The effect of nanocrystallites in the pores of PEO coatings on their magnetic properties

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ABSTRACT

The coatings manifesting ferromagnetic characteristics have been formed on titanium and aluminum by plasma electrolytic oxidation in alkaline electrolytes additionally containing iron oxalate and cobalt or nickel acetate. The metals of iron subgroup are found be concentrated in pores of PEO coatings, as a rule, in a form of crystallites. In a number of cases the relation between crystallite compositions and magnetic properties of the coatings has been established.

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1. Introduction

The 'ferromagnetic oxide coating/titanium' composites are of interest as absorbers of electromagnetic radiation and micro-transformers [1,2]. To obtain such composites one can use plasma electrolytic oxidation (PEO) technique [1,3–5] that is electrochemical oxidation of valve metals under spark and microarc electric discharges [6–13].

There are two possibilities of PEO application for obtaining magneto-active oxide layers on valve metals (Fig. 1). The first is one-stage PEO technique when precursors of magneto-active compounds are directly involved into forming electrolyte as complex compounds ($[Co(EDTA)]^-$ [5], $[Fe(P_6O_{18})]^{3-}$ [14]) or in the compositions of solid micro- and nanosized particles (Fe^0, Co^0 or Fe_2O_3) [1,4]. Furthermore, the conditions for the formation of solid particles can be created directly in the electrolyte for PEO, for example, as a result of iron or cobalt hydroxide precipitation in phosphate–borate–tungstate solution after addition of appropriate oxalate or acetate [3,14,15] and their hydrolysis in alkaline medium. During PEO the dispersed (colloidal) particles of negatively charged metal hydroxides were maintained in suspended state by stirring the electrolyte. By analogy with Ref. [16] we called such dispersed systems as 'slurry electrolytes'.

Other known approaches for obtaining magneto-active coatings with the help of PEO are multistage. According to [17], magneto-active nanoparticles of Co can be embedded in inert PEO coating as a result of its modification by rubbing. The impregnation in appropriate solution following by annealing can impart magnetic properties to inert PEO coatings too [18].

In all cases there are micro- or nanoaggregates which are responsible for the magnetic properties of the coatings. The structures of such aggregates can be different. The nanoparticles in the coatings obtained by combination of PEO and rubbing consist of Co ferromagnetic core and a CoO antiferromagnetic shell [17]. When 'PEO + impregnation + annealing' is used, magneto-active elements are located in dispersed particles on the coating surface [18].

Upon one-stage PEO technique the magneto-active elements are concentrated in the pores [3,5] or the defects of the surface [14]. In this case the simulation showed [19] that the composites 'Fe-containing PEO coating/valve metal' can have ferromagnetic clusters which consist of chemically inhomogeneous particles or a mixture of particles with very different magnetic properties. Scanning electron microscopy of high resolution confirmed the presence of agglomerates of nanoparticles in the pores of PEO coatings [15,20–22]. The particles in the pores of the coatings formed on titanium in phosphate–borate–tungstate electrolyte (PBW-electrolyte) with addition of iron oxalate contain (at. %) 51.0 Fe, 13.5 Ti, 19.2 O, 7.2 C, 2.2 P, 1.7 Na, 5.2 W and seem to be the species of reduced metals encapsulated in oxide–hydroxide shell [20]. X-ray diffraction (XRD) [21] and X-ray photoelectron spectroscopy (XPS) [20] confirm the presence of reduced iron in PEO coatings.

The objective of the work is summarizing the available data and confirming that the magnetism of composites 'PEO coating/valve metal' is associated with the presence of nano- and microagglomerates in the pores of the coatings.

2. Experimental

2.1. Materials

The PEO layers were formed on the samples of AMg5 aluminum alloy (4.8–5.8% Mg, 0.02–0.01% Ti, and the balance Al) and VT1-0

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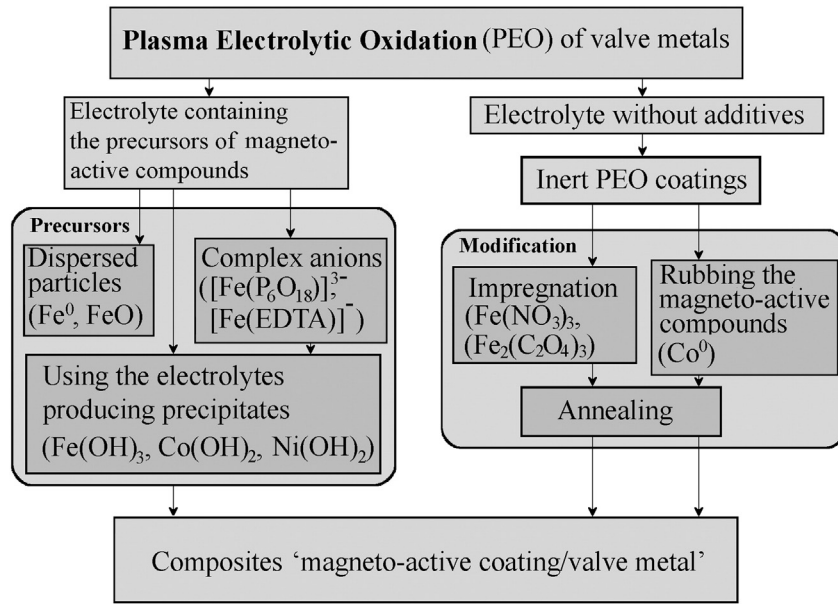E-mail address: rudnevvs@ich.dvo.ru (V.S. Rudnev).

