# Electrochemical Study of Sintered Aluminum-Based Materials and MAO Coatings on Their Surfaces

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Received June 21, 2020; revised August 14, 2020; accepted August 20, 2020

**Abstract**—The electrochemical behavior of sintered materials from powder aluminum, its compositions with copper (1, 2, and 3%), and coatings on their surfaces formed by micro-arc oxidation (MAO), is studied in a 3% NaCl solution. The values of the anodic and cathodic current densities on the polarization dependences for compact aluminum samples are approximately 4 and 2 times lower compared to sintered powder aluminum, which, in turn, is less corrosive than aluminum-copper composites. MAO coatings lead to a decrease in anodic and cathodic currents, which indicates their positive effect on the corrosion resistance of these materials. Using scanning electron microscopy and X-ray phase analysis, the structure of aluminum-copper composites with MAO coatings after electrochemical studies is examined.

**Keywords:** powder metallurgy, aluminum-copper composites, micro-arc oxidation, MAO coatings, surface morphology, structure, phase composition, corrosion-protective ability, scanning electron microscopy, X-ray phase analysis, electrochemical-polarization test

**DOI:** 10.1134/S1027451021020130

## **INTRODUCTION**

The development of industry and new technologies requires the creation of new structural materials and their surface modification by various methods to impart special properties. Research in the field of creating composite materials based on the aluminum matrix opens up great prospects. Powdered aluminum materials are promising in terms of their low weight and low capital costs of production. However, their use is limited to applications that do not require high strength and corrosion resistance. An increase in the operating characteristics of powder aluminum-matrix composites is facilitated by their modification with alloving additions of metals (Cu, Zr, Cr, Co, Ti, etc.), as well as nanoparticles of refractory substances [1-4]. Alloving with copper strengthens aluminum due to the formation of a solid solution, Guinier-Preston zones, and precipitates of the Al<sub>2</sub>Cu phase but significantly reduces its corrosion resistance [1]. The surface treatment of sintered aluminum-copper composites by micro-arc oxidation (MAO) can significantly increase their corrosion resistance. In this case, ceramic-like coatings are formed on the modified surface, which also contribute to an increase in wear resistance and heat resistance of the treated materials [5-9]. MAO coatings, as a rule, consist of an inner working layer, which is responsible for their corrosion-protective ability, and an outer technological layer.

The thickness and structure of MAO coatings formed on sintered aluminum-copper composites differ from those obtained on compact aluminum alloys. This is manifested in the presence of oxide films and pores along grain boundaries, as well as hardening phases of different natures [8-10]. For example, in [9], it was shown that, upon the oxidation of a sintered aluminum-copper composite for 60 min, metal inclusions remain in the coating, completely disappearing with an increase in the duration of the process to 180 min, and an increase in the copper concentration leads to a slowdown in the rise of the anode voltage at the initial stage of MAO-coating formation. In [11, 121, the negative effect of strengthening intermetallic phases in aluminum-copper composites on the protective properties of the formed coatings was noted due to a decrease in the thickness and an increase in the porosity of MAO coatings. However, even for powder composites, the MAO treatment of their surface promotes the inhibition of corrosion. Sintered aluminum-copper composites with MAO coatings are used to increase the efficiency and service life of various units in mechanical engineering (engine impellers, gear wheels, bushings, spacers, etc.), including aggressive corrosive conditions.

To understand the limits of the possible application of the "aluminum-copper composite – MAO-coating" system, it is necessary to study its physicochemical properties.

The aim of this study is to perform a comparative analysis of the electrochemical behavior of compact aluminum, sintered powder samples of aluminum, and its compositions with copper (1, 2, and 3%) without and with MAO coatings formed on their surface.

## **EXPERIMENTAL**

Samples of sintered powder materials without additives (Al) and composites alloyed with copper (Al + 1%, 2%, or 3% Cu) were obtained using powder metallurgy methods (cold pressing and sintering in vacuum). The matrix used was aluminum powder with an average particle size of  $\sim 4 \,\mu m$  (ASD-4, technical standard (TU) 48-5-226 87). For alloying, copper powder with an average particle size of  $\sim 2 \,\mu m$  (PMS-V, the State standard (GOST) 4960-75) was used. Aluminum powder was sieved through a sieve with a mesh size of 14  $\mu$ m and then mixed in hexane with copper powder in a ball mill with a ball-to-powder weight ratio of 1:4. Then the mixture was placed in an ultrasonic bath (20 kHz) and homogenized using a rotating stirrer (400 rpm). Drying was carried out in air at 60°C for 24 h. The resulting mixture was pressed in cylindrical molds 14 mm in diameter and 17 mm in height on a hydraulic press under a pressure of 400 MPa. The resulting powder samples were sintered in a low vacuum furnace at a temperature of 650°C for 180 min.

