

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

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Received July 3, 2015

Abstract—The composition, structure, and magnetic characteristics of oxide layers on titanium formed in electrolytes containing colloid particles of iron hydroxo-compounds and their filtrates have been investigated. The obtained results corroborate that formation of Fe-containing crystallites in coating pores occurs due to ingress of negatively charged particles of hydroxo-compounds of transition metals from the electrolyte into breakdown channels and their transformation in local spaces of electric breakdowns. The presence of crystallites in pores is responsible for coatings ferromagnetic properties. Fe-containing crystallites were not found in pores of coatings formed in the electrolyte after filtering of iron hydroxides and hydroxo-salts, whereas coatings contained small concentrations of iron homogeneously distributed over the surface and manifested paramagnetic properties at room temperature.

DOI: 10.1134/S2070205116030023

INTRODUCTION

“Oxide layer with ferromagnetic characteristics/metal” composites are promising as materials protecting from electromagnetic radiation. The method of plasma electrolytic oxidation (PEO) [1–12]—formation of oxide layers in electrolytes under effect of electric spark and microarc discharges—enables one to obtain coatings of the above type on valve metals (Al, Ti, Nb, Zr, Mg, etc.). One can single out four types of fabrication of oxide coatings with certain magnetic characteristics using the PEO method. The first one consists in introduction of precursors of magnetic compounds directly into the electrolyte as micro- and nanosized particles of Fe⁰ [1], Co⁰ [6], or Fe₂O₃ [4]. The second one is concerned with application of electrolytes containing water-soluble complex compounds, such as [Fe(EDTA)][−] [7] and [Fe(P₆O₁₈)]^{3−} [3]. The third constitutes the creation of conditions for formation of colloid particles directly in the electrolyte for PEO, for instance, the formation of negatively charged colloid particles of Fe(III) and Co(II) hydroxides as a result of hydrolysis of respective oxalates and acetates added into alkaline electrolytes [2, 3, 5, 8–11]. In all cases, iron and cobalt become embed-

ded into coatings under the effect of electric spark and microarc discharges. The fourth is related to modification of preliminarily formed PEO coatings, for example, by mechanical rubbing onto the surface of Co⁰ nanoparticles [6] or through coating impregnation in aqueous acetate or nitrate solutions of trivalent iron with subsequent annealing [10].

In our opinion, the application of electrolytes spontaneously releasing colloid particles of transition metals into the precipitate has some advantages over other above-described approaches. In this case, there is no requirement for the presence of prepared in advance dispersed powders or complexing agents while the process is single-stage and allows the introduction of both individual metals and their mixtures from the electrolyte to the coating [2, 9, 11]. The latter is important for targeted changing of the magnetic characteristics of the formed oxide layers.

During application of electrolytes with colloid particles of iron and/or cobalt hydroxides, metals are concentrated in PEO coatings' pores in compositions of micro- and nanosized crystallites [3, 5, 8–12]. Crystallites contain significant excesses of metals from electrolyte and substrate as compared to the quantity of oxygen. For example, the crystallites of a size of ~50 nm

in pores of coatings formed on titanium in the electrolyte $0.066 \text{ M Na}_3\text{PO}_4 + 0.034 \text{ M Na}_2\text{B}_4\text{O}_7 + 0.006 \text{ M Na}_2\text{WO}_4 + 0.04 \text{ M Fe}_2(\text{C}_2\text{O}_4)_3$ contain, at %: 5.3 O, 10.1 Ti, 76.9 Fe, and 7.6 W. Here, the average iron content on the coating surface is 6.5 at % [8, 11]. In an analogous similar electrolyte containing $0.025 \text{ mol/L Fe}_2(\text{C}_2\text{O}_4)_3$, coatings with an average iron content of ~6 at % were obtained on the aluminum alloy: crystallites of a size of ~1 μm containing (at %) 30.1 O, 43.8 Fe, and 26.1 Al in their pores [12]. The data on the element composition allow it to be concluded that crystallites are made up of chemically heterogeneous multiphase systems containing both reduced and oxidized metals. Crystallites may consist of a metal core surrounded by an oxide-hydroxide shell [8]. Note that the presence of the reduced iron in coatings has been corroborated by data of X-ray diffraction analysis and X-ray photoelectron spectroscopy [8, 12].

