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NEW SUBSTANCES,  
MATERIALS AND COATINGS

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## Iron Distribution and Ferromagnetic Characteristics of Fe-Containing PEO Coatings on Aluminum

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**Abstract**—Fe-containing oxide coatings fabricated by the plasma-electrolytic oxidation (PEO) method have been studied by means of scanning electron and magnetic force microscopy. The data comparison has demonstrated that ferromagnetic properties of the coatings are mainly associated with concentrating of iron in specific pores. A scheme has been suggested that would explain iron distribution in the course of the coating growth.

**Keywords:** aluminum, plasma-electrolytic oxidation, iron distribution, ferromagnetic domains

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### INTRODUCTION

Materials of the “ferromagnetic oxide coating + metal” type can find application as electromagnetic wave absorbers, in medicine, in design of separation units, and in catalysis. It was shown [1–5] that the plasma-electrolytic oxidation (PEO) method could be applied to form oxide coatings with ferromagnetic and antiferromagnetic characteristics on paramagnetic titanium and aluminum. PEO comprises an electrochemical oxidation of metal surface under effect of spark and microarc discharges in the anode area.

We suggested to form ferromagnetic PEO coatings on valve metals, including aluminum and its alloys, in alkali electrolytes-sols with dispersed particles of iron hydroxides [2, 6]. Analysis of the published experimental data allowed us to suggest that ferromagnetism of these coatings was associated with iron that tended to concentrate mainly in pores [7–9]. However, iron was present not only in pores, but also in other surface areas, albeit less concentrated, as well as in the coatings' bulk. The ferromagnetic characteristics of the samples presumably represented a superposition of contributions from varied Fe-containing formations and compounds on the coatings surface and in bulk.

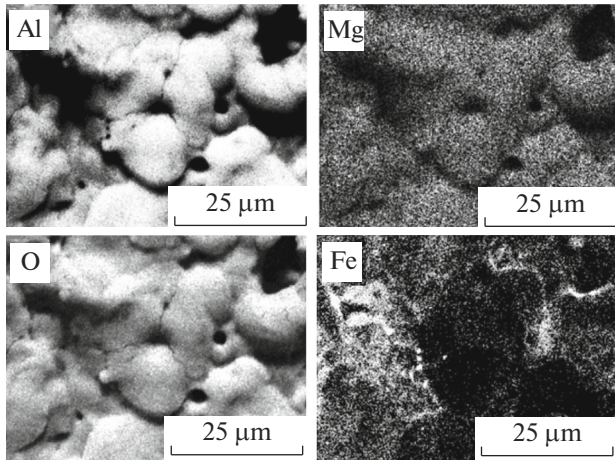
Distribution of ferromagnetic domains in the surface layer of the coating can be found by means of magnetic force microscopy. To specify a correlation between iron concentration sites and ferromagnetic characteristics of PEO coatings, we cross-referenced

them by comparing iron distribution maps obtained via an energy-dispersive spectrometer to a scanning electron microscope and maps of ferromagnetic domains allocation along the coating surface that were determined by means of magnetic force microscopy.

### MATERIALS AND METHODS

Fe-containing oxide coatings of a thickness of 12–14 μm were formed in PBWFe aqueous alkali electrolyte that contained (mol./L) 0.066 of Na<sub>3</sub>PO<sub>4</sub> + 0.034 of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 0.006 of Na<sub>2</sub>WO<sub>4</sub> + 0.015 of Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> under constant current density of 0.1 A/cm<sup>2</sup> for 10 min on AMg5 anode-polarized aluminum alloy (wt %: 4.8–5.8 of Mg, 0.5–0.8 of Mn, 0.02–0.1 of Ti, 0.5 of Fe, 0.5 of Si, 0.1 of Cu, 0.2 of Zn, the rest Al), all other conditions were in accordance with [9]. Note that such a concentration of ferrous oxalate was selected to provide maximum concentration of iron in the resulting composition of coatings [9]. The synthesis was performed at the Institute of Chemistry of the Far East Division of the Russian Academy of Sciences.

