

## Nanocrystallites in the pores and magnetic properties of PEO coatings

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

### 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 one-stage plasma electrolytic oxidation (PEO) technique [1, 3-5] that is electrochemical oxidation of valve metals under spark and microarc electric discharges. In this case the precursors of magneto-active compounds must be directly involved into forming electrolyte as complex compounds ( $[\text{Co}(\text{EDTA})]^-$  [5]) or in the compositions of solid micro- and nanosized particles ( $\text{Fe}^0$ ,  $\text{Co}^0$  or  $\text{Fe}_2\text{O}_3$ ) [1, 4]. 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, 6, 7] and their hydrolysis in alkaline medium.

The simulation showed [7] 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. As a rule, the metals of iron subgroup are concentrated in the pores of the PEO coatings in form of nano- and microcrystallites [3, 6].

The objective of the work is to establish that the magnetism of composites ‘PEO coating/valve metal’ is related with the presence of nano- and microcrystallites in the coating pores.

### Experimental

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 titanium (Ti content >99.6%) in alkaline solutions additionally containing iron oxalate and cobalt or nickel acetate using anodic or anodic-cathodic polarization with the effective current density  $i=0.1\text{--}0.3\text{ A/cm}^2$  for 5–30 min.

The coatings element compositions were obtained using on a JXA 8100 X-ray spectral microanalyzer (XSA) (Japan) equipped with an INCA energy-dispersive (X-ray spectral) attachment (United Kingdom). Using a Hitachi S5500 (Japan) high resolution scanning electron microscope (SEM) with a Thermo Scientific (USA) microscope accessory for energy-dispersive analysis (EDA), we determined the element composition of individual coating parts. In both cases, gold was preliminarily sputtered on films to prevent the surface charging.

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

## Results and discussion

The correlation between the presence of micro- or nanocrystallites in PEO coatings and magnetic properties of the latter has been studied by way of example of PEO coatings formed on titanium in  $\text{PBWFe}_{0.08}$  electrolyte. As can be seen from the elemental composition of the surface structures (Fig. 1, Table 1), iron is concentrated in the pores in form of nanocrystallites of  $\sim 50$  nm in size. The sample under study is ferromagnetic with coercive force 137 Oe at room temperature (Fig. 1d). Since the pores occupy about 30 % of the coating, the magnetic properties associated with the formations in the pores.

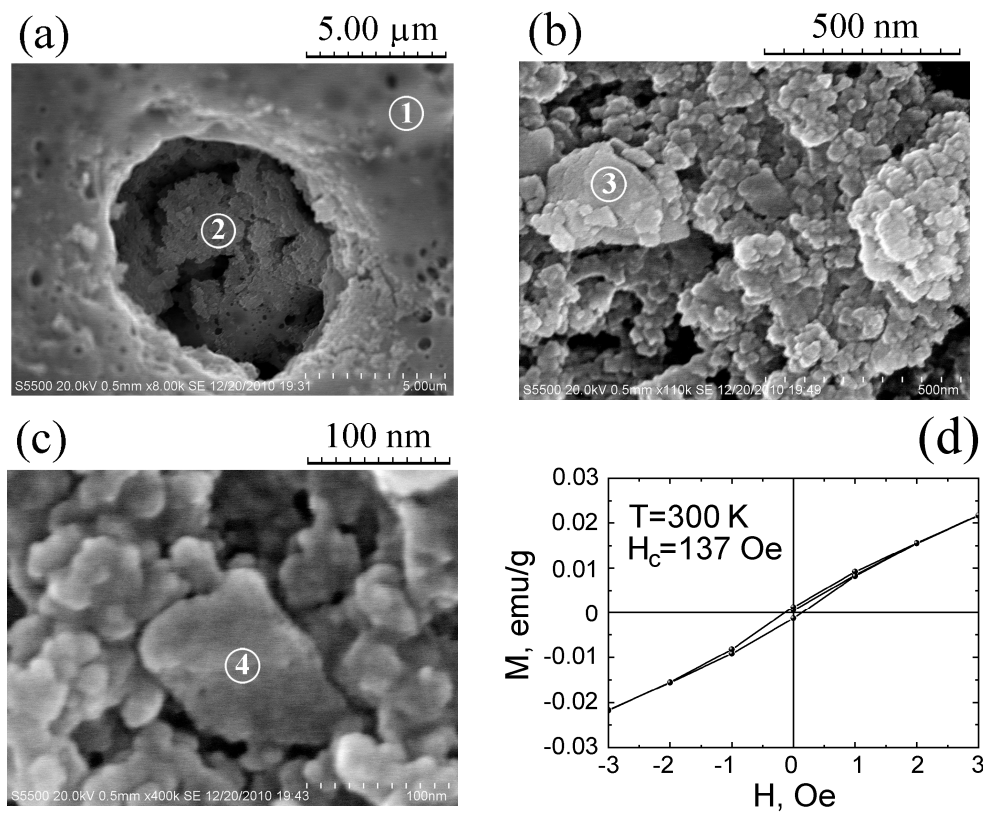


Fig. 1. SEM images (a) of a pore and crystallite agglomerates in the pore (b, c), and the dependence (d) of magnetic moment  $M$  on the strength of external magnetic field  $H$  at 300 K for the coating formed on titanium in  $\text{PBWFe}_{0.08}$  electrolyte at  $0.1 \text{ A/cm}^2$  for 30 min.

