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Investigation of copper-doped aluminum composites with ceramic-like oxide coatings corrosion resistance

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Abstract. The effect of MAO coatings on the electrochemical behavior of aluminum composites without additives and doped with copper (1, 2, 3 wt%) in 3% NaCl solution compared to uncoated aluminum composites has been studied. A comparison of the polarization dependences of the current density lgi on the potential *E* of coated and uncoated aluminum composites showed the positive effect of MAO coatings on the electrochemical properties. It is shown that the presence of copper affects the electrochemical characteristics of composites with MAO coatings as compared to composites without additives. The values of current densities on the anode curves of MAO-coated aluminum composites with 1, 2, and 3% copper are not significantly different. On the local areas of the coatings the oxide-chloride compound islands were found after electrochemical tests.

1. Introduction

Aluminum alloys are widely used in aviation and astronautics in the design of existing and the development of advanced aircraft [1–3]. They combine high strength, low weight and good processability [4]. However, to increase the life time of jet engines and various pumps used in mechanical engineering, it is necessary to find ways to improve the mechanical properties of traditional and the development of new aluminum materials. One of the most important components of rocket engines is the turbopump assembly. Introduction of new materials will be promoted to increase life time of its parts (impellers, bearings, bushings, etc.). Aluminum matrix composites are promising to solve these problems. Doping with metals and small additives of refractory nanoparticles introducing into aluminum can significantly improve its functional and strength properties [5–8]. The application of anticorrosive oxide coatings will lead to an increase in the duration of its operation in aggressive environments [9, 10].

One of the methods of aluminum composite materials wear resistance and corrosion resistance increasing is the formation of protective oxide coatings on their surface by micro arc oxidation (MAO) [11–13]. MAO is an electrochemical process using the energy of electrical microdischarges functioning on the surface of the processed material. It allows to obtain oxide coatings with high wear resistance, corrosion resistance, heat resistance, etc.

The doping of aluminum composites with copper significantly affects the MAO process and the properties of the formed coatings. In this paper, we studied the effect of MAO coatings on the electrochemical behavior of aluminum composites without additives and doped with copper (1, 2, 3%) compared to untreated aluminum composites.

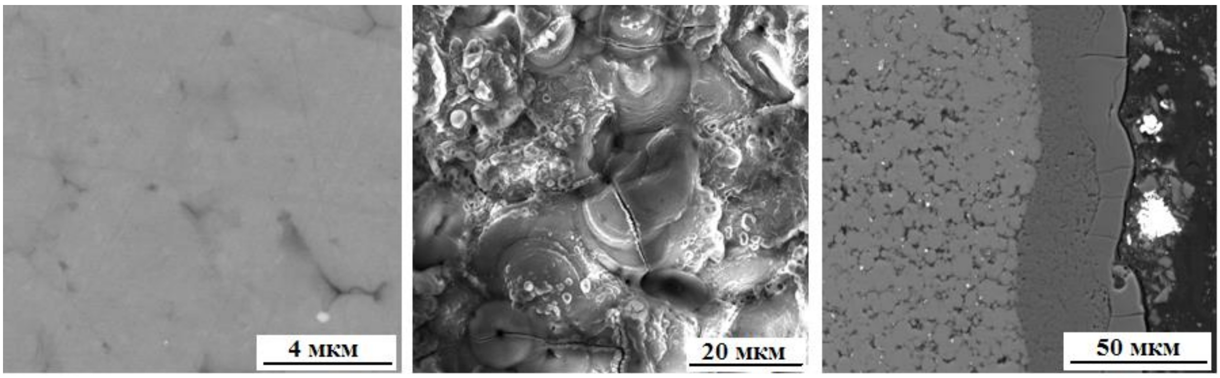
2. Experimental setup and characterization techniques

Samples of aluminum composites without additives and alloyed with copper (Al + 1, 2, 3 wt% Cu) were obtained by powder metallurgy (cold pressing and sintering in low vacuum). Aluminum powder (99,95%) with an average particle size of 4 μm was used as a matrix. Copper powder (99,5%) with a particle size of 0.2 μm was used for doping. The powders were mixed in a ball mill in a steel beaker with steel balls (5 mm) in ethanol for a day with powder to balls ratio P:B = 1:3. Sintering was carried out in low vacuum in a laboratory oven at 650 ° C for 180 minutes. MAO coatings were obtained in an electrolyte containing 2 g/l of potassium hydroxide and 9 g/l of sodium silicate in AC mode at the MAI installation. The total current density was 12.5 A/dm^2 with equal anodic and cathodic currents. The duration of the MAO process was 60 minutes.

Electrochemical studies were performed for coated and uncoated composites Al, Al + 1; 2; 3% Cu in a three-electrode cell using a potentiostat in a 3% NaCl solution at a potential sweep rate of 1 mV/s. The structure of the coatings before and after electrochemical studies were analyzed using a Quanta 600 scanning electron microscope and an X-ray diffractometer (Empyrean PANalytical, CuKa radiation).

