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Structure and magnetic characteristics of iron-modified titania layers on titanium

V.S. Rudnev [a,b,*], M.V. Adigamova [a], I.V. Lukiyanchuk [a], I.A. Tkachenko [a], V.P. Morozova [a]

[a] *Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, 159, Prosp. 100-letya Vladivostoka, Vladivostok 690022, Russia*
[b] *Far East Federal University, 8, Sukhanova Str., Vladivostok 690950, Russia*

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ABSTRACT

Iron-containing titania coatings manifesting ferromagnetic characteristics have been formed on titanium by combining plasma electrolytic oxidation with impregnation technique. Iron is concentrated in the composition of dispersed particles of a size of 1–10 μm distributed over the coating surface. The values of the coercive force of 'coating/titanium' samples are equal to 20–70 Oe. The composition, structure and magnetic properties of the samples obtained by combining the methods of PEO and impregnation with subsequent air annealing have been compared with those formed by one-stage PEO technique. The impregnation and annealing can be applied to impart specific magnetic characteristics to various functional PEO-coatings.

1. Introduction

The 'ferromagnetic oxide coating/titanium' composites can be of interest as absorbers of electromagnetic radiation, micro-transformers, catalytically active systems, protective systems, etc. [1,2]. As was demonstrated recently, iron- and/or cobalt-containing coatings with ferri-, ferro-, and antiferromagnetic properties can be deposited on aluminum or titanium substrates by one-stage anodization in aqueous electrolytes at voltages of spark and microarc electric discharges (micro arc or plasma electrolytic oxidation, hereinafter referred to as PEO) [1,3–9]. Here, the precursors containing iron or cobalt compounds are added to electrolytes whether in the compositions of solid micro- and nanosized particles (Fe^0, Co^0 or Fe_2O_3) [1,5,6] or as complex compounds ($EDTA + Co^{3+}$) [7].

Earlier, to obtain ferromagnetic oxide coatings on aluminum and titanium by PEO technique, we proposed to use a basic alkaline solution $Na_3PO_4 + Na_2B_4O_7 + Na_2WO_4$ (hereinafter referred to as PBW, pH 11), into which Fe(III) oxalate and or Co(II) acetate had been added [3,4,8,9]. Hydrolysis of these salts in alkaline medium resulted in the precipitation of metal hydroxides. During PEO the dispersed (colloidal) particles of negatively charged metal hydroxides were maintained in suspended state by stirring the electrolyte. Really the electrolyte was a dispersed system; therefore we shall call it slurry electrolytes by analogy with Ref. [10].

In all above cases, transition metals from electrolytes were built up into coatings under electric discharges. For example, when dispersed iron particles with sizes no larger than 5 μm were added to a base electrolyte, these particles observed on the surface of PEO coatings formed on aluminum alloy as inclusions in alumina matrix [1]. Such composite coatings absorbed microwave radiation of certain wavelengths. The ferromagnetic coatings obtained through mechanical rubbing of nanosized (~70 nm) particles of metallic cobalt on the surface of PEO coatings preformed on titanium in phosphate electrolyte seem to have a similar structure too [6].

But a different structure is typical for the ferromagnetic iron-containing coatings on aluminum and titanium formed in the suspension electrolyte based on PBW-solution with colloidal particles of hydroxides of iron or cobalt spontaneously precipitated [4,8,9]. In this case, the transition metals from the electrolyte are concentrated in surface defect sites, mainly in pores formed by the electrical discharges. Within the pores they are located in the composition of conglomerates of nanoparticles or microcrystals containing reduced iron or cobalt, Fig. 1 [9]. It was established that the presence and composition of the crystallites in the pores determine the magnetic characteristics of the coatings [8,9]. Concentrating iron in the pores is also observed when coatings are formed in the electrolyte with complex ions $EDTA + Fe^{3+}$ [7]. Note that the

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* Corresponding author at: Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, 159, Prosp. 100-letya Vladivostoka, Vladivostok 690022, Russia.