Investigation of the coatings by means of magnetic force and scanning microscopy methods and measurements of the coercive force values of the samples were performed using the equipment at the Research Park of St. Petersburg State University. An INTEGRA AURA magnetic-force microscope (NT-MDT, Russia), a Hitachi S-3400N (Japan) scanning electron



**Fig. 1.** Distribution of main elements along the coating surface on the aluminum alloy.

microscope with dispersive spectrometer, and an MPMS 3 SQUID-magnetometer (Quantum Design, United States) were used. To measure the coercive force, the samples surface planes were positioned in parallel to the external magnetic field.

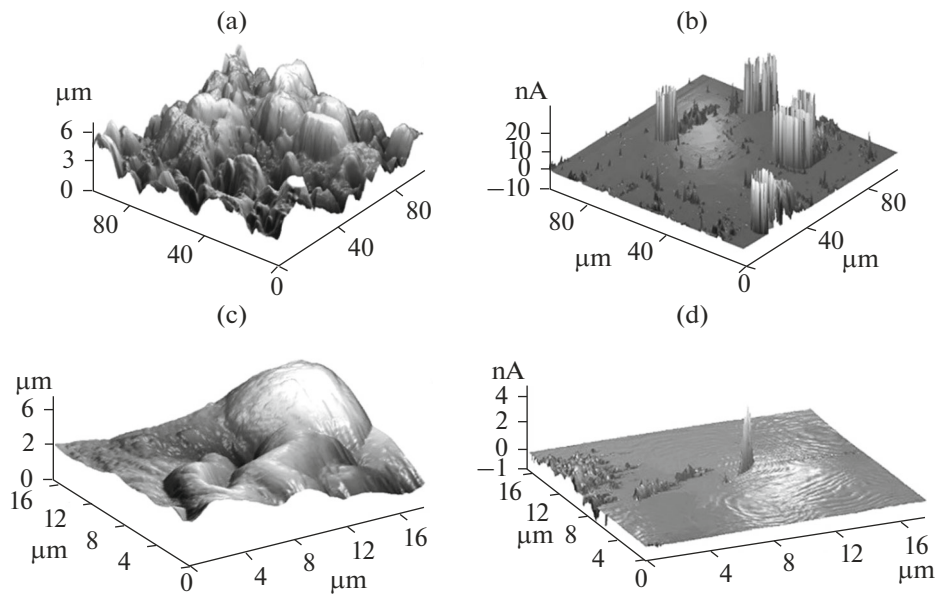
## RESULTS AND DISCUSSION

According to measurements performed in St. Petersburg, the coercive force value at 300 K equaled to 54–123 Oe for certain samples of the series, which was close to the previously obtained values for similar samples [9].

As seen from Fig. 1, the surface distribution of Al and Mg contained in the alloy composition and O in the surface layer were synchronous. These elements were present throughout all sites of the relief, except pores and cavities. On the contrary, Fe was distributed mainly in cavities, where many fine pores were located, and along the perimeter of large pores. This result is in compliance with the maps of Fe, Ti, and O distribution for similar Fe-containing coatings on titanium [7].

The magnetic force microscopy data are provided in Fig. 2. The image on the left demonstrates the surface relief, and the one on the right the distribution of the ferromagnetic domains along the surface. Maxima of the magnetic field distribution were observed along the perimeter of the pores that were located on flat-topped heights of the relief (Figs. 2a, 2b; the pore was not displayed) and inside the pores (Figs. 2c, 2d). The surface sites exhibiting weak ferromagnetic qualities must be related to iron having been distributed mainly in relief lows with a large number of fine pores.