Pores in coatings are the channels of spark or microarc breakdowns during the PEO process. Concentration of metals in pores and formation of crystallites inside them result from electric breakdowns inducing intense mass transfer, temperature increase, and pressure difference in local breakdown areas. Sharp cooling of these areas upon discharge attenuation promotes formation of amorphous phases. Reduction of metals in pores must be initiated by hydrogen formed at water thermolysis under effect of spark and microarc discharges. According to [13, 14], at formation of anode coatings on the aluminum alloy in KOH solutions under the effect of spark discharges, hydrogen is the main component of the anode gas (about 90%).

The range of experimental data obtained in [3, 5, 8–12] enables one to conclude that coatings' magnetic characteristics (their ferro-, ferri-, or antiferromagnetism) are determined by the presence of metal-oxide crystallites (as well as their size and composition) in the coatings pores. The formation of crystallites occurs due to ingress of negatively charged particles of transition metals into breakdown channels and their transformations in local electric breakdown spaces. However, interrelation between the presence of transition metal hydroxides in the electrolyte, formation of metal-oxide crystallites in PEO coatings pores, and magnetic characteristics of the formed coatings has not yet been corroborated experimentally. The objective of the present work was to compare the composition, structure, and magnetic characteristics of PEO coatings formed on titanium in electrolytes containing colloid particles of iron hydroxide with those of coatings in the same electrolytes upon colloid particles removal.

MATERIALS AND METHODS

The samples to be treated comprised flat plates of VT1-0 technical grade titanium of a size of $2.2 \times 2.2 \times 0.1$

and $0.7 \times 3 \times 0.1 \text{ cm}^3$. Pretreatment of titanium samples included polishing in a mixture of concentrated acids $\text{HNO}_3 : \text{HF} = 3 : 1$ (by volume) at 70°C , washing by distilled water, and drying at 70°C in air.

To form PEO coatings, the base alkaline PBW-electrolyte of the composition (mol/L) $0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7 + 0.006 \text{ Na}_2\text{WO}_4$ was prepared (pH ~11). The electrolyte was added (as in [3, 8]) with $0.04 \text{ mol/L Fe}_2(\text{C}_2\text{O}_4)_3$ (PBWFe electrolyte). Each of the components of the PBW-electrolyte was preliminarily dissolved in distilled water. Thereafter, solutions were mixed at a preset ratio. Thereafter, the solution of $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ was added, and the final mixture was held under stirring for at least 1 h. The PBW-electrolyte was a transparent colorless solution, while the PBWFe electrolyte comprised a brownish suspension (pH ~8), in which colloid and suspension contained insoluble iron compounds, including hydroxo-salts and hydroxides.

To establish the effect of colloid particles on the coatings' structure, composition, and magnetic properties, the PBWFe electrolyte was twice fed through the "blue ribbon" paper filter. The obtained filtrate was transparent and light-yellowish and had pH ~8–9. Upon holding for a week at room temperature, the filtered solution did not produce a precipitate.

The coatings formed in the PBWFe will be thereafter referred to as no. 1; those formed in the filtrate will be referred to as no. 2.

In both cases, coatings on titanium anodes were formed in the galvanostatic mode at an effective current density of 10 A/dm^2 for 10 min. A PC-controlled TER4-100/460N thyristor device (Russia) operating in the unipolar mode served as the current source. The electrochemical cell comprised a vessel made of thermally resistant glass of a volume of 1 L, into which the sample (anode), the cathode in the form of a hollow coil made of nickel alloy, and a thermometer were placed. The electrolyte was stirred using a magnetic stirrer and cooled by feeding cold tap water through the coil. The electrolyte temperature during the PEO process did not exceed 30°C .

The layers' thicknesses were determined using a VT-201 thickness meter (Russia). Each measurement was made 12 times from each sample side, and the obtained data were averaged. The coatings' element compositions and surface images were obtained using a JXA 8100 X-ray spectral analyzer (Japan) with an INCA energy-dispersive accessory (United Kingdom). The averaged element composition was determined on the basis of the results of scanning from three to five surface areas of ~250 μm^2 each. In addition, the coatings' surface and pore structures were studied using a Hitachi S5500 high-resolution scanning electron microscope (Japan). Using a Thermo Scientific energy-dispersive analysis attachment for a microscope (United States), maps of element distri-

