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The influence of micro plasma oxidation (MPO) process conditions on creation of the Al_2O_3 coatings on aluminum alloy D16 was studied using EPR technique. Aluminum alloy D16 contains alloyed transition metals such as Cu, Mn, Fe, Ni, Ti, being incorporated into the coatings structure during MPO processes. EPR data on transition metal ions allow estimating an appearance of a high temperature phase of Al_2O_3 due to difference in incorporation coefficients and in the EPR parameters of transition metal ions in low and high temperature Al_2O_3 phases of MPO coatings. These data show that no high temperature Al_2O_3 phases were created during anodic MPO process.

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1. Introduction

Micro plasma oxidation processes are electrochemical processes producing oxidation of metal surface in the canals of micro discharges, where high temperature plasma occurs. Micro plasma oxidation coatings containing a high temperature phase of aluminum α - Al_2O_3 have many interesting applications. Such coatings can be obtained both from material of aluminum details and by introducing aluminates into electrolyte. The properties of the coatings created depend on various anode and cathode regimes, current discharge values, temperature and composition of electrolyte. The coatings structure consists of two layers. The outer layer at the boundary of electrolyte containing mainly a low temperature phase of Al_2O_3 is a technological layer. The inner layer close to metal surface containing α - Al_2O_3 is responsible for a wide range of interesting macroscopic characteristics of the MPO coatings, such as microhardness, friction, wear resistance [1]. In this communication, we discuss EPR data for micro plasma oxidation coatings on aluminum alloy D16. Since aluminum alloy D16 involves transition metals – copper, iron, titanium, manganese and chromium, we hope to gain an information about the peculiarities of the MPO processes at different stages of the coating growth using EPR data on the oxidizing states of the transition metal ions. MPO coatings on the surface of aluminum alloy D16 were obtained with a semi-industrial plant, developed at the Institute of Inorganic Chemistry SB RAS.

2. Results

The MPO coatings under EPR study were obtained :

- 1) during anodic MPO process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$;
- 2) during anodic – cathodic MPO process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$.

EPR spectra were prepared with automatized Varian EPR spectrometer E-109 at X-band at 300 K. EPR spectra analysis was performed with WinEPR and Simfonia programs. The following is a table of the contents of alloying elements.

Table 1. Content of alloying elements in aluminum alloy D16

Aluminum alloy	Mg, %	Mn, %	Cu, %	Si, %	Zn, %	Fe, %	Ti, %	Cr, %	Ni, %
D16	1,2-1,8	0,3-0,9	3,8-4,9	0,5	0,3	0,5	0,1	-	-

MPO oxidized aluminum alloy D16 plates of sizes $0.5 \times 5 \times 10$ mm were prepared to perform their EPR examinations. Thickness was measured with thickness gauge “Quanix 5000”. EPR spectrum of DPPH ($g = 2.0036$) was used as a g -value comparison standard.

Anodic MPO process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$ electrolyte

The EPR spectra of MPO coatings obtained with anodic micro plasma process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$ are shown in Fig. 1. They are identical to the Cu^{2+} EPR spectrum in γ - Al_2O_3 [4]. EPR spectrum of the coating is observable as an asymmetrical single line with g -value 2.07 and of 160 Gauss linewidth. Lack of hyper fine structure (HFS) is due to high concentration of copper ions and exchange interaction between them. Increasing coating thickness (ranging from 10 up to 30 microns) results in the decrease of the concentration of the paramagnetic copper ions. Hereafter, (thick above 30 microns) the concentration of the paramagnetic copper ions has a valid level (Fig.2). Such a