Fig. 1. The examples of using PEO technique for obtaining magneto-active structures on valve metals.

titanium (Ti content > 99.6%). Planar samples of $2 \times 2 \times 0.1$ or $1 \times 0.5 \times 0.1$ cm in size were used.

To standardize pre-coating sample surfaces, they were chemically polished to high luster (surface finish classes 8–9) in a mixture of concentrated acids. A mixture of $H_3PO_4:H_2SO_4:HNO_3 = 4:2:1$ (by volume) at 110–120 °C and a mixture of $HF:HNO_3 = 1:3$ (by volume) at 70 °C were used for treating aluminum and titanium, respectively. Then the samples were washed with distilled water and dried by air at 70 °C.

2.2. PEO treatment

PEO coatings were formed using anodic polarization with the effective current density $i = 0.1–0.3$ A/cm^2 for 5–30 min. In some cases, anode–cathode polarization was used. The electrolyte compositions and the formation conditions are given in Table 1.

The electrochemical treatment of titanium and aluminum samples was carried out in a thermal glass of 1 L volume. The computer-controlled thyristor unit TER-100/460N (Russia) with unipolar pulse current was used as a power source. The sample under treatment was connected with a positive pole of the power supply while a spiral-shaped stainless steel coil cooled with tap water served as a cathode. The electrolyte in a glass was agitated using a magnetic mixer. The electrolyte temperature was maintained below 35 °C during the process.

2.3. Coatings characterization

To characterize the coatings we used measurements of the thickness, X-ray spectrum analysis (XSA), energy-dispersive analysis (EDA), scanning electron microscopy (SEM).

The thickness of coatings was measured using an eddy-current thickness gage VT-201 (Russia).

The element composition and coating surface images were obtained using an electron probe micro-analyzer JXA 8100 (Japan) with an INCA energy spectrum analyzer (United Kingdom) (hereinafter referred to as XSA). The averaged element composition was determined on the basis of the results of scanning 3–5 surface parts of an area of ~250 μm^2 each. In some cases, we obtained surface images using a Hitachi S5500 (Japan) high resolution scanning electron microscope (SEM). Using a Thermo Scientific (USA) microscope accessory for energy-dispersive analysis (EDA), we determined the element composition of individual coating parts by focusing the probe beam at the site radius of 1 to 10 nm (the example is given in Fig. 2). In both cases, gold was preliminarily sputtered on films to prevent the surface charging.

2.4. Magnetic properties

Magnetic measurements were performed on a SQUID MPMS 7 (Germany) magnetometer at temperatures 300 or 340 K. The samples

Table 1
The conditions of PEO coatings formation.

No.	Substrate	Electrolyte	C, mol/L	Current mode	i, A/cm^2	τ, c	t, min	Ref.
1	VT1-0	PBWFe$_{0.08}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.06 Na$_2$WO$_4$ + 0.04 Fe$_2$(C$_2$O$_4$)$_3$	A	0.1		30	[20]
2	AMg5	PBWFe$_{0.05}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.06 Na$_2$WO$_4$ + 0.025 Fe$_2$(C$_2$O$_4$)$_3$	A	0.1		10	[21]
3	AMg5	PBWFe$_{0.03}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.06 Na$_2$WO$_4$ + 0.015 Fe$_2$(C$_2$O$_4$)$_3$	A	0.1		10	[21]
4	AMg5	PBWFe$_{0.04}$Co$_{0.04}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.06 Na$_2$WO$_4$ + 0.02 Fe$_2$(C$_2$O$_4$)$_3$ + 0.04 Co(CH$_3$COO)$_2$	A	0.1		10	[15]
5	AMg5	PBFe$_{0.04}$Co$_{0.04}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.02 Fe$_2$(C$_2$O$_4$)$_3$ + 0.04 Co(CH$_3$COO)$_2$	A	0.1		10	[22]
6	AMg5	BFe$_{0.04}$Co$_{0.04}$	0.1 Na$_2$B$_4$O$_7$ + 0.02 Fe$_2$(C$_2$O$_4$)$_3$ + 0.04 Co(CH$_3$COO)$_2$	A	0.3		5	[22]
7	AMg5	SiFe$_{0.04}$Co$_{0.04}$	0.05 Na$_2$SiO$_3$ + 0.02 Fe$_2$(C$_2$O$_4$)$_3$ + 0.04 Co(CH$_3$COO)$_2$	AC	±0.1	0.02	10	[22]
8	AMg5	PBWFe$_{0.04}$Ni$_{0.04}$	0.66 Na$_3$PO$_4$ + 0.34 Na$_2$B$_4$O$_7$ + 0.06 Na$_2$WO$_4$ + 0.02 Fe$_2$(C$_2$O$_4$)$_3$ + 0.04 Ni(CH$_3$COO)$_2$	A	0.1		10	New data

τ — duration of cathodic and anodic pulses.
A — anodic, AC — pulse anodic–cathodic current mode.
Indexes in electrolyte symbolic representation mean the concentration of iron or cobalt or nickel species.