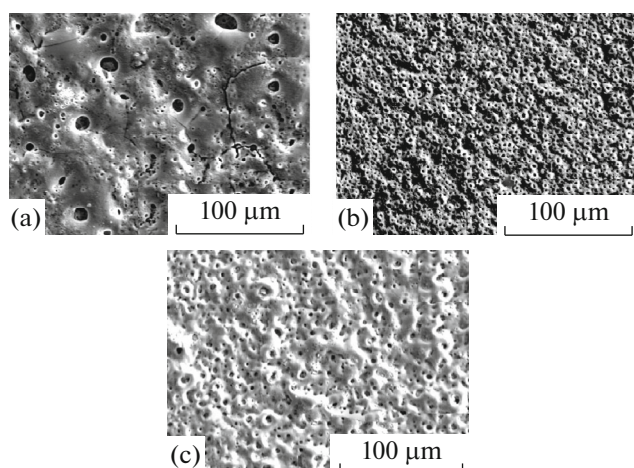


Fig. 1. SEM images of the surface of coatings formed on titanium in (a) the PBWFe electrolyte, (b) its filtrate, and (c) the PBW-electrolyte.

bution over a surface were obtained and the element composition of individual coatings' areas, including formations in pores and pore bottoms, were determined. In both cases, prior to measurements, coatings were sputtered with gold to prevent surface charging.

X-ray diffraction patterns were obtained using a D8 ADVANCE X-ray diffractometer (Germany) in the CuK_α -radiation (hereinafter referred to as XRD). At the X-ray diffraction analysis, the EVA search program with the PDF-2 database was used.

Magnetic measurements were performed using a SQUID MPMS 7 magnetometer (United States) at temperatures in the range of 3–300 K. Samples were magnetized in parallel to the magnetic field direction. In magnetization calculations, the measured magnetic moment was normalized on the mass of the sample with coating. The coating mass fraction in the samples was ~1–3%.

RESULTS AND DISCUSSION

Thicknesses, averaged surface element compositions (from microprobe analysis data, analysis depth up to 5 μm), and coercive forces of PEO coatings formed on titanium in the PBWFe electrolyte and its

filtrate are shown in the table. For comparison, earlier-obtained [8, 10] data on composition and parameters of coatings formed in the PBW and PBWFe electrolytes are presented.

According to X-ray diffraction analysis, the coatings formed in the PBWFe electrolyte and its filtrate contain titanium dioxide in anatase and rutile modifications.

As is seen in the table, addition of Fe(III) oxalate into the PBW-electrolyte results in embedding of iron (5–9 at %) into coatings and reduction of the titanium content in them. The reduction of the coating thickness must occur due to the etching effect of oxalate ions.

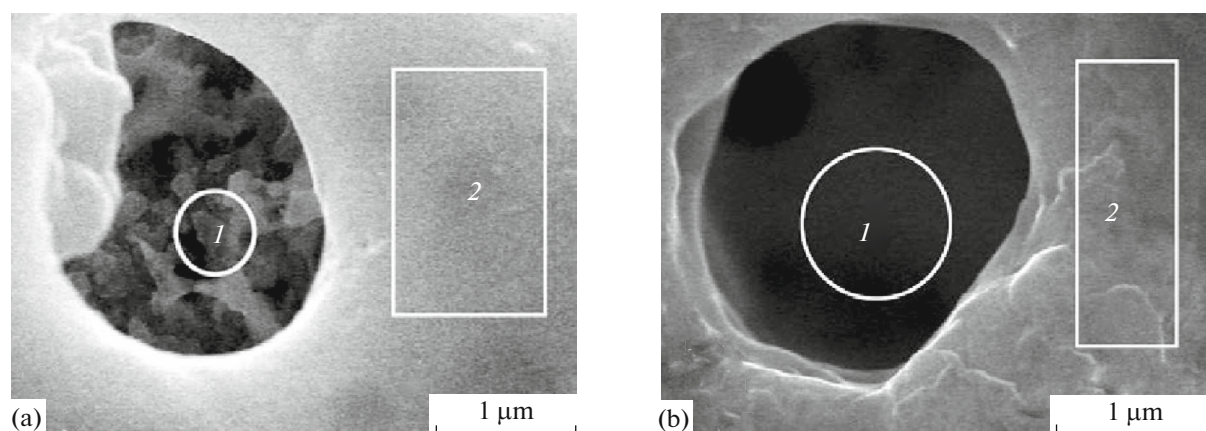
Thicknesses, averaged surface element compositions, and coercive forces of coatings formed in the present work and in [8] are similar, taking into consideration the multifactor character of the experiment (see table); i.e., the coatings' parameters are reproducible.