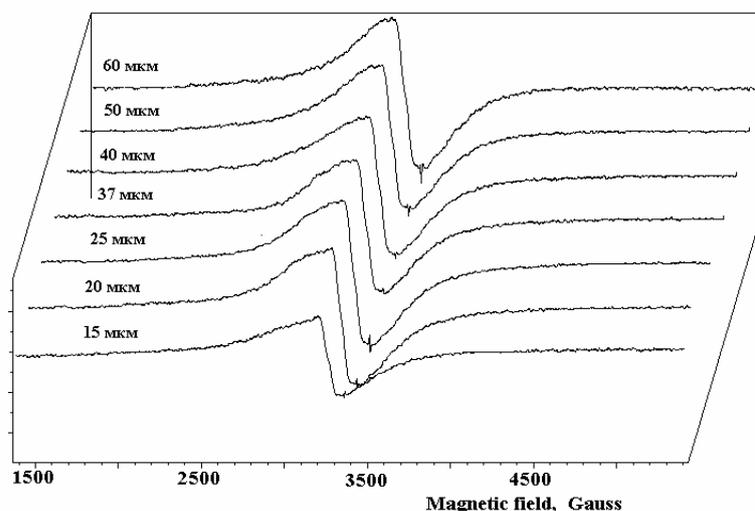


Fig. 1 Dynamics of EPR spectra changes with changing MPO coating thickness. Anodic MPO process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$ electrolyte.

behavior of the copper ions is due to the transformation of hydroxide copper complex into copper oxide, having no EPR spectra. On the other hand, an existence of the EPR spectrum with $g = 2.07$ says that this anodic MPO coating contains only a low temperature Al_2O_3 phase.

Anodic – cathodic MPO process in aqueous solution of KOH + Na_2SiO_3 electrolyte

The EPR spectra of the MPO coating obtained during the anodic – cathodic MPO process differ from the spectra of the anodic coatings. Fig. 3 shows the dependence of paramagnetic centers concentration on the thickness of coatings obtained. As illustrated in Fig. 4, at a low magnetic field ($g = 4.3$) Fe^{3+} EPR spectrum occurs. It's known and has been observed in γ -phase of Al_2O_3 [5]. Nearby $g = 2.00$ a complicated spectrum consisting of six lines can be seen. Deconvolution of the experimental spectrum and simulation of individual spectra showed that this complicated spectrum is produced by overlap of the Cu^{2+} EPR spectra with HFS from the Mn^{2+} manganese ion.

Figs. 4a to 4c show the experimental spectrum deconvolved into spectra of manganese and copper ions. Simulation of the Cu^{2+} EPR spectrum allows estimating $g_{\parallel} = 2.2876$ and $g_{\perp} = 2.050$ at the linewidth $\Delta H_{1/2} = 90$ G. The similar spin-Hamiltonian parameters were observed for the copper ions in α -phase of Al_2O_3 [4]. Subtraction of the copper ions spectrum from experimental that gives a typical EPR spectrum of the manganese ions Mn^{2+} with $g = 2.00$ and HFS parameter $A = 83.7$ G. EPR spectrum with the same parameters was observed for α -phase of Al_2O_3 [6]. Fig. 5 exhibits the experimental and simulated Mn^{2+} EPR spectra.

3. Discussion

As it follows from previous results [1], the produced MPO coatings contain different ratio of low and high temperature Al_2O_3 phases depending on the conditions of MPO process. Since the structure of these Al_2O_3 phases has different symmetry, transition metal ions incorporating into coating serve as paramagnetic probes for diagnosing phase types and peculiarities of their distributions in the structure of the MPO coatings.

Our data showed that anodic MPO process produced mainly low temperature Al_2O_3 phases of poor quality. In this case a typical EPR spectrum of copper ions with $g = 2.07$ is observed. It should be noted that the increase in coating thickness up to 40 microns led to decreased the concentration of Cu^{2+} paramagnetic centers. But beginning with 40 microns their concentration has a stable level. Copper, manganese and iron ions among alloy impurities show paramagnetic properties. With the content 5% of copper in aluminum alloy D16 paramagnetic states of the Cu^{2+} , Mn^{2+} and Fe^{3+} ions give a single exchange line with $g = 2.07$. As the coatings grow, decreasing paramagnetic states concentration is due to the transformation of hydroxide complexes of copper into CuO , which did not show EPR spectra. But at increased the coatings thickness there is existed an equilibrium between these two forms of copper compounds and beginning with 40 microns concentration of the paramagnetic centers became stable. The same situation is observed in the anode-cathode coatings, but the decay of copper paramagnetic states stopped with a more decreased thickness of coatings (beginning with 20 microns). Differences between the EPR spectra of anodic and anodic-cathodic coatings arise from the presence in the latter of high temperature α -phase of Al_2O_3 . At the same time in the anodic- cathodic coatings together with exchange line are observed individual EPR spectra of copper, iron and manganese ions. These results show that the resolved EPR spectra are due to isolated parts of coatings with a low concentration of the copper ions. Such parts of the coatings are related to an appearance of α - Al_2O_3 polycrystalline phase. Recrystallization of low temperature phases within high temperature phases produces a redistribution of the impurities due to the difference in the coefficients of incorporation into various Al_2O_3 phases.

