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The Iron Distribution and Ferromagnetic Areas in PEO Coatings

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Abstract. Oxide coatings formed on aluminum alloy in electrolyte with colloidal particles of iron hydroxides show ferromagnetic properties. Iron distribution have been studied using electron scanning microscopy and magnetic force microscopy. It is found that the iron localized in the areas exposed to spark and microarc electric discharges makes the main contribution to the ferromagnetic properties of coatings.

Introduction

The 'ferromagnetic oxide coating/metal' composites can find application in designs of absorbers of electromagnetic radiation, separators, catalysts, and microtransformers. As was shown in Refs. [1-5], plasma electrolytic oxidation (PEO) technique could be used to form the oxide coatings with ferromagnetic or antiferromagnetic characteristics on paramagnetic titanium and aluminum. PEO is the electrochemical oxidation of the metal surface under spark and microarc electric discharges occurring in near-anode area [6-8].

One of the methods proposed for the formation of ferromagnetic PEO coatings on valve metals is associated with the use of slurry electrolytes containing Fe(III) hydroxide colloidal particles [2, 9]. In this case, iron is unevenly distributed over the coating surface. For example for coated aluminum samples, its average concentration is about 6 at. % in the coatings, whereas that is about 50 at. % in the pores. The scope of experimental data suggests that iron concentrated in the pores is responsible for the ferromagnetism of Fe-containing PEO coatings [10-12].

This paper presents the data, which allows one to compare the distribution of the ferromagnetic areas and that of characteristic components of the coating relief.

Experimental

Fe-containing oxide PEO coatings were formed the anode-polarized AMg5 aluminum alloy (wt.%: 4.8-5.8 Mg, 0.5-0.8 Mn, 0.02-0.1 Ti, 0.5 Fe, 0.5 Si, 0.1 Cu, 0.2 Zn, the rest of Al) at the effective current density i = 0.1 A/cm^2 for 10 min in the aqueous alkaline PBWFe electrolyte containing (mol /L): 0.066 Na_3PO_4 + 0.034 $Na_2B_4O_7$ + 0.006 Na_2WO_4 + 0.015 $Fe_2(C_2O_4)_3$, similarly to [12].

The distribution of magnetic fields over the surface of the sample was visualized by magnetic force microscopy using an atomic force microscope INTEGRA AURA (NT-MDT, Russia) with a CoCr magnetic probe. Backscattered electron images were collected and analysis of the chemical composition of the samples was performed using a Hitachi S-3400N SEM with a wavelength dispersive spectrometer WDS-INCA 500, a field emission cathode SEM Zeiss Merlin and a QUANTA System 200 3-D with an analytic complex Pegasus 4000.

Results and Discussion

The measured value of the coercive force of the composites "Fe-containing coating / aluminum alloy" at 300 K was 54-123 Oe for individual samples in the series. During the PEO, iron from the electrolyte is concentrated in coating pores, as a rule, in form of crystallites. The nanoparticles contain (at. %) 51.6 Fe, 12.0 Al, 20.5 O, 15.9 W. Fig. 1 shows SEM image of crystallites in the pores PEO coating.

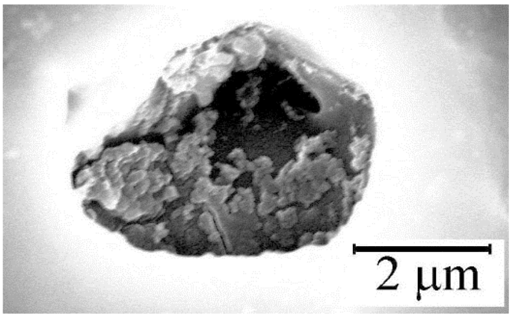

Fig. 1. SEM image of crystallites in the pores

Fig. 2 presents the data of magnetic force microscopy. The images on the left are the surface reliefs, on the right - the distribution of the ferromagnetic areas over the surface. Maxima in the distribution of magnetic fields are observed on the elevations with a flat top (pore is not mapped, Fig 2a, b) and in the pores (Fig. 2c, d). The presence of areas with minimal ferromagnetic responses on the surface is apparently related to the iron distribution in relief depressions with a large number of fine pores.

