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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 magnetoactive 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 (Fe⁰, Co⁰ or Fe₂O₃) [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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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 H₃PO₄:H₂SO₄:HNO₃ = 4:2:1 (by volume) at 110–120 °C and a mixture of HF:HNO₃ = 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 $i = 0.1-0.3 \text{ A/cm}^2$ 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 computercontrolled 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 μ m² 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
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The	conditions	of PFO	coatings	formation
IIIC	contaitions	ULLO	coatings	iormation.

Ma	Cubatnata	El e et relute	C mal//	Cumunt made	: 1 /		*	Def
INO.	Substrate	Electrolyte	C, 11101/L	Current mode	I, A/CIII ⁻	τ, ε	ι, ππ	Kel.
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	А	0.1		30	[20]
2	AMg5	PBWFe _{0.05}	$0.66 \text{ Na}_3 \text{PO}_4 + 0.34 \text{ Na}_2 \text{B}_4 \text{O}_7 + 0.06 \text{ Na}_2 \text{WO}_4 + 0.025 \text{ Fe}_2 (\text{C}_2 \text{O}_4)_3$	Α	0.1		10	[21]
3	AMg5	PBWFe _{0.03}	$0.66 \text{ Na}_3 \text{PO}_4 + 0.34 \text{ Na}_2 \text{B}_4 \text{O}_7 + 0.06 \text{ Na}_2 \text{WO}_4 + 0.015 \text{ Fe}_2 (\text{C}_2 \text{O}_4)_3$	Α	0.1		10	[21]
4	AMg5	PBWFe _{0.04} Co _{0.04}	$0.66\ \text{Na}_3\text{PO}_4 + 0.34\ \text{Na}_2\text{B}_4\text{O}_7 + 0.06\ \text{Na}_2\text{WO}_4 + 0.02\ \text{Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04\ \text{Co}(\text{CH}_3\text{COO})_2$	Α	0.1		10	[15]
5	AMg5	PBFe _{0.04} Co _{0.04}	$0.66 \text{ Na}_3 \text{PO}_4 + 0.34 \text{ Na}_2 \text{B}_4 \text{O}_7 + 0.02 \text{ Fe}_2 (\text{C}_2 \text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3 \text{COO})_2$	Α	0.1		10	[22]
6	AMg5	BFe _{0.04} Co _{0.04}	$0.1 \text{ Na}_2\text{B}_4\text{O}_7 + 0.02 \text{ Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3\text{COO})_2$	Α	0.3		5	[22]
7	AMg5	SiFe _{0.04} Co _{0.04}	$0.05 \text{ Na}_2 \text{SiO}_3 + 0.02 \text{ Fe}_2 (\text{C}_2 \text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3 \text{COO})_2$	AC	± 0.1	0.02	10	[22]
8	AMg5	PBWFe _{0.04} Ni _{0.04}	$0.66\ \text{Na}_3\text{PO}_4 + 0.34\ \text{Na}_2\text{B}_4\text{O}_7 + 0.06\ \text{Na}_2\text{WO}_4 + 0.02\ \text{Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04\ \text{Ni}(\text{CH}_3\text{COO})_2$	Α	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.

(a) 5.00 µ	m (b)		50	(c)	100 nm				
2 55500 20 OAV D Brim x8 OVA EF: 12/20/20/17/201									
Surface site	No.	No. Elemental composition, at %							
		Ο	С	Na	Р	Ti	Fe	W	
Coating, averaged data as to XSA		55.4	24.7	3.2	5.1	4.5	6.5	0.7	
*The surface near the pore (site 1))	1	57.7	27.6	5.5	3.2	1.3	4.4	0.4	
*Agglomerates of	2	5.3	-	-	-	10.1	76.9	7.6	
(sites 2)	3	7.0	-	-	-	12.6	73.9	6.5	
*Crystallites in the pore (sites 3 and 4)	e 4	6.6	-	-	0.9	8.2	76.8	7.5	

Fig. 2. SEM images (a) of a pore and crystallite agglomerates in the pore (b, c) of the coating formed on titanium in PBWFe_{0.08} electrolyte at 0.1 A/cm² for 30 min and elemental composition of the coating surface structures as to EDA and XSA. * – the averaged data obtained by EDA for 3–5 measurements in different sites.

were magnetized in parallel to the magnetic field direction. During the magnetization calculations, the magnetic moment was normalized on the weight of a sample with coating. Mass fraction of the coatings in the samples was about 1–3%.