3. Results and discussion

The average grain size of the composite (~5 μm) was estimate by the secant method using SEM images (figure 1(a)). The surface morphology of MAO coatings on composites corresponds to that typical for coatings on compact aluminum alloys [11, 12]. It is characterized by crater-shaped areas of aluminum oxide and areas with a globular structure, mainly consisting of elements that make up the components of the electrolyte (figure 1(b)). Coatings consist of 3 main layers: a barrier layer at the border with the substrate about 0.5 μm thick, a middle polycrystalline layer and an outer layer penetrated by crater channels (figure 1(c)). The average coating thickness on aluminum composite without additives was ~ 35 μm. The thickness of the MAO coatings for copper doped composites varied from 20 to 50 μm. The heterogeneity of thickness increases with copper content increasing. It can be assumed that the presence of copper in the composite accelerated the MAO coating formation due to its lower electrical resistance and greater thermal conductivity.



(a) **(b)** **(c)**

Figure 1. SEM images of the aluminum composite without additives **(a)**; the surface **(b)** and the cross-section structure **(c)** of the MAO coating obtained for 60 minutes.

A comparison of the polarization dependences of the current density lgi on the potential *E* of coated and uncoated aluminum composites has showed their positive effect on the electrochemical properties (figure 2). The values of currents for all cathodic and anodic polarization curves for MAO coatings are approximately an order of magnitude smaller than for samples without coatings. The smallest anode and cathode currents were obtained for MAO-coated aluminum composite without additives. These features of the electrochemical behavior can be due to both the absence of inclusions and lower through porosity of this coating. The current density on the cathode curves is an order of magnitude less, and on the anodic curves is three orders of magnitude less for MAO-coated composites as compared to the untreated materials. A great difference in current values indirectly indicates a compact MAO coatings, which has high adhesion to the composite and relatively low through porosity. The doping of copper has worsened the electrochemical characteristics of MAO-coated composites. An analysis of the anodic polarization curves shows an increase in the values of currents for MAO-coated Al-Cu composites compared to the MAO-coated Al composite. The values of current densities on the anode curves of MAO-coated aluminum composites with 1, 2, and 3% copper are not significantly different.

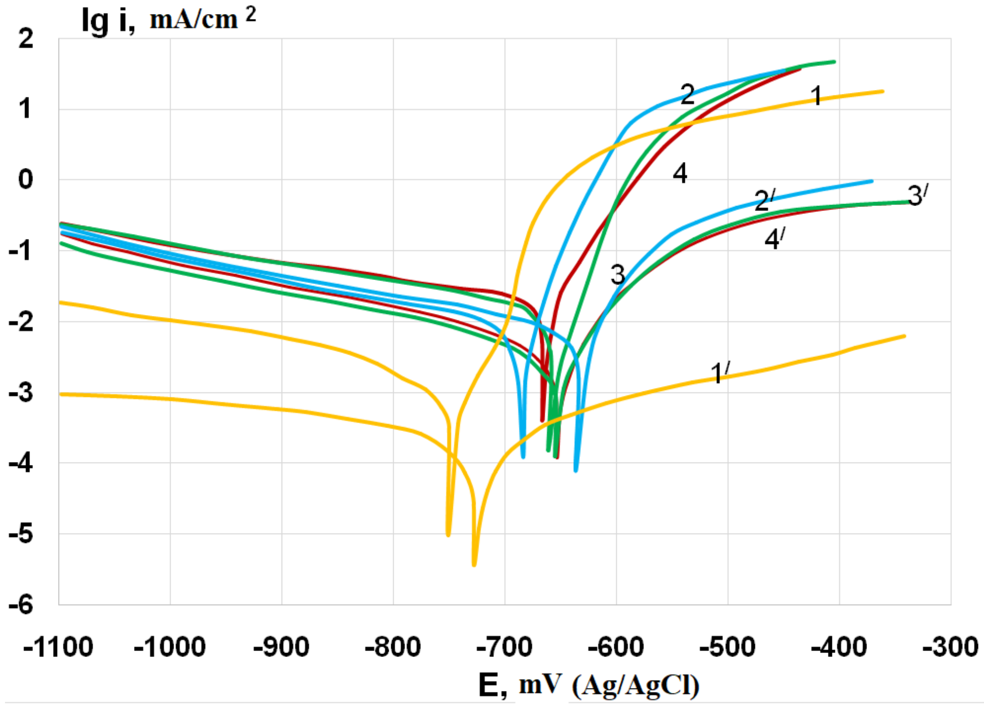


Figure 2. Polarization curves of current density lgi on potential *E* of uncoated composites Al (1), Al + 1% Cu (2), Al + 2% Cu (3), Al + 3% Cu (4) and MAO-coated composites (1'), Al + 1 Cu% (2'), Al + 2% Cu (3'), Al + 3% Cu (4') in 3% NaCl at a potential sweep rate of 1 mV/s.

