating has a great interest [4–8]. Thus, additions to the alkaline electrolyte of oxides nanoparticles Al₂O₃, ZrO₂, and CeO₂ during the formation of MAO coatings on zirconium contribute to an increase in their corrosion-protective ability. For example, when CeO₂ nanoparticles were added to the electrolyte, the corrosion currents for the samples with the PEO coating decreased by four orders of magnitude compared to untreated zirconium [4]. The addition of yttria submicron and nanoparticles to the electrolyte provides the formation of high-temperature modifications of zirconia in MAO coatings, which improves their thermal stability and makes them promising for aviation and rocket technology [6–8].

In this work, we investigated the corrosion resistance in 0.2 M LiOH of zirconium alloy samples with MAO coatings obtained in suspension electrolyte with the addition of fine particles of yttrium oxide.
2. Experimental

Samples of zirconium-niobium alloy (Nb – 1%) were used as substrates for coatings. MAO treatment was carried out in an aqueous solution of sodium hypophosphite (5 g/l) and sodium silicate (9 g/l) with addition of submicron yttrium oxide powder (6 g/l). Average particle size of the powder was ~ 0.28 μm. Coatings were formed in AC electrical mode at equal values of anode and cathode currents and total current densities 20, 30, and 40 A/dm² for 20 min.

The thicknesses of MAO coatings were measured using the eddy current thickness gauge VT-201 and on cross-sections using a scanning electron microscope (SEM). The structure of the coatings was studied by SEM Quanta 600. Phase analysis of the coatings was carried out in copper λKα₁,2 radiation using x-ray diffractometer PANalytical Empyorean. Phases were identified using database ICDDPDF-2. The electrochemical behavior of the coatings was studied in an aqueous solution of 0.2M LiOH at temperatures of 25 and 100 °C. Polarization was carried out using a PI-50-1 potentiostat in a standard three-electrode cell with a silver chloride reference electrode and a platinum auxiliary electrode from the cathode to the anode region at a rate of 1 mV/s. Roughness assessment was carried out using a portable roughness meter TIME TR100. Ten measurements were done on each coating samples.

3. Results and discussion

Study of coatings cross-sections showed that the thicknesses of MAO coatings increased with an increase in the processing current density from 15 to 35 μm. The surface morphology of the coatings is characterized by areas of a crater-like structure with pores in the crater centers (figure 1, a), a globular structure, and adsorbed particles of yttrium oxide ~ 600 nm in size (figure 1, b).

![Figure 1. SEM images of MAO coatings formed at a current density of 30 A/dm²: a - surface microstructure; b - globular structure; c - surface microstructure after electrochemical studies; d - cross-section structure.](image-url)
There are three coating layers in the cross-section coatings structure: barrier layer, a medium porous layer and an outer layer with current-discharge channels (figure 1, d). The thickness of the barrier layer at the interface with the alloy is \( \sim 1.5 \mu m \). The surface roughness of the obtained coatings increases with an increase in the MAO current density. Thus, for the coating obtained at 20 A/dm², the roughness parameter \( R_a \) is 1.5 \( \mu m \), for the coatings obtained at 30 and 40 A/dm², \( R_a \) is 2.6 and 4.2 \( \mu m \), respectively. The coatings surface morphology did not change after electrochemical studies (figure 1, c).

After MAO treatment for 20 minutes, monoclinic and tetragonal phases of zirconia with the predominance of the monoclinic modification have been formed in the coatings (figure 2). An increase in the current density of the MAO process practically does not lead to a change in the content of phases in the coating. After MAO treatment in this electrolyte without adding of yttrium oxide particles, only the monoclinic modification of zirconia was found in the coating [9].

![Figure 2. X-ray diffraction patterns of MAO-coated sample at 30 A/dm².](image)

Polarization studies in 0.2M LiOH solution at room temperature have shown that the anode currents on samples with coatings are 1.5-2 orders of magnitude lower than on the E110 alloy without coating. With an increase in the potential above +600 mV, it is already 4 orders of magnitude lower (figure 3). The cathode currents on MAO coatings are 3 orders of magnitude lower then on samples without coatings. Very low current densities on the anodic polarization curves for MAO coatings indicate that the coated alloy is in a deep passive state and, therefore, the coatings provide its protection. Since the corrosion rate is a superposition of the cathodic and anodic reactions, it can be assumed that the corrosion rate on the coatings should be less than on the alloy by at least 2 orders of magnitude.

With an increase in the temperature of the 0.2M LiOH solution to 100 °C, the anodic currents on the coating increase by \( \sim 3 \) times, but they still correspond to the values of the current density for the passive state. The difference in the current density values on the anodic polarization curves for MAO coatings formed at different current densities is insignificant, as in conditions without heating. When the electrolyte is heated, an uncoated alloy behaves in a fundamentally different way. Anodic currents increase, and after anodic polarization, local corrosion products are observed in the form of white flakes. No external changes in MAO coatings were found during the study. Considering this, it can be assumed that the formed MAO coatings can effectively protect the E110 alloy from corrosion under real operating conditions.
Figure 3. Polarization curves for an uncoated alloy (1) and samples with MAO coatings obtained at current densities 20 A/dm² (2), 30 A/dm² (3), and 40 A/dm² (4).

4. Conclusions
The thicknesses of MAO coatings increased with an increase in the processing current density from 15 to 35 μm. Monoclinic and tetragonal phases of zirconia with the predominance of the monoclinic modification have been found in the coatings. The MAO coatings formed for 20 minutes at current densities of 20, 30, and 40 A/dm² showed good corrosion resistance. At a polarization study of 0.2M LiOH at room temperature, the anode currents on the coating are 4 times lower than on the uncoated alloy. Increasing the electrolyte temperature to 100 °C, leads to an increase in the anode currents on the samples with coatings, but still correspond to the current density values for the passive state.

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