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

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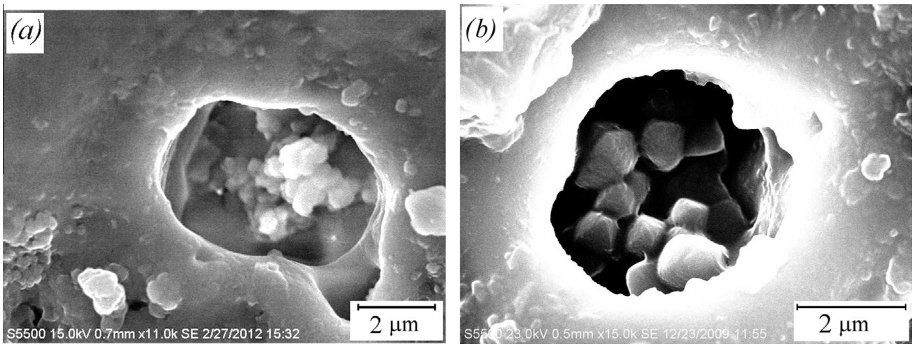

Fig. 1. SEM images of Fe-containing crystallites (a and b) located in the pores and determining ferromagnetic properties of PEO coatings [9].

formation of ferromagnetic coatings in the electrolytes containing colloidal hydroxide particles does not require preformed nano- or microparticles of metals or their oxides and allows one to introduce various metals or their mixtures into the pores by adding salts desired to alkaline electrolyte. For example, the crystallites containing both iron and cobalt are revealed in pores of PEO coatings produced in electrolyte with hydroxides of iron and cobalt [8]. Changing the ratio of magnetoactive elements in crystallite compositions enables controlling the magnetic properties of the coatings [8,9].

Other methods can evidently be applied to impart magnetic properties to PEO coatings. In particular, impregnation in respective aqueous solutions followed by air annealing or deposition of additional layer by extraction pyrolysis can be among them. These approaches have been used to modify the PEO coatings with noble and transition metals and impart catalytic or protective properties to them [11–13].

The objective of the present work was to modify the surface of PEO coatings on titanium with iron using impregnation in aqueous solutions followed by air annealing and to compare the magnetic properties of modified coatings with those of iron-containing coatings obtained by a one-stage PEO technique in slurry electrolytes with colloidal particles of iron hydroxides.

2. Materials and methods

2.1. Coatings manufacturing

To obtain the coatings, flat samples of titanium of a technical grade (VT1-0, 99.2–99.7% Ti) of sizes of $2.2 \times 2.2 \times 0.1$ cm^3 or $0.7 \times 1.3 \times 0.1$ cm^3 were used to study the coatings thickness, morphology, elemental and phase composition or to carry out the magnetic measurements, respectively. The sample pretreatment included chemical polishing in a mixture of concentrated acids at a volume ratio HNO_3:HF = 3:1 at 70 °C. Thereafter, the samples were washed with distilled water and dried at 70 °C in air.

Anodic coatings on the titanium substrates were formed galvanostatically at an effective current density of 8–10 A/dm^2 for 5 or 10 min. The two-electrode electrochemical cell comprised a glass of a volume of 1 L made of thermally resistant glass, in which the processed sample as an anode, the cathode as a hollow coil made of nickel alloy, and the thermometer were placed. The power source was a computer-controlled TER4-100/460N (Russia) thyristor aggregate working in the unipolar mode.

2.2. Electrolytes

For the PEO-coatings formation, aqueous electrolytes of three types were used (mol/L):

(I) 0.066 Na_3PO_4 + 0.034 $Na_2B_4O_7$ + 0.006 Na_2WO_4 (PBW [14]).
(II) PBW + 0.04 $Fe_2(C_2O_4)_3$ (PBWFe [4,8,9]).
(III) 0.098 $Na_5P_3O_{10}$ + $Ca(CH_3COO)_2 \cdot H_2O$, the molar ratio in the electrolyte was $n = [P_3O_{10}^{5-}]/[Ca^{2+}] = 0.625$ (PCa [15]).