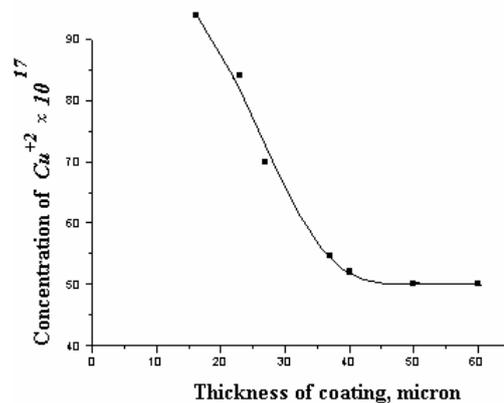


Fig. 2 The dependence of the Cu^{2+} ions concentration on the thickness of MPO coating in anodic process. Electrolyte is aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$.

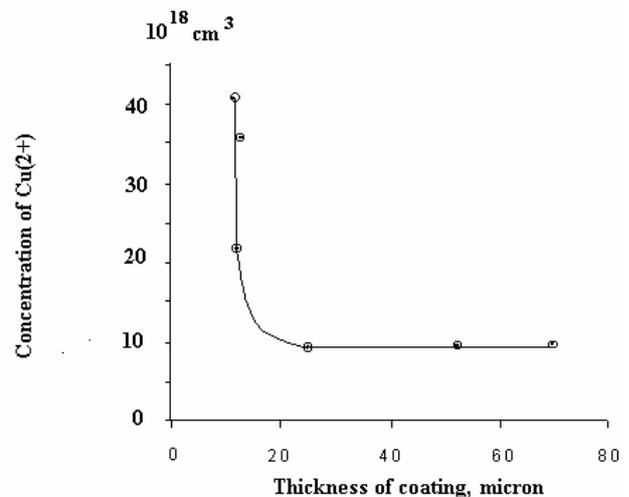


Fig. 3 The dependence of the copper ions concentration on the coatings thickness on alloy D16 obtained by anodic- cathodic MPO process in aqueous solution of $\text{KOH} + \text{Na}_2\text{SiO}_3$.