Table 1. Elemental composition of the coating and surface structures (1-4 in Fig. 1) as to XSA and EDA, respectively

Coating site	C [at. %]						
	O	C	Na	P	Ti	Fe	W
	55.4	24.7	3.2	5.1	4.5	6.5	0.7
1	57.7	27.6	5.5	3.2	1.3	4.4	0.4
2	5.3	-	-	-	10.1	76.9	7.6
3	7.0	-	-	-	12.6	73.9	6.5
4	6.6	-	-	0.9	8.2	76.8	7.5

The most of ferro- and ferrimagnetic coatings on aluminum contain the crystallites in the pores too (Fig. 2). The crystallites consist of the components of electrolyte and substrate, so the magnetic properties of the coatings depend on both base electrolyte and precursors added to it as well as on metal substrate (Table 2).

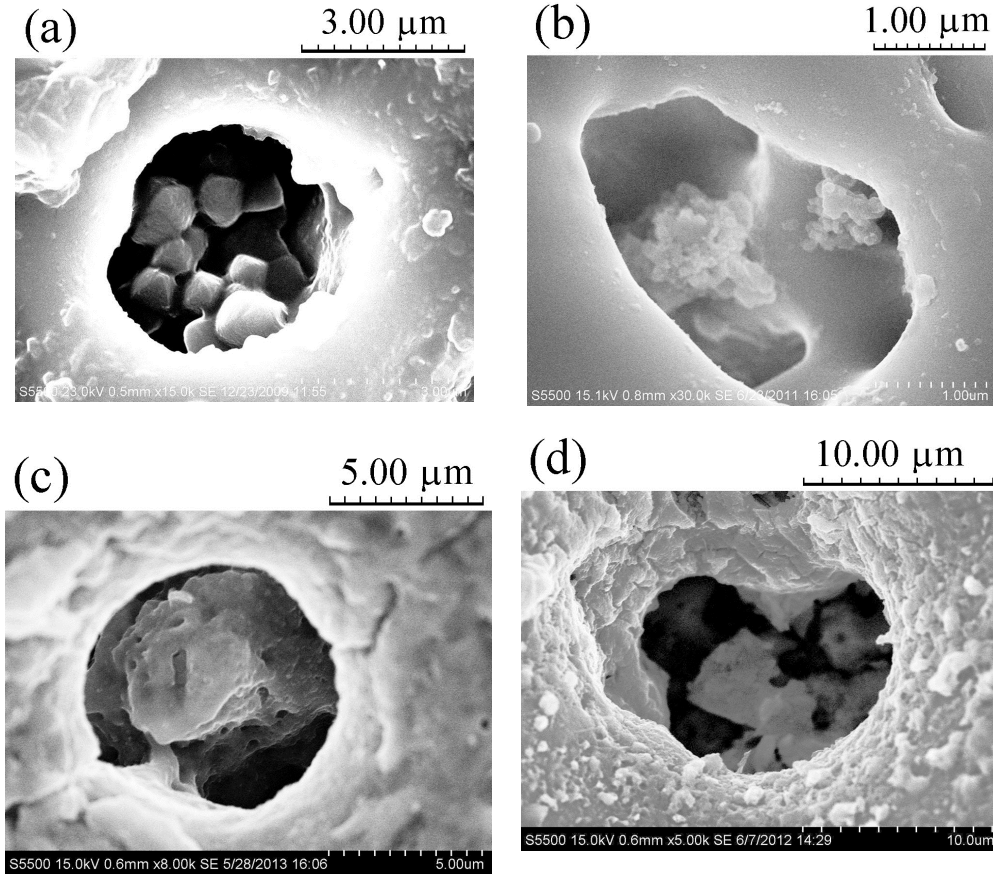


Fig. 2. SEM images of the pores with crystallite agglomerates for the coatings formed on aluminum alloy in the electrolytes: (a)  $\text{PBWFe}_{0.05}$ , (b)  $\text{PBWFe}_{0.04}\text{Co}_{0.04}$ , (c)  $\text{PBFe}_{0.04}\text{Co}_{0.04}$ , (d)  $\text{SiFe}_{0.04}\text{Co}_{0.04}$ .