Removal of dispersed particles by filtering the PBWFe electrolyte results in reduction of the iron concentration in the electrolyte (just soluble forms of iron(III) are preserved) and changes in characteristics of the coatings formed in it (see table). The thickness of coating no. 1 is equal to $11 \pm 1 \mu\text{m}$, whereas that of coating no. 2 formed in the filtrate is twice as small, $7 \pm 1 \mu\text{m}$. Upon the electrolyte filtering, the quantity of iron embedded into coatings decreases dramatically. The average quantity of iron embedded into coating no. 1 is equal to 5.2 at %, whereas for coating no. 2 it does not exceed 1 at %. Here, the content of titanium (substrate metal) increases. The coatings formed in the filtrate are similar in composition to those obtained in the PBW-electrolyte.

Figure 1 shows scanning electron microscopy images of coatings formed in the PBWFe electrolyte (no. 1, Fig. 1a) and its filtrate no. 2, Fig. 1b). Coating no. 1 has a developed heterogeneous surface with large pores, beads around them, and cracks. The surface relief of coating no. 2 is closer to that of the coating formed on titanium in the PBW-electrolyte (Fig. 1c). Here, the surface has a rather regular structure with pores of a size of 1–5 μm . Smaller pore sizes and thickness of coating no. 2, as compared to those of the coating formed in the PBW-electrolyte, may be related

Thickness, averaged element composition of the surface (from microprobe analysis data), and coercive force of PEO coatings formed on titanium in the electrolytes PBW and PBWFe, as well as filtrate of the latter

Electrolyte	$h, \mu\text{m}$	Element concentrations, at %							H_c, Oe	
		C	O	Na	P	Ti	Fe	W	300 K	3–10 K
PBW [10]	15 ± 2	13.6	64.2	1.2	4.8	15.4	–	0.7	–	–
PBWFe [8]	12 ± 1	15.2	59.7	2.2	7.0	5.8	9.0	1.1	70	261 (10 K)
PBWFe (coating no. 1)	11 ± 1	7.9	69.9	1.5	6.1	8.2	5.2	1.2	50	300 (3 K)
Filtrate (coating no. 2)	7 ± 1	10.9	67.2	0.7	2.1	16.8	0.8	1.5	–	~12 (4 K)



Electrolyte	Object	Averaged element composition, at %						
		C	O	Na	P	Ti	Fe	W
PBWFe, coating no. 1	Surface	23.5	48.1	1.6	4.8	5.1	16.3	0.3
	Pore	–	14.0	–	1.4	23.3	61.3	–
Filtrate, coating no. 2	Surface	33.3	38.9	0.9	1.4	21.8	1.3	2.4
	Pore	5.0	10.0	0.2	0.6	76.0	1.9	6.3

Fig. 2. SEM images of pores in the coatings nos. (a) 1 and (b) 2 and the composition of crystallites in pores (coating no. 1), pore bottom (coating no. 2), and coating surface. In all cases, the average values of 4–13 independent measurements for different pores and surface areas are shown. (1, 2) Examples of analyzed areas of pores and surface, respectively.

to the etching effect of oxalate ions remaining in the filtrate.

As was mentioned in the Introduction, in pores of coatings formed in the PBWFe electrolyte, metals are present in the composition of crystallites that are linked into agglomerates and determine magnetic properties of the produced composites [3, 5, 8–12]. Figure 2 shows SEM images of the coatings formed in the PBWFe electrolyte and its filtrate. One can observe crystallites in pores of the coatings obtained in the initial electrolyte (Fig. 2a), in accordance with the earlier obtained data. No crystallites were found in pores of the coatings formed in the filtrate (Fig. 2b). The insert of the figure contains the element composition of crystallites (coating no. 1), pore bottom (coating no. 2), and individual areas on the surface of coatings obtained using the energy-dispersive accessory of the scanning electron microscope. For each case, the averaged data from the results of 4–13 independent measurements are presented.

Compositions of crystallites in pores of coating no. 1 and the pore bottom in coating no. 2 are dramatically different from that of the coating surface. In both of the above cases, the contents of electrolyte transition metals (Fe, W) and the substrate (Ti) are elevated. Iron is predominant (61 at %) in coating no. 1, while titanium is predominant (76 at %) in coating no. 2. Insufficient quantity of oxygen to form oxides indi-

cates to the fact that in pores metals exist predominantly in the reduced state. As was mentioned in the Introduction, reduction of metals in pores must be initiated by hydrogen formed during water thermolysis in breakdown channels. The presence of the reduced iron, aside from the oxidized one, in the composition of PEO coatings formed in the PBWFe electrolyte was earlier corroborated using the method of X-ray photoelectron spectroscopy [8].