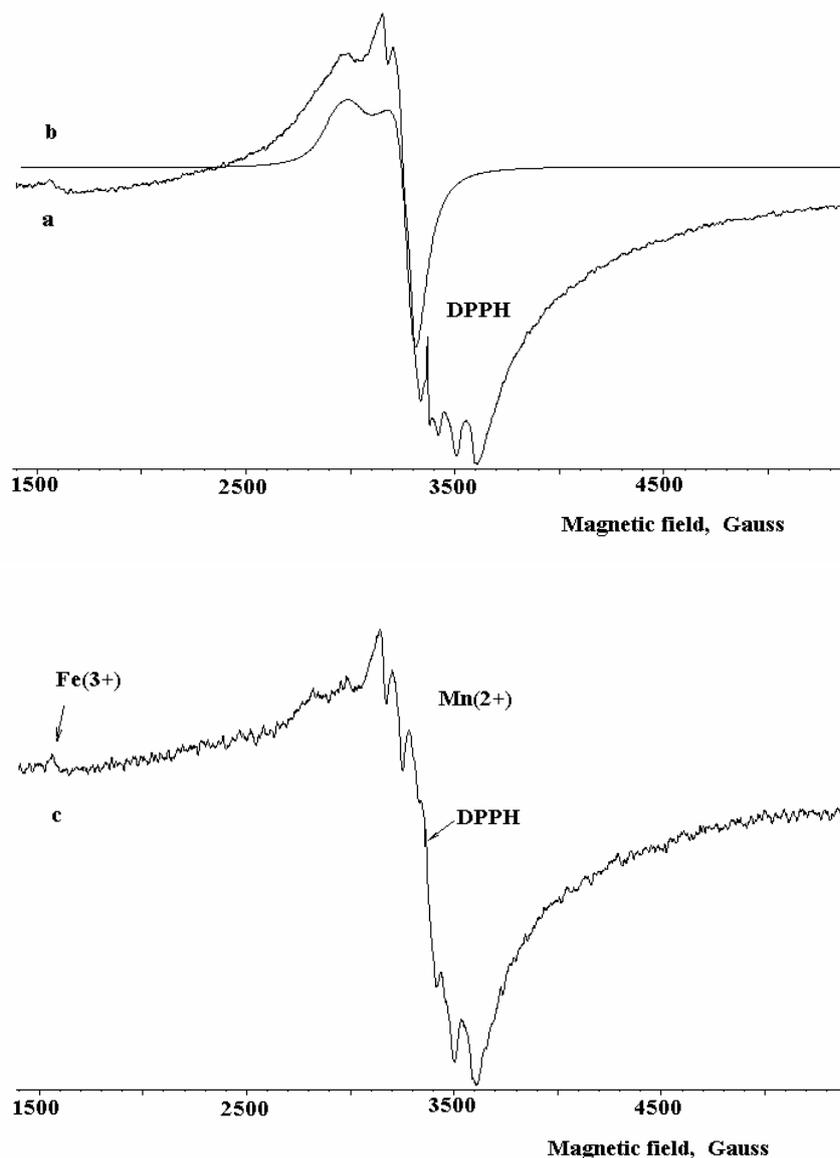


Fig. 4 EPR spectra of the transition metal ions in MPO coatings obtained with anodic – cathodic process in aqueous solution of KOH + Na₂SiO₃: a – experimental spectrum; b – simulated spectrum of Cu²⁺ ions; c – difference spectrum (a – b) due to HFS from the Mn²⁺ ions.

To test our assumptions, we removed a technological portion of the coating obtained by anodic-cathodic MPO process. The EPR data show that after such a treatment copper ions content drops by 10%, at the same time contents of the iron and manganese ions remain invariable. The reason of 10% changing the copper ions content is due to loose structure and a small density of a technological layer of the coatings.

The EPR data obtained demonstrate that the coatings grown by anodic and anodic-cathodic MPO processes differed in the states of the copper, iron and manganese ions. It allows using a nondestructive EPR technique for diagnosing the MPO coatings.

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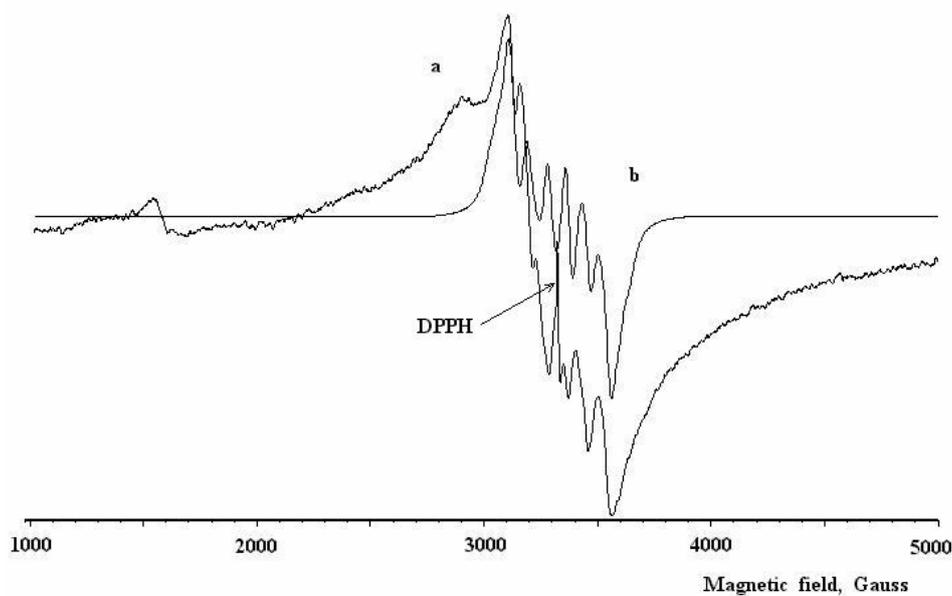


Fig. 5 Experimental (a) and simulated (b) EPR spectra of the Mn^{2+} ion in the MPO coating on aluminum alloy D16.

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