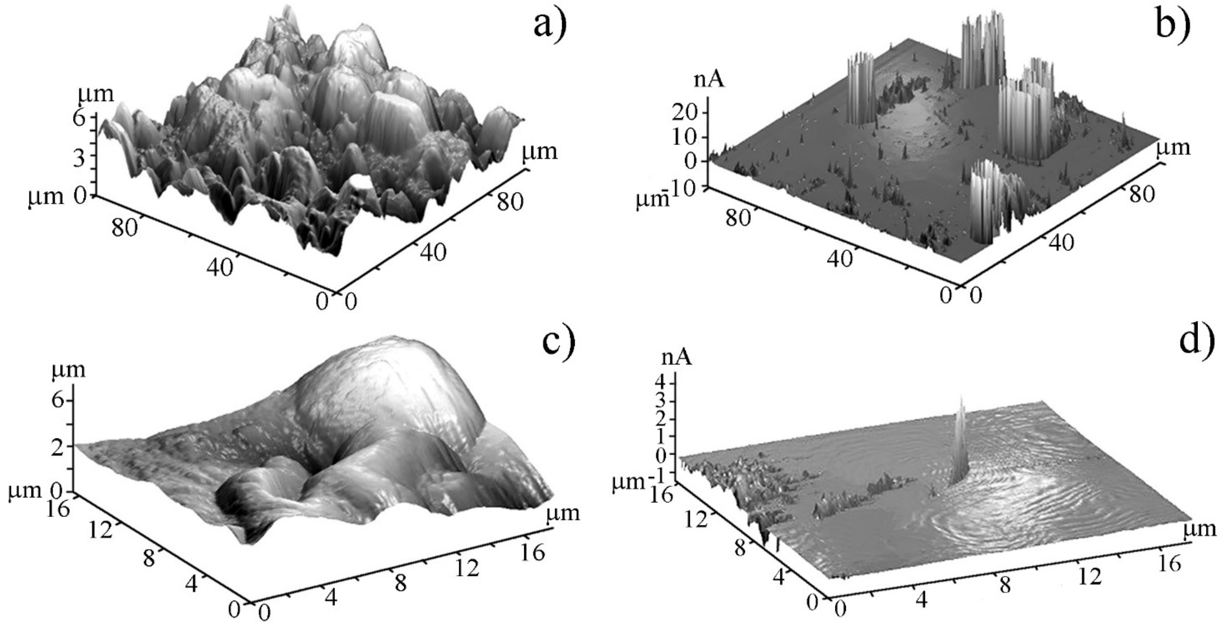

Fig. 2. The surface relief (a, c) and the distribution
of the ferromagnetic areas on the coatings surface (b, d)

Thus, it is the areas of iron concentration in the pores that makes the main contribution to the ferromagnetic properties of the coatings as a whole. According to [11, 12], iron in the pores is in a partially reduced state. As follows from the data obtained (Fig. 2), in other coating constituents, iron is found in compounds that do not possess ferromagnetic properties. Given the composition of the electrolyte and the parameters of PEO treatment, it can be phosphates, borates, tungstates, oxides or spinels. The high temperature in the coating bulk necessary to form such compounds based on the electrolyte components and the substrate to be treated is maintained by ensembles of spark and microarc electric discharges permanently operating in the surface layer.

The formation of elevations with pores on the surface of PEO coatings is also associated with the action of electrical discharges. The pore (breakdown channel) with the surrounding elevation consisting of solidified melt ("volcanic-like" formation), remains after discharge attenuation. Not all elevations contain ferromagnetic inclusions on the surface (Fig. 2). This fact can be accounted for the following reasons. First, during the formation of the PEO coating and increase in its thickness, the Fe-rich areas formed earlier and associated with the action of electric discharges gradually move into the coatings depth. Elevated temperatures result in the diffusion of iron from such areas and that of aluminum from the substrate. In the depth of the coating, the material of such Fe-rich areas is gradually mixed with the main oxide layer bulk, which leads to averaging the iron concentration in the coating bulk and forming the non-ferromagnetic compounds. Fig. 3 shows the scheme of the assumed process.

According to [13], including the iron into the coating pores is a result of the capture of iron hydroxide particles from the electrolyte by electric discharges. Therefore, another possible reason for the absence of ferromagnetic properties in many elevations is that not all discharges capture and involve into coatings the dispersed particles of iron hydroxides from the electrolyte. It can be expected that an increase in the concentration of dispersed particles in the electrolyte will cause an increase both in the iron concentration in the elevations and in the number of Fe-containing elevations and, respectively, in the number of ferromagnetic areas.