Table 2. Effect of electrolyte on the crystallite element composition and coercive force value ( $H_c$ ) for the coatings formed on aluminum alloy

Electrolyte	Crystallite element composition [at. %]	$H_c$ [Oe] ( $T$ [K])
$\text{PBWFe}_{0.05}$	43.8 Fe; 26.1 Al; 0.3 P; 4.9 C; 24.9 O	101-110 (300) 200-245 (10)
$\text{PBWFe}_{0.04}\text{Co}_{0.04}$	29.3 Fe; 45.6 Co; 13.1 Al; 12.1 O	113 (300) 260 (2)
$\text{PBFe}_{0.04}\text{Co}_{0.04}$	46.4 Fe; 49.6 Co; 0.5 Al; 0.7 P; 2.7 O	177 (300)
$\text{SiFe}_{0.04}\text{Co}_{0.04}$	78.8 Fe; 5.9 Co; 0.1 Al; 3.3 Si; 0.2 C; 11.7 O	31 (300)
$\text{PBWFe}_{0.04}\text{Ni}_{0.04}$	15.3 Fe; 50.6 Ni; 18.8 Al; 0.1 W; 0.3 P; 11.7 O	34-42(300) 322-325 (2)

Notes: the electrolytes contain (mol/L):

$\text{PBWFe}_{0.05} = 0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7 + 0.006 \text{ Na}_2\text{WO}_4$  (PBW)+  $0.025 \text{ Fe}_2(\text{C}_2\text{O}_4)_3$ ;

$\text{PBWFe}_{0.04}\text{Co}_{0.04} = \text{PBW} + 0.02 \text{ Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3\text{COO})_2$ ;

$\text{PBFe}_{0.04}\text{Co}_{0.04} = 0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7$  (PB) +  $0.02 \text{ Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3\text{COO})_2$ ;

$\text{SiFe}_{0.04}\text{Co}_{0.04} = 0.05 \text{ Na}_2\text{SiO}_3$  (Si)+  $0.02 \text{ Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04 \text{ Co}(\text{CH}_3\text{COO})_2$ ;

$\text{PBWFe}_{0.04}\text{Ni}_{0.04} = \text{PBW} + 0.02 \text{ Fe}_2(\text{C}_2\text{O}_4)_3 + 0.04 \text{ Ni}(\text{CH}_3\text{COO})_2$ .

The exclusion of sodium tungstate from  $\text{PBWCo}_{0.04}\text{Fe}_{0.04}$  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. The use of silicate electrolyte as a base solution changes the ratio of cobalt/iron in the pores. The additional appearance of silicon in the crystallite composition together with decrease in cobalt concentration dramatically reduces the coatings coercive force.

For the aluminum samples with PEO coatings formed in  $\text{PBWFe}_{0.05}$  [8] and  $\text{PBWFe}_{0.04}\text{Ni}_{0.04}$ -electrolytes the phenomenon of instable magnetization has been observed at room temperature. In the fields up to 5 kOe the samples behave as ferro- or ferrimagnetic materials. When  $5\text{kOe} < H < 20\text{kOe}$ , the samples behave as ferrimagnetics. At certain external field intensities ( $>20\text{kOe}$ ) 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 ( $>40\text{kOe}$ ), the state with a magnetization opposite to external field prevails. Special studies are required to determine the nature of the effect of magnetization instability. It should be noted that such structures are characterized by a rather high content of aluminum in the crystallites, which is comparable with the content of iron in them.

The magnetic instability depends on temperature too (Fig. 3). As the temperature was less than or equal to 30 K the samples behave like ferromagnetics. At temperatures from 100 to 300 K, they showed ferrimagnetism, but when the external magnetic field was greater than 20 kOe the samples also showed a magnetic instability.

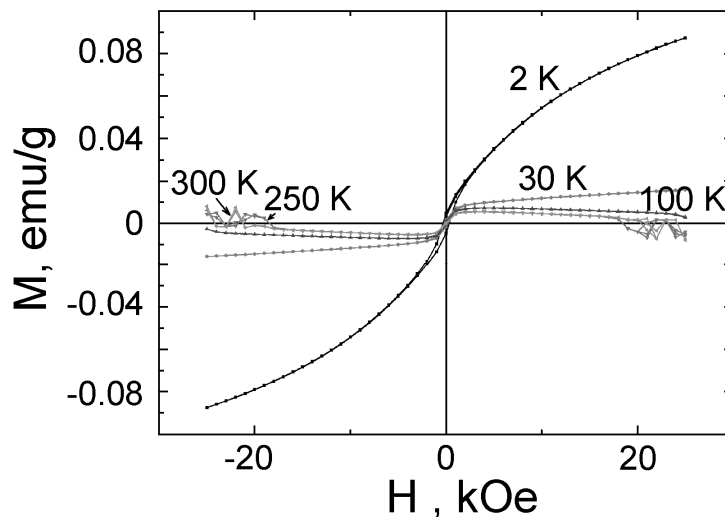


Fig. 3. The dependences of magnetic moment  $M$  (emu/g) (b) on the strength of external magnetic field  $H$  (Oe) at different temperatures  $T$  (K) for aluminum sample with PEO coating formed in  $\text{PBWFe}_{0.04}\text{Ni}_{0.04}$  electrolyte.

### Summary

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. All available data indicate that the crystallites in the pores are responsible for the magnetic properties of the coatings.

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