The micro-arc oxidation of samples made of compact aluminum and sintered powder materials was carried out in electrolytes containing 2 g/L of potassium hydroxide and 9 g/L of sodium liquid glass in the anode-cathode mode. The total current density during MAO treatment, ensuring a stable course of the process, was  $10 \text{ A/dm}^2$  at equal anodic and cathodic currents. The duration of the MAO process was 60 min.

The surface morphology of the sintered materials before and after MAO treatment and the cross-sectional structure of the aluminum-copper composites with coatings were investigated by scanning electron microscopy (SEM) using a Quanta 600 scanning electron microscope. The phase composition was determined using an Empyrean PANalytical X-ray diffractometer (CuK $\alpha$  radiation). Electrochemical polarization studies of the samples were carried out in a standard three-electrode cell using an IPC PRO L potentiostat. Polarization was carried out from the cathode to the anode region in a 3% NaCl solution with a potential sweep rate of 1 mV/s.

### **RESULTS AND DISCUSSION**

The outer appearance of the samples of sintered aluminum with MAO coatings differs from those of composites with copper, which is due to the presence of copper oxide in the coating. Thus, the MAO coating on aluminum is white and its upper layer contains predominantly amorphous silicon oxide, which is incorporated into an electrolyte coating containing liquid glass [13, 14]. The introduction of copper into the aluminum base of the composites in an amount of 1, 2, and 3% affects the composition and structure of the formed coatings and changes the nature of the MAO process. There is a slowdown in the growth of the forming voltage and, probably, a change in the temperature-time characteristics of micro-arc discharges. Visually, the coatings change color from white (for aluminum) to brown with a burgundy tint (for composites with copper). Alloying with copper leads to the formation of inclusions of copper oxide and spineltype compounds in the MAO coating.

Similar processes were observed for titanium samples during their MAO in silicate-alkaline electrolytes with nickel sulfate additives [13, 14]. At low NiSO<sub>4</sub> concentrations, MAO proceeded according to the mechanism with the predominant formation of silicon dioxide coming from the electrolyte and the coating had a characteristic white color. With an increase in its concentration, the MAO coating consisted mainly of titanium dioxide with a fraction of nickel oxides. In this case, the color of the coating changed from white to black or grey-green (depending on the valence of nickel in its oxide).

Here, for composites containing copper, elongated copper-containing inclusions were noted along the boundaries of aluminum grains with an average size of  $\sim$ 5 µm (Figs. 1a, 1b). The structure of MAO coatings on a powder material without additives (Al) and a composite doped with copper (Al + 1% Cu) was almost identical. It is characterized by crater-like islands, some of which contain pores in their center, which remained after the completion of micro discharges and solidification of the molten coating material (Fig. 1c). With an increase in copper content in composites to 2-3%, the crater structure becomes less pronounced, the density of craters on the coating surface decreases, open porosity increases, and a large area is occupied by areas with a fine globular structure (Fig. 1d). As shown in [8], these areas predominantly



Fig. 1. SEM images of the surface morphology of sintered Al (a) and Al + 3% Cu (b) powder materials and MAO coatings on sintered Al + 1% Cu (c) and Al + 3% Cu (d).

contain electrolyte components. SEM studies of the structure of cross sections of MAO coatings showed that their thickness is about  $35 \,\mu$ m.

The results of the polarization studies are shown in Figs. 2, 3, and Table 1. It can be seen that the addition of copper to aluminum decreases the corrosion resistance of sintered powder materials due to an increase in electrochemical heterogeneity. Thus, current densities in the anodic polarization (-500 mV) increased approximately 3 times, and upon cathodic polarization (-900 mV) by 5–10 times, depending on the copper content in the composite (Table 1). MAO coatings in all cases shifted the corrosion potential to more noble values, which indirectly indicates their protective effect. The values of the current on all cathodic (left side) and anodic (right side) polarization curves obtained for the samples with coatings are lower than those for samples made of sintered powder materials

(Fig. 2). This directly testifies to the positive effect of MAO coatings on corrosion resistance. For example, for a sintered powder material (Al), the current density extracted from the cathodic polarization curves is an order of magnitude lower for samples with MAO coatings. In the case of the anodic curves, the current decrease was three orders of magnitude (Fig. 2a, Table 1). This indicates a very strong inhibition of the anodic dissolution process of the base metal by the coatings.