The composition of the coating bulk obtained using the energy-dispersive analysis is in satisfactory agreement with the results of its determination using the X-ray spectral microprobe analysis (see Table). Some difference in the results of elements determination can be caused by the fact that the X-ray spectral microprobe method is used to analyze surface areas of a size of $\sim 250 \times 250 \mu\text{m}^2$ and layers of a thickness of up to $5 \mu\text{m}$. During the energy-dispersive analysis, the data were averaged for areas of sizes from 1×1.5 up to $50 \times 65 \mu\text{m}^2$, while the depth of the probing beam penetration was not larger than $1 \mu\text{m}$.

General surface view and maps of some elements distribution over the surface of coating no. 2 are shown in Fig. 3. One can see that titanium and iron are distributed over the surface rather homogeneously. The melted formations surrounding the pores are enriched with oxygen, phosphorus, and carbon.

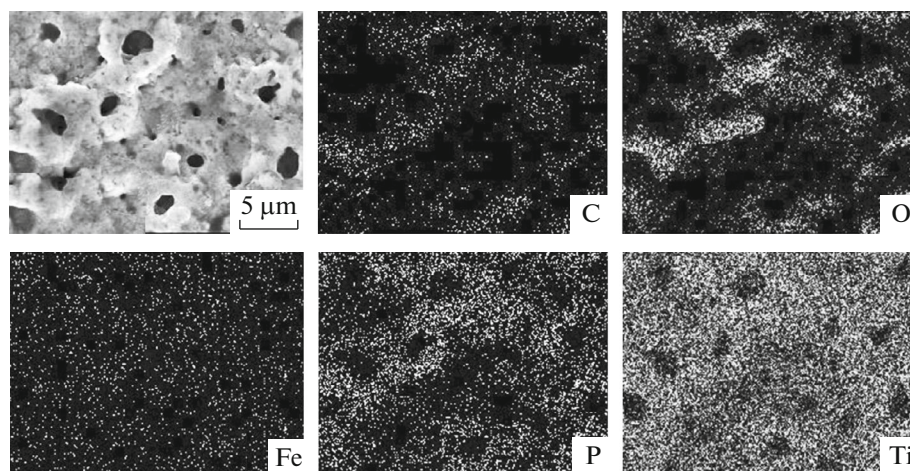


Fig. 3. General surface view and maps of elements distribution over coating no. 2.