After electrochemical tests in 3% NaCl solution the MAO coatings retained their integrity, and there were no significant changes in the surface structure (figure 3(a)). On the local areas of the coating, there are islands of the film, apparently related to oxide-chloride complexes. On the coatings cross-sections in local areas characterized by a smaller thickness (~20 μm), a delamination of coatings into 2 layers (middle and outer) occurred. In these areas there are film islands embedded through the pores of the outer coating layer as a result of electrochemical tests (figure 3(c)). In areas of greater thickness the islands of the oxide-chloride film are observed on the surface of the coating (figure 3(b)). Their formation could happen during the migration of chlorine ions through the oxide coating or due to the chemisorption of chloride ions on the coating surface that contributed to the dissolution of the oxide coating through the formation of oxide-chloride compounds [14]. Embedded sections of the film led to an increase in the number of cracks in the coatings.

Before electrochemical tests, MAO coatings were contained γ-Al_2O_3, mullite and CuO on composites doped by more than 1% copper. After tests in NaCl composites x-ray patterns contain reflexes of the base – Al, Al_2Cu, and reflexes of the coating – γ-Al_2O_3, mullite, and CuO. It is also possible the presence of spinel $AlCu_2O_4$ confirmation of which requires further research. The coating is characterized by a high content of amorphous component. An amorphous halo with a maximum at $2\theta = 27$ ° most likely refers to oxide-chloride compounds in the coatings.

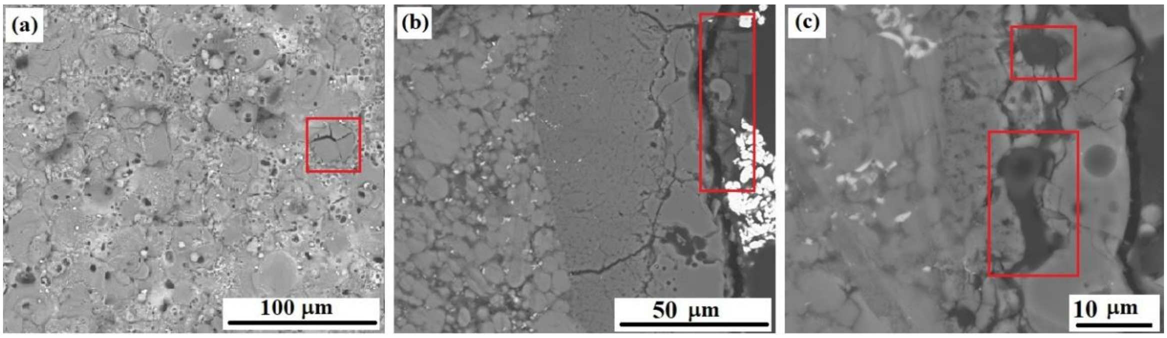


Figure 3. SEM images of the surface **(a)** and cross-section structure **(b), (c)** of the MAO-coated Al + 3% Cu composite after electrochemical tests in 3% NaCl solution (the areas of the oxide-chloride film are highlighted).

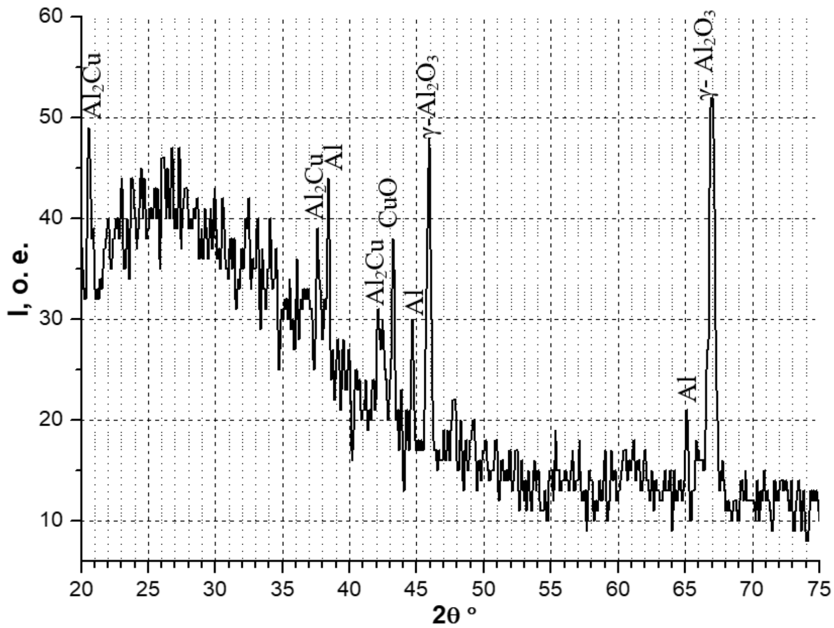


Figure 4. X-ray diffraction spectrum of the MAO-coated composite Al-3% Cu after electrochemical tests

4. Conclusion

This research results have shown a positive effect of MAO coatings on the electrochemical behavior of aluminum composites compared to untreated samples. It is shown that the presence of copper affects the electrochemical characteristics of composites with MAO coatings. The influence of oxide-chloride compound films on the formation of cracks in coatings was revealed.

Acknowledgments
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