3. Results and discussion

3.1. The correlation between the presence of micro- or nanocrystallites in the pores and magnetic properties of PEO coatings

This correlation has been studied by way of example of PEO coatings formed on titanium in $PBWFe_{0.08}$ electrolyte (no. 1 in Table 1). As can be seen from the elemental composition of the surface structures (Fig. 2),

iron is concentrated in the pores in the nanostructures of ~50 nm in size. The crystallite composition sharply differs from the average composition of the coatings and other surface structures (swells around pores). The crystallites contain not only iron, but also other elements from electrolyte and the metal under treatment: tungsten, titanium, phosphorus etc. Insofar as the oxygen content is insufficient for the formation of oxides, metals are present in the crystallites in a partially or predominantly reduced state. The presence of reduced iron in PEO coatings was found previously by XPS [20] and XRD [21].

The mechanism of embedding the titanium and of formation of metal crystallites in the coatings pores is debatable. At first, titanium can be injected to the electrolyte by the action of spark or arc electric discharges, than its hydroxocomplexes or other compounds can get to



Fig. 3. The dependences of magnetic moment *M* (emu/g) (a) on the strength of external magnetic field *H* (Oe) and (b) temperature *T* (K) for titanium sample with the coating formed in PBWFe_{0.08} electrolyte at 0.1 A/cm² for 30 min.

Table 2

		h		Crystallite/coating elemental composition, at.%											H Oe		
No.	Substrate	Electrolyte	μm	С	0	Na	Mg	Al	Si	Р	Ti	Fe	Со	Ni	W	(<i>T</i> , K)	Ref.
1	VT1-0	PBWFe _{0.08}	51.2	<u>0.0</u> 24.7	<u>6.3</u> 55.4	<u>0.0</u> 3.2	-	-	-	<u>1.0</u> 5.1	<u>18.5</u> 4.5	<u>64.5</u> 6.5	-	-	<u>9.7</u> 0.7	137 (300) 66 (10)	[20]
2	AMg5	PBWFe _{0.05}	7.3	<u>4.9</u> 14.2	<u>24.9</u> 57.6	<u>0.0</u> 0.3	<u>0.0</u> 1.0	<u>26.1</u> 22.3	-	<u>0.3</u> 1.0	-	<u>43.8</u> 3.4	-	-	<u>0.0</u> 0.2	101–110 (300) 200–245 (10)	[21]
3	AMg5	PBWFe _{0.03}	13.3	<u>0.0</u> 12.4	<u>20.5</u> 56.1	-	<u>0.0</u> 1.1	<u>12.0</u> 23.6	-	<u>0.0</u> 1.4	-	<u>51.6</u> 4.2	-	-	<u>15.9</u> 0.3	174 (300) 263 (10)	[21]
4	AMg5	PBWFe _{0.04} Co _{0.04}	12.7	<u>0.0</u> 9.0	<u>12.1</u> 60.2	-	-	<u>13.1</u> 25.3	-	<u>0.0</u> 0.5	-	<u>29.3</u> 1.9	<u>45.6</u> 2.2	-	<u>0.0</u> 0.2	113 (300) 260 (2)	[15]
5	AMg5	PBFe _{0.04} Co _{0.04}	39	<u>0.0</u> 32.6	<u>2.7</u> 47.7	<u>0.0</u> 1.6	<u>0.0</u> 0.3	<u>0.5</u> 6.0	-	<u>0.7</u> 3.5	-	<u>46.4</u> 4.6	<u>49.6</u> 3.8	-	-	177 (300)	[22]
6	AMg5	BFe _{0.04} Co _{0.04}	29	<u>2.4</u> 24.7	<u>3.7</u> 52.6	-	<u>0.0</u> 0.5	<u>8.0</u> 9.4	-	-	-	<u>65.1</u> 2.2	<u>20.8</u> 10.7	-	-	89 (300)	[22]
7	AMg5	SiFe _{0.04} Co _{0.04}	25	<u>0.2</u> 21.1	<u>11.7</u> 55.6	<u>0.0</u> 0.6	-	<u>0.1</u> 1.7	<u>3.3</u> 10.5	-	-	<u>78.8</u> 10.1	<u>5.9</u> 0.6	-	-	31 (300)	[22]
8	AMg5	PBWFe _{0.04} Ni _{0.04}	_	<u>0.0</u> 16.3	<u>11.7</u> 55.6	_	<u>0.0</u> 1.1	<u>18.8</u> 25.0	-	<u>0.3</u> 0.5	-	<u>15.3</u> 0.9	-	<u>50.6</u> 1.5	<u>0.1</u> 0.1	34–42(300) 325–322 (2)	New data