Each of the components was preliminarily dissolved in distilled water; thereafter the solutions were mixed at a specified ratio and held with stirring for at least 1 h. At PEO treatment the electrolyte solution was cooled by feeding cold tap water through the coil and stirred using a magnetic stirrer. The electrolyte temperature during the PEO process did not exceed 30 °C.

2.3. Modifying the coatings

To modify the samples with PEO-coatings, they were immersed into an aqueous solution of either iron nitrate $Fe(NO_3)_3$ (1 mol/L) or iron oxalate $Fe_2(C_2O_4)_3$ (0.04 mol/L) and held there for 1 h. The concentration of iron oxalate was similar to that used at a one-stage formation of coatings in the PBWFe electrolyte [4,8,9]. Salts of the chemically pure grade were used. Upon impregnation, the samples were dried above an electric stove and annealed in air in a muffle furnace at 500 °C for 2 h.

2.4. Coatings characterization

To characterize the coatings we used measurements of the thickness, X-ray spectrum analysis (XSA), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

The thickness of coatings was measured using an eddy-current thickness gage VT-201 (Russia). The element composition, element distribution maps, 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, we determined the element composition of individual coating parts. In both cases, gold was preliminarily sputtered on films to prevent the surface charging.

X-ray patterns were recorded on a D8 ADVANCE (Germany) X-ray diffractometer using Cu Kα-radiation (hereinafter referred to as XRD analysis). During the XRD analysis, the EVA search program with the PDF-2 database was used.

2.5. Magnetic properties

Magnetic measurements were performed on a SQUID MPMS 7 (Germany) magnetometer at temperatures 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. Mass fraction of the coatings in the samples was about 1–3%.

3. Results

3.1. Fe-modified PEO coatings formed in PBW-electrolyte

The thickness, phase and element compositions of PEO coatings formed for 5 min before and after impregnation with subsequent annealing are shown in Table 1. The samples impregnation and annealing do not affect the coatings thicknesses. According to the XSA method data (the depth of penetration of the probing beam ~2–5 μm), the average amount of iron embedded into coatings

Table 1
Effect of electrolyte for PEO forming and impregnation solution on the thickness, element (from XSA data) and phase composition of PEO coatings on titanium formed for 5 min at i = 8 A/dm^2.

Electrolyte		PBW			PCa		
Impregnation solution		–	$Fe(NO_3)_3$	$Fe_2(C_2O_4)_3$	–	$Fe(NO_3)_3$	$Fe_2(C_2O_4)_3$
h (μm)		15 ± 2	15 ± 1	17 ± 1	14 ± 1	14 ± 1	13 ± 2
Phase composition		TiO_2(a)	TiO_2(a)	TiO_2(a)	TiO_2(a)	TiO_2(a, r)	TiO_2(a, r)
Element composition (at.%)	C	13.6	11.4	9.6	10.4	12.4	9.2
	Fe	–	0.1	0.1	–	0.6	1.0
	O	64.2	66.9	68.3	65.7	65.9	68.4
	Na	1.2	0.8	0.9	0.6	0.4	0.6
	P	4.8	4.3	4.9	3.2	2.9	2.9
	Ti	15.4	15.5	15.5	17.6	15.9	16.4
	Ca	–	–	–	2.4	2.0	1.4
	W	0.7	0.7	0.7	–		

Note: a – anatase; r – rutile.

under experimental conditions did not exceed 1 at.%. Similar results were obtained for the coatings formed during 10 min.