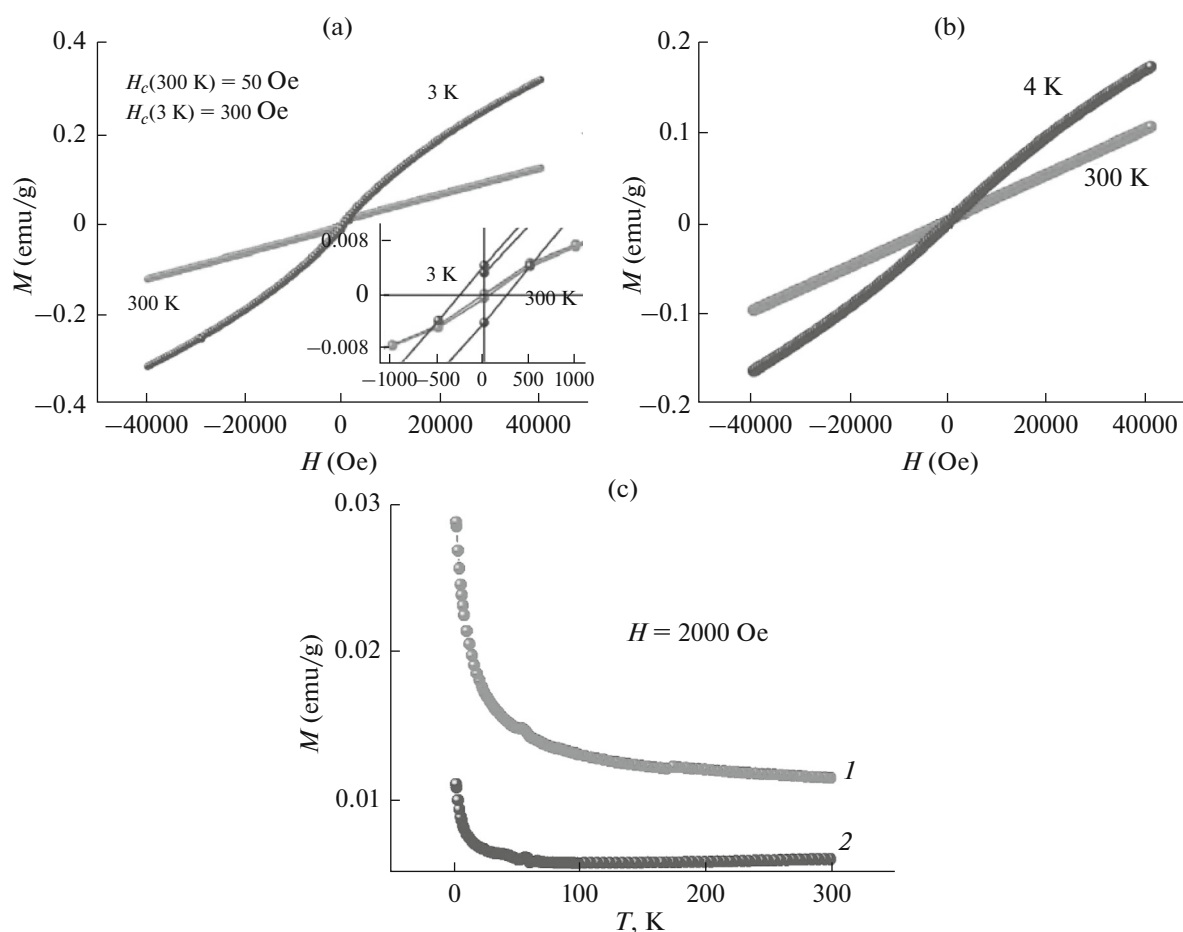


Fig. 4. Magnetization curves for sample with coatings nos. (a) 1 and (b) 2 and (c) the temperature dependence of magnetization for samples nos. 1 (curve 1) and 2 (curve 2). The insert shows the area of low fields.

The results of studying magnetic properties of the samples with PEO coatings are shown in table and Fig. 4. According to the obtained data, the sample with coating no. 1 manifests ferromagnetic properties. The

value of coercive force H_c measured at room temperature is equal to 50 Oe. The temperature decrease down to 3 K yields an increase of H_c : its value becomes equal to 300 Oe (Fig. 4a). As was demonstrated in studies of

magnetic characteristics of the sample with coating no. 2, this sample was paramagnetic at room temperature (Fig. 4b); i.e., iron present in the coating composition does not impart ferromagnetic properties to the sample. Measurements performed at 4 K demonstrated deviation of the field dependence of magnetization from linearity and the emergence of a small coercive force ($H_c \sim 12$ Oe).

In general, the obtained magnetization temperature dependences (Fig. 4c) corroborate conclusions that have been drawn on the magnetic properties of the samples under study. The curves contain the following bends: around ~ 180 and ~ 60 K on curve 1 and around ~ 60 and ~ 45 K on curve 2. The bend at ~ 180 K on curve 1 may be related to the Morin transition, which is characteristic of such iron oxide as hematite [15]. Significant shift of such transition temperature can be explained by small sizes of hematite particles. The bend around ~ 45 K on curve 2 must be related to whether the ferromagnetic phase with the Curie temperature near this temperature or the superparamagnetic phase with the blocking temperature in the same range. Deviation of the magnetization field dependence for the sample with coating no. 2 from linearity at low temperature could be related to the presence of the above phases. A small peak around 60 K on both curves is explained, most probably, by the presence of oxygen in the measurement system. Additional studies are required to examine these assumptions.

CONCLUSIONS

The obtained results demonstrate that coatings with Fe-containing crystallites in their pores are formed in the PEO process in the presence of iron hydroxo-compounds particles in the electrolyte. Formation of crystallites proceeds due to ingress of negatively charged transition metals hydroxides particles from the electrolyte to breakdown channels as a result of their transformations in local spaces of electric breakdowns. In this case, coatings manifest clearly expressed ferromagnetic properties.

Upon removal of particles of iron hydroxide and hydroxo-salts from the electrolyte, coatings contain low concentrations of iron homogeneously distributed over the surface and manifest paramagnetic properties at room temperature. With respect to composition and surface morphology, such coatings are similar to those formed in base alkaline phosphate-borate-tungstate electrolyte (without addition of iron oxalate).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no, 15-03-03271 and the program "Far East".

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Translated by D. Marinin