Average elemental composition^a (at.%) of the coatings (denominator) and crystallites (numerator) on the pore bottom.

Samples numbers and their formation conditions correspond to those in Table 1.

^a Elemental compositions of the coatings and the crystallites in the pores were determined by XSA and EDA, correspondingly. The data for crystallites were averaged for three or more pores.

the anode surface and be processed by the same electric discharges. Reduction of metals in the coating pores may be due to the thermolysis of water and the action of hydrogen in the releasing moment. Since the pores occupy about 30% of the coating, the magnetic properties associated with the formations in the pores. As to the dependences of magnetic moment on the external magnetic field and



Fig. 4. SEM images of the pores with crystallite agglomerates for the coatings formed on aluminum in the electrolytes: (a) $PBWFe_{0.05}$, (b) $PBWFe_{0.04}Co_{0.04}$, (c) $PBFe_{0.04}Co_{0.04}$, and (d) $SiFe_{0.04}Co_{0.04}$.

temperature (Fig. 3), the sample under study is ferromagnetic with coercive force 137 Oe at room temperature.

3.2. The factors influencing the composition of the crystallites in the pores and on magnetic properties of the coatings

The ferro- and ferrimagnetic coatings on titanium and aluminum can be formed in the electrolytes of various compositions (Table 2). The most of them contain the crystallites in the pores (Fig. 4).

Since the crystallites contain not only components of electrolyte but also those of substrate, it is clear that the substrate nature will be one of the factors determining both the crystallite composition and the magnetic properties of the coatings (examples nos. 1 and 2 in Table 2).

The influence of concentration of the precursors of magnetically active compounds can be seen from examples 2 and 3 (Table 2). When the concentration of Fe³⁺ species in PBW electrolyte is equal to 0.03 mol/L (example 3), the coatings obtained demonstrate ferromagnetic properties, Fig. 5a–c. When it is 0.05 mol/L (example 2), they are ferromagnetic at low temperature (10 K), Fig. 5e, and ferrimagnetic at room temperature (300 K) before the strength of external magnetic field $H \sim 20$ kOe, Fig. 5d. When H is >20 kOe magnetic characteristics of the samples become instable. This fact will be discussed below. In the second case (example 3) the crystallites in the pores of the coatings contain more iron and less aluminum than in the first one (example 2). The results of investigation of Fe-containing PEO coatings on aluminum and titanium indicate that the coatings manifest ferromagnetic properties at a noticeable excess of iron with respect to paramagnetic metals, such as Al, Ti, and W in crystallites. More details on this issue have been discussed in Ref. [21].

Additional introduction of cobalt acetate into electrolyte significantly affects the crystallite composition but not significantly affects the magnetic properties of the coatings formed during 10 min (see examples 2, 3 and 4). Note, when forming duration was 5 min the coercive force of the samples formed in PBWFe_{0.04}Co_{0.04} electrolyte was greatly higher [15]. This fact was explained by small sizes of crystallites in the pores close to the single-domain state. In contrast, the additional introduction of nickel acetate into Fe-containing electrolyte reduces the concentration of iron in the pores of the coatings and results in decreasing coercive force at room temperature (examples 2, 3 and 8). Such various effects of the addition of cobalt and nickel salts may be related with the formation of the crystallites of different composition, for example with formation of alloys in the systems Fe–Co or Fe–Ni.