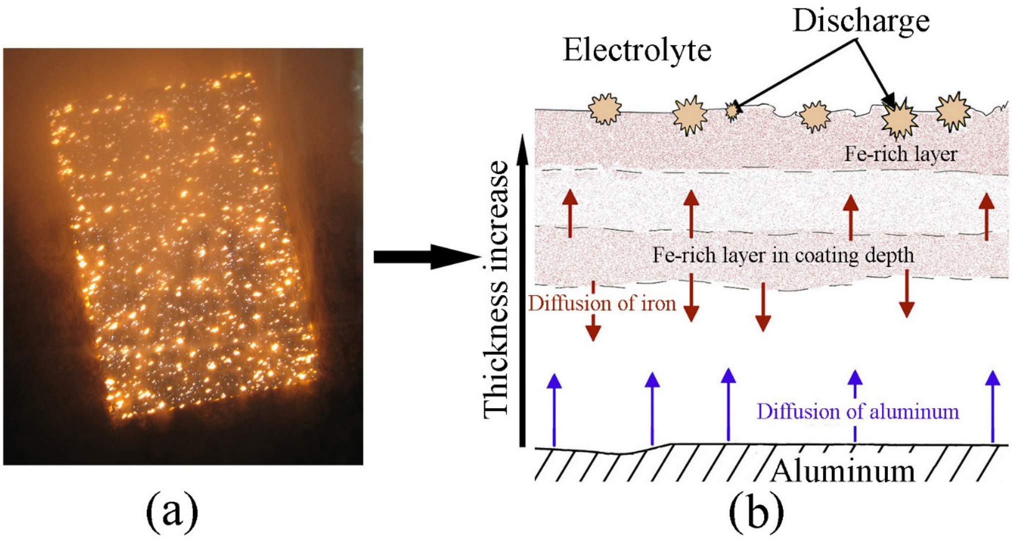

Fig. 3. Spark and micro arc discharges on the aluminum surface (a) and the proposed scheme of inclusion and distribution of iron in the PEO coating during its growth (b).

To test the proposed scheme (Fig. 3), a SEM image of the cross-section of the coating was obtained and maps of the distribution of the chemical elements were constructed (Fig. 4). The internal structure of the coating is heterogeneous; one can see cracks and pores, including those with dispersed particles (inset, Fig. 4a). The iron concentration in the outer part of the coating is higher than in the depth. At the outer boundary (the ‘coating / polymer’ interface, Fig. 4b), the Fe-rich areas duplicate the outlines of the pore boundaries or concentrate near the pores. The data obtained do not contradict our suggestion made about the mechanism of averaging the iron concentration in the coating bulk during its growth under electric discharges (Fig. 3).

The relationship established between the concentrating the iron from the electrolyte in the areas, exposed to electric discharges (in the pores and their vicinity), and the ferromagnetism of the coatings, as well as the model proposed for the iron distribution on the surface and in the bulk of the coating (Fig. 3) should be of a general nature and performed during obtaining the PEO coatings of different composition. The regularities established may be performed when antiferromagnetic PEO coatings are obtained in electrolytes with dispersed particles of Fe_2O_3 [3], the coatings absorbing microwave radiation are formed in electrolytes with dispersed particles Fe^0 [1], or ferromagnetic coatings are synthesized in electrolytes with complex compounds EDTA-Fe^{3+} [5]. In the last case, concentrating the iron (including iron in reduced state) was noted in the pore vicinities.

It is worth noting that the increased concentrations of electrolyte elements in the near-surface layer of the growing PEO coating are reported in the literature [14-16]. For example, concentrating Si(IV) in the surface layer of the coatings formed on aluminum in the aqueous electrolyte with Na_2SiO_3 was shown in Ref. [14]. Concentrating Zr (IV) during the formation of coatings on titanium in the aqueous electrolyte with $Zr(SO_4)_2$ was mentioned in Ref. [15]. Enrichment of the surface layer with ceria was observed during the formation of the coatings on magnesium alloy in the electrolyte with dispersed ceria particles in Ref. [16].