The addition of copper to powdered aluminum leads to a decrease in the protective effect of MAO coatings, apparently, due to an increase in through porosity. Thus, the current densities on the anodic polarization curves for all aluminum-copper composites decrease in comparison with the uncoated samples by only two orders of magnitude (Figs. 2b–2d, Table 1). The current densities on the cathodic polarization curves for the composites (Al + 2% Cu) and (Al + 3% Cu)



**Fig. 2.** Polarization dependences obtained in 3% NaCl solution at a potential sweep rate of 1 mV/s of sintered Al (a), Al + 1% (b), Al + 2% (c), and Al + 3% Cu (d) powder materials without (1) and with (2) MAO coatings.

decreases by half an order of magnitude (Figs. 2c, 2d, Table 1), and for the composite (Al + 1% Cu) the MAO coating has practically no effect on the cathodic currents (Fig. 2b, Table 1).

Thus, the smallest anodic and cathodic currents in the polarization dependences were obtained for a sintered powder material (Al) with a MAO coating (Fig. 2a, curve 2), apparently associated with the absence of copper compounds, which introduce elec-



**Fig. 3.** Polarization dependences obtained in 3% NaCl solution at a potential sweep rate of 1 mV/s of compact Al (*1*) and powder Al (*3*) without a coating, and compact (*2*) and powder Al (*4*) with a MAO coating.

trochemical heterogeneity in the substrate and structural heterogeneity in the coating.

Figure 3 shows for comparison the polarization dependences for samples of compact aluminum and sintered powder material (Al) without and with MAO coatings. For uncoated samples of compact aluminum, the anodic current density is approximately four times lower and the cathodic current density is two times lower (Fig. 3, Table). This may be due to the lower imperfection (development of morphology, porosity, presence of inclusions, fracturing, etc.) of the surface of compact aluminum in comparison with the powder material (Al). The values of the anodic and cathodic current densities for samples of compact aluminum with MAO coating are almost two orders of magnitude lower than those for samples coated with sintered powder Al (Fig. 3, Table 1).

Figures 4a and 4b show SEM images (in backscattered electrons) of the surface morphology of the sintered composites (Al + 1% Cu) and (Al + 3% Cu) without coatings after electrochemical polarization in a 3% NaCl solution. On the surface of the samples, there are regions covered with a film, most likely, of oxide-chloride complexes (Fig. 4a, region 2). They are formed as a result of the chemisorption of chloride anions on the surface of the composites. Fragments of the structure of sintered composites are also observed (Figs. 4a, 4b, region 1). Investigation of the surface

Sample	$E_{\rm corr}$ , mV (vs sat. Ag/AgCl)	<i>i</i> , mA/cm <sup>2</sup> (at -500 mV)	$\log i$ , mA/cm <sup>2</sup> (at -500 mV)	<i>i</i> , mA/cm <sup>2</sup> (at -900 mV)	$\log i$ , mA/cm <sup>2</sup> (at -900 mV)
Al (c)	-704	5.1286	0.71	0.0033	-2.48
Al(c) + MAO	-640	$5.86 \times 10^{-5}$	-4.232	$1.81 \times 10^{-5}$	-4.742
Al (p)	-754	18.6209	1.27	0.0072	-2.14
Al(p) + MAO	-737	0.0030	-2.53	0.0007	-3.14
Al + 1% Cu (p)	-834	54.9541	1.74	0.0363	-1.44
Al + 1% Cu (p) + MAO	-647	0.8892	-0.051	0.0398	-1.4
Al + 2% Cu (p)	-673	53.7032	1.73	0.0891	-1.05
Al + 2% Cu (p) + MAO	-668	0.5495	-0.26	0.0339	-1.47
Al + 3% Cu (p)	-680	43.6516	1.64	0.0891	-1.05
Al + 3% Cu (p) + MAO	-666	0.4677	-0.33	0.0427	-1.37

 Table 1. Results of polarization tests (c is compact Al and p is powder Al)

 $E_{\rm corr}$  is the corrosion potential; sat. Ag/AgCl is the reference electrode; *i* is the current density.