Fig. 5. Magnetization curves of the samples formed in PBWFe electrolytes with Fe(III) concentration (a–c) 0.03 mol/L and (d–f) 0.05 mol/L: (a, d) T = 300 K, (b, e) T = 10 K, and (c, f) H = 1 kOe. H_c values are estimated from the magnetization curves.



Fig. 6. The dependences of magnetic moment M (emu/g) (b) on the strength of external magnetic field H (Oe) at different temperatures T(K) for aluminum sample with PEO coating formed in PBWFe_{0.04}Ni_{0.04} electrolyte.

Base electrolyte has a noticeable influence too. Thus, the exclusion of sodium tungstate from PBWCo_{0.04}Fe_{0.04} electrolyte leads to an increase in cobalt and iron concentration both in pores and coating composition, which is accompanied by an increase of coercive force value at room temperature (examples 4 and 5). The use of borate and silicate electrolytes (examples 6 and 7 compare with 4 and 5) as base solutions changes the ratio of cobalt/iron in the coatings and pores. The additional appearance of silicon in the crystallite composition together with decrease in cobalt concentration dramatically reduces the coercive force of the coatings. Note that the presence of silicon in the crystallites may be due to the lower volatility of silica than that of oxides of boron and phosphorus.

Thus all these factors (the nature and concentration of the precursor, the nature of substrate metal or alloy, the composition of the base electrolyte) affect both the composition of the crystallites and the value of the coercive force. However, at this stage of research it is difficult to establish a direct correlation between the composition of the crystallites and the coercive force of the samples with PEO coatings.

3.3. Instability of magnetic properties of the samples with PEO coatings

For some samples with PEO coatings the phenomenon of instable magnetization has been observed at room temperature (example 2 in Table 2, and Fig. 5d). In the fields up to 5 kOe the samples behave as ferro- or ferrimagnetic materials. When 5 kOe < H < 20 kOe, the samples

behave as ferrimagnetics. At certain external field intensities (>20 kOe) the magnetic state of the samples becomes unstable: magnetization jumps accompanied by the change in the magnetization direction with respect to the external field are observed from time to time. In still stronger external field (>40 kOe), the state with a magnetization opposite to external field prevails. Such structures are characterized by a rather high content of aluminum in the crystallites, which is comparable with the content of iron in them.

A similar phenomenon (Fig. 6) was observed for the samples coated by PEO in PBWFe_{0.04}Ni_{0.04}-electrolyte (example 8 in Table 2). In addition to nickel and iron the pores of the coatings contain a high aluminum quantity too. As the temperature was less than or equal to 30 K the samples behave like ferromagnetics. At temperatures from 100 K to 300 K, they showed ferrimagnetism, but when the external magnetic field was greater than 20 kOe the samples also showed a magnetic instability.

The absence of magnetic instability at low temperatures (Figs. 5e and 6.) indicates that this phenomenon is temperature-dependent.

We can assume that such change in magnetic properties is related to the peculiarities of exchange interactions between the lattices of ferromagnetic and paramagnetic metals under conditions when one metal or another prevails in nano- and microcrystallites of coatings. The possible cause of magnetic instability is the presence of two sublattices in the domains or the presence of domains with different magnetization directions, Fig. 7.

4. Conclusions

- 1. The scope of the data presented in this paper clearly shows that the use of slurry electrolytes with colloidal particles of hydroxides of iron, nickel or cobalt allows one to form PEO coatings with ferro- or ferrimagnetic properties.
- The metals of iron subgroup are concentrated in pores of PEO coatings in form of crystallites preferably in the reduced state. All available data indicate that the crystallites are responsible for the magnetic properties of the coatings.
- 3. We obtained the coatings manifesting ferro- and ferrimagnetic properties as well as those exhibiting magnetic instability. The magnetic instability is observed for the coatings on aluminum with a high content of aluminum in the crystallites. Perhaps in this case the crystallites consist of combined lattices of aluminum and metal of iron subgroup.

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Fig. 7. Schemes of (a) antiferromagnetic and (b) ferromagnetic structures.

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