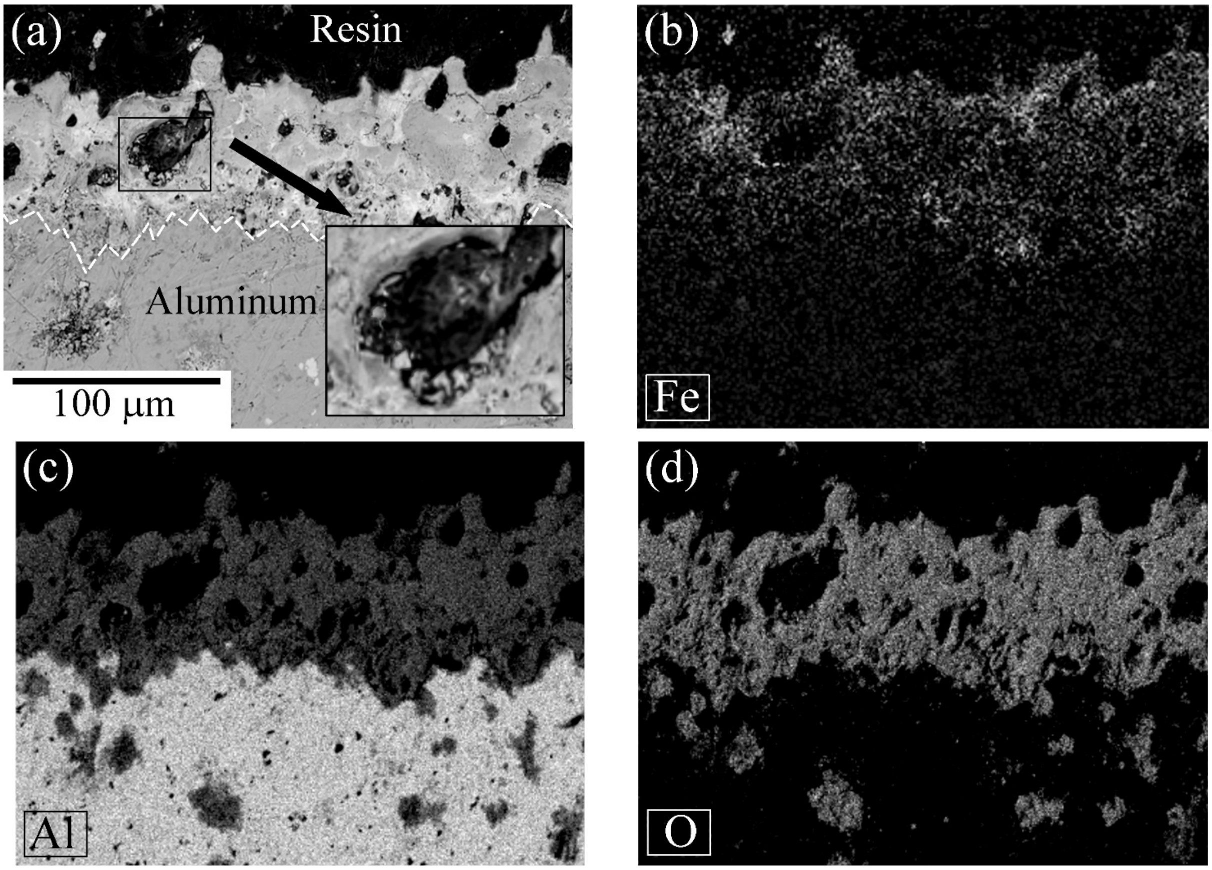

Fig. 4. The SEM image of the cross-section of the coating (a) and the element distribution map (b-d); inset (a) shows a pore with dispersed particles.

Summary

Thus, a comparison of the distribution of ferromagnetic areas and the surface topography shows that the ferromagnetic properties of the Fe-containing PEO coatings formed on aluminum in slurry electrolytes are related to iron concentration areas located in individual pores. The main bulk of such coatings does not possess ferromagnetic properties. Using slurry electrolytes with colloidal particles of metal hydroxides of different nature enables one to concentrate the necessary metals or their combinations in the pores, thereby regulating the magnetic properties of the "PEO-coating / Al" samples.

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References

[1] F.Y. Jin, H.H. Tong, J. Li, L.R. Shen and P.K. Chu, Structure and microwave-absorbing properties of Fe-particle containing alumina prepared by micro-arc discharge oxidation, Surf. Coat. Technol. 201 (2006) 292-295.

[2] V.S. Rudnev, A.Yu. Ustinov, I.V. Lukiyanchuk, P.V. Kharitonskii, A.M. Frolov, V.P. Morozova, I.A. Tkachenko, V.I. Sergienko, Magnetic properties of plasma electrolytic iron-containing oxide coatings on aluminum, Dokl. Phys. Chem. 428 (1) (2009) 189–192.