In other words, despite the fact that iron in different concentrations was present throughout all the coating bulk, the sites of iron concentration in pores and along the perimeter at certain heights made the main contribution to overall ferromagnetic properties of the coating. The results obtained in [8, 9] enable one to suggest that iron contained in the pores is in a partially reduced state. According to the present study, iron in other components of coatings contained in the compounds that did not exhibit ferromagnetic properties (Fig. 2). Taking into account the electrolyte composition and peculiarities of PEO processing, those compounds may be phosphates, borates, tungstates,



**Fig. 2.** (a, c) Relief of the surface and (b, d) distribution of ferromagnetic domains along the coating surface.

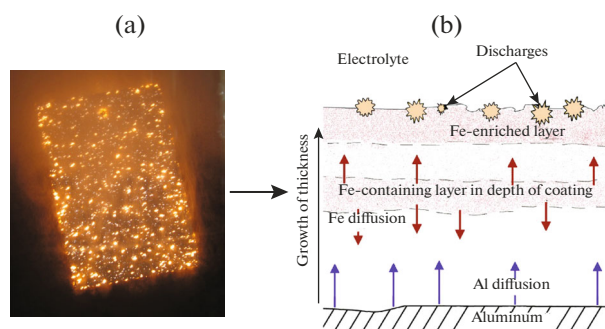
oxides, or spinels. The high temperature in the bulk of the coatings necessary for the formation of such compounds based on components of the electrolyte and the processed substrate was maintained by constantly active groups of spark and microarc discharges.

The heights with pores on the PEO-coating surface were also considered to be related to an impact of electric discharges. Upon the discharge attenuation, a pore remained (a trace of a penetration path) with surrounding heights that were formed of hardened melt (volcano-like formation). According to the measurements performed earlier for similar Fe-containing coatings by means of energy-dispersive accessory, upon probe beam focusing on the bottom, pore walls, and crystallites contained in pores, it was discovered that all these objects contained iron in high concentrations (about 50 at % [8–10]). Here, measurements performed in the bulk of the coating by the same method demonstrated that it consisted mainly of aluminum oxide and contained about 6 at % of iron. The iron content in the heights surrounding the pore was close to that in the coating bulk and much lower than inside the pore [9, 10].

As seen from the magnetic force microscopy data (Fig. 2), not all the heights contained ferromagnetic inclusions. This may be due to the following factors. First, the areas of elevated iron concentration that had appeared earlier due to discharge activity were moving into the depth of the oxide PEO coatings, while the latter were forming and growing in thickness. Due to iron diffusion from these sites and aluminum from the substrate, which was caused by elevated temperatures, a material of these formations gradually mixed with the bulk of the oxide layer. The iron concentration in the coating bulk leveled. Figure 3 shows a tentative scheme of the process.

After iron hydroxide particles were removed from the electrolyte by filtration, iron was not observed in the pores of the formed coatings and the samples became paramagnetic [11]. Consequently, iron incorporation in pores of the coatings in the investigated case was related to the iron hydroxide particles being captured by electric discharges from the electrolyte. This is why the second possible reason for many heights missing ferromagnetic domains is that not all the discharges were captured and incorporated dispersed iron hydroxide particles into the coating. It can be expected that an increase of the concentration of the dispersed particles in the electrolyte will cause an increase in both iron concentration in heights and the number of Fe-containing heights and, consequently, a number of ferromagnetic domains.

If the scheme provided in Fig. 3 is correct, then the distribution of iron and other electrolyte components throughout the coating cross section can be assumed to be nonhomogeneous. The iron concentration in the subsurface layer of the coating must be increased. Note that an elevated concentration of the electrolyte



**Fig. 3.** (a) Spark and microarc discharges on the aluminum surface and (b) the suggested scheme of the iron incorporation and distribution in the PEO coating in the course of its growth.

elements in the subsurface layer of the growing PEO coating has been noted in the published works. For instance, Si(IV) concentration has been observed in the subsurface layer of the coatings formed in an aqueous electrolyte with  $\text{Na}_2\text{SiO}_3$  [12], concentration of Zr(IV) upon the formation of coatings in aqueous electrolyte with  $\text{Zr}(\text{SO}_4)_2$  [13], and concentration of cerium upon the formation of coatings on magnesium alloy in an electrolyte with dispersed particles of cerium oxide [14].

## CONCLUSIONS

To sum up, a comparison of the distribution maps of iron and ferromagnetic domains has demonstrated that ferromagnetic properties of the investigated Fe-containing PEO coatings on aluminum formed in electrolyte–sols are related to the iron concentration sites in certain pores. A majority of these coatings have not exhibited ferromagnetic properties.

## ACKNOWLEDGMENTS

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