morphology of aluminum-copper composites with MAO coatings after polarization showed the absence of any defects (Figs. 4c, 4d). Nevertheless, on the surface of the coatings, there are islands up to  $100 \,\mu\text{m}$  in size, most likely, of the same oxide-chloride complexes (Figs. 4c, 4d). Fragments of an oxide-chloride film (Fig. 4e), the formation of which can occur as a result of the chemisorption of chloride anions after electrochemical polarization in a 3% NaCl solution, were observed on cross-sectional images of composites with thick MAO coatings. In the local areas of the MAO coatings, characterized by a smaller thickness (up to  $30 \,\mu$ m), their stratification was noted into inner (Figs. 4e, 4f, layer 3) and outer (Figs. 4e, 4f, layer 4) layers with an intermediate oxide-chloride film as a result of the penetration of chloride anions through the pores of the outer layer of the coating (Fig. 4f). The wedging of this film into the MAO coating can lead to its cracking [15].

Figure 5 shows X-ray diffraction patterns of sintered aluminum-copper composites after electrochemical polarization in a 3% NaCl solution. The Xray diffraction pattern of the uncoated powder composite (Al + 3% Cu) contains reflections of Al and the Al<sub>2</sub>Cu intermetallic phase (Fig. 5a). There are no reflections of the oxide-chloride film, which may indicate its amorphous state. The X-ray diffraction patterns of the powder composite (Al + 1% Cu) with a MAO coating (Fig. 5b) showed peaks of Al and Al<sub>2</sub>Cu, as well as reflections of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and mullite aluminosilicate. For the composite (Al + 3% Cu) with a MAO coating (Fig. 5b), peaks of copper oxide CuO were also revealed (Fig. 5b). This diffraction pattern is characterized by a high content of the amorphous component, as evidenced by a halo with a maximum at  $2\theta = 27^{\circ}$ , which is (most likely) related to oxide-chloride compounds that got into the coating after electrochemical polarization. In [9], the phases  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mullite, and CuO were also observed in MAO coatings on aluminum–copper composites containing more than 1% Cu [9].

## CONCLUSIONS

The densities of the anodic and cathodic currents on the polarization dependences for the compact aluminum samples are approximately 4 and 2 times lower than those for sintered powdered aluminum. Powdered aluminum, in turn, corrodes less than aluminum-copper composites. The current densities at anodic polarization increase by approximately 3 and 5-10 times for the case of cathodic and anodic polarization, respectively, depending on the copper content in the composite. The formation of MAO coatings on sintered powder materials in all cases nobles the corrosion potential and leads to a decrease in the anodic and cathodic currents on the polarization curves, which indicates the positive effect of MAO treatment on the corrosion resistance of these materials. The smallest polarization currents were obtained for sintered powder aluminum with a MAO coating, which is associated with the absence of copper compounds in them, which introduce electrochemical heterogeneity into the substrate and structural heterogeneity into the coating. The study of the surface morphology of alu-



**Fig. 4.** SEM backscattering images of the surface after polarization in 3% NaCl solution of sintered powder composites Al + 1% Cu (a) and Al + 3% Cu (b) and MAO coatings on Al + 1% Cu (c) and Al + 3% Cu (d), and MAO coatings cross-sectional SEM images of Al + 1% Cu (e) and Al + 3% Cu (f). Structure of composites (1), oxide-chloride film regions (2), inner layer of MAO coating (3), and (4) top layer of MAO coating.



**Fig. 5.** XRD diffraction patterns of sintered composites after electrochemical polarization in 3% NaCl: Al + 3% Cu without a coating (a), Al + 1% Cu with a coating (b), Al + 3% Cu with a coating (c). Symbols correspond to ( $\blacksquare$ ) Al, ( $\square$ ) Al<sub>2</sub>Cu, ( $\bullet$ )  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ( $\Delta$ ) mullite, and ( $\bigcirc$ ) CuO.

minum-copper composites with MAO coatings after electrochemical polarization in a 3% NaCl solution showed that they did not contain any defects (in general). Nevertheless, islands of oxide-chloride complexes were present on the surface of the coatings. The X-ray phase analysis of MAO coatings on aluminumcopper composites revealed the presence of Al, the CuAl<sub>2</sub> intermetallic compound,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CuO, and mullite aluminosilicate.

### FUNDING

This work was financially supported by The Grant Council of the President of Russia (grant no. MK 54.2019.8).

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Translated by D. Kharitonov