[3] A. Jagminas, R. Ragalevicius, K. Mazeika, J. Reklaitis, V. Jasulaitiene, A. Selskis and D. Baltrunas, A new strategy for fabrication Fe_2O_3/SiO_2 composite coatings on the Ti substrate, J. Sol. State Electrochem. 14 (2) (2010) 271-277.

[4] S.V. Gnedenkov, S.L. Sinebryukhov, I.A. Tkachenko, D.V. Mashtalyar, A.Yu. Ustinov, A.V. Samokhin, Yu.V. Tsvetkov, Magnetic properties of surface layers formed on titanium by plasma electrolyte oxidation on titanium, Inorg. Mater.: Appl. Res. 3 (7) (2012) 151–156.

[5] A.B. Rogov, O.P. Terleeva, I.V. Mironov, A.I. Slonova, Iron-containing coatings obtained by microplasma method on aluminum with usage of homogeneous electrolytes, Appl. Surf. Sci. 258 (7) (2012) 2761–2765.

[6] V.I. Belevantsev, O.P. Terleeva, G.A. Markov, E.K. Shulepko, A.I. Slonova, V.V. Utkin, Micro-plasma electrochemical processes, Prot. Met. 34 (5) (1998) 416–430.

[7] A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S.J. Dowey, Plasma electrolysis for surface engineering, Surf. Coat. Technol 122 (1999) 73–93.

[8] F.C. Walsh, C.T.J. Low, R.J.K.Wood, K.T. Stevens, J. Archer, A.R. Poeton, A. Ryder, Plasma electrolytic oxidation (PEO) for production of anodised coatings on lightweight metal (Al, Mg, Ti) alloys, Trans. Inst. Met. Finish. 87 (3) (2009) 122–135.

[9] Patent RF No. 2420614: The method of fabrication of magnetoactive oxide coatings on valve metals and alloys / V.S. Rudnev, I.V. Lukiyanchuk, A.Yu. Ustinov / Published 10.06.2011. Bull. Izobr. No. 16.

[10] V.S. Rudnev, A.Yu. Ustinov, I.V. Lukiyanchuk, P.V. Kharitonskii, A.M. Frolov, I.A. Tkachenko, V.P. Morozova, Magnetoactive oxide layers formed on titanium by plasma electrolytic technique, Prot. Met. Phys. Chem. Surf. 46 (5) (2010) 566–572.

[11] V.S. Rudnev, M.V. Adigamova, I.V. Lukiyanchuk, A.Yu. Ustinov, I.A. Tkachenko, P.V. Kharitonskii, A.M. Frolov, V.P. Morozova, The effect of the conditions of formation on ferromagnetic properties of iron-containing oxide coatings on titanium, Prot. Met. Phys. Chem. Surf. 48 (5) (2012) 543—552.

[12] V.S. Rudnev, V.P. Morozova, I.V. Lukiyanchuk, I.A. Tkachenko, M.V. Adigamova, A.Yu. Ustinov, P.V. Kharitonskii, A.M. Frolov, S.A. Boev, Magnetic properties of plasma-electrolytic iron-containing oxide coatings on aluminum alloy, Prot. Met. Phys. Chem. Surf. 49 (3) (2013) 309–318.

[13] M.V. Adigamova, V.S. Rudnev, I.V. Lukiyanchuk, V.P. Morozova, I.A. Tkachenko, A.A. Kvach, The effect of Fe-containing colloid particles in electrolyte on the composition and magnetic characteristics of oxide layers on titanium formed using the method of plasma electrolytic oxidation, Prot. Met. Phys. Chem. Surf. 52 (3) (2016) 526–531.

[14] F. Monfort, A. Berkani, E. Matykina, P. Skeldon, G.E. Thompson, H. Habazaki, K. Shimizu, Development of anodic coatings on aluminium under sparking conditions in silicate electrolyte, Corrosion Science. 49 (2007) 672–693.

[15] V.S. Rudnev, K.N. Kilin, I.V. Malyshev, T.P. Yarovaya, P.M. Nedozorov, A.A. Popovich, Plasma-electrolytic oxidation of titanium in $Zr(SO_4)_2$-containing bath, Prot. Met. Phys. Chem. Surf. 46 (6) (2010) 634–639.

[16] Z.U. Rehman, M. Uzair, H.T. Lim, B.H. Koo, Structural and electrochemical properties of the catalytic CeO_2 nanoparticles-based PEO ceramic coatings on AZ91 Mg alloy, J. Alloy. Compd. 726 (2017) 284-294.