According to the XRD analysis, the coatings formed in the PBW electrolyte contain titanium dioxide in the anatase modification, Table 1 and Fig. 2. Upon the impregnation and annealing operations, on X-ray patterns one can see an increase in heights of reflections corresponding to anatase, which indicates an increase in the content of the titanium dioxide crystalline phase in the coatings. The growth of reflection heights corresponding to titanium may be caused by cracking the coating under annealing conditions (arrows C in Fig. 3b) and by increasing the signal from titanium substrate.

Fig. 3 shows SEM images of PEO-coating formed in PBW-electrolyte before (Fig. 3a) and after (Fig. 3b) impregnation in aqueous solution of $Fe_2(C_2O_4)_3$ as well as a map of iron distribution at surface of the coating modified (Fig. 3c). The initial coatings have developed heterogeneous fused surface with pores of a size of ~1–10 μm and elevations and recesses around them (Fig. 3a), which is typical for many of PEO coatings. Visible pores occupy up to 30% of total coating surface. As follows from comparison of Fig. 3b and c, iron is concentrated on the surface in the composition of dispersed particles of sizes in the range 1–10 μm. Iron-containing particles are located around pores, but do not enter them. These sites must have the most favorable conditions for surface wetting with the impregnation solutions. The liquid drops remained upon impregnation are condensed into solid iron-containing dispersed particles in the process of annealing. Thus, under the experimental conditions, the impregnation and annealing operations yield not a solid 'crust', but individual iron-containing dispersed particles. Since the peaks characterizing crystalline iron or its compounds are absent on X-ray patterns (Fig. 2), these particles can be amorphous or fine-crystalline or their amount is too low for their detection by XRD. The particles seem to consist of iron oxides that are the product of thermolysis during air annealing of $Fe_2(C_2O_4)_3$ or $Fe(NO_3)_3$ or products of their hydrolysis containing in the impregnation solutions.

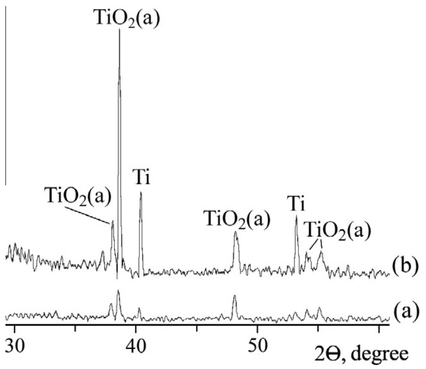

Fig. 2. X-ray patterns of the coatings obtained by PEO in PBW-electrolyte before (a) and after impregnation in solution of 0.04 mol/L $Fe_2(C_2O_4)_3$ and air annealing (b). PEO coatings are formed at i = 8 A/dm^2 for 5 min.

As seen from the data of Fig. 3c and d and Table 2, upon the impregnation and annealing operations, the coatings manifest ferromagnetic properties, whereas the value of coercive force H_c for the systems formed is in the range from 20 up to 70 Oe at 300–340 K. Since the initial coatings do not have such characteristics, it is evident that ferromagnetic properties are determined by iron compounds present on the surface in the composition of disperse particles.

3.2. Fe-modified PEO coatings formed in PCa-electrolyte

Results similar to those listed in Section 3.1 were obtained upon the modification of PEO coatings formed in PCa-electrolyte by impregnation with subsequent annealing, Tables 1 and 2.

Fig. 4 shows a general view of the surface and map of iron distribution over the surface of PEO-coatings formed in the PCa-electrolyte and additionally impregnated in aqueous solution of 1 M $Fe(NO_3)_3$. As in the case of Fe-modified PEO coating obtained in PBW-electrolyte, iron is concentrated in the composition of disperse particles located near the pores and nonuniformly distributed over the surface.

Fe-modified 'PCa' coatings manifest ferromagnetic properties too, Fig. 4c and d.

3.3. Fe-containing coatings formed by one-stage PEO technique in PBWFe-electrolyte (as to Refs. [4,9])

In this case the PBW electrolyte is added with 0.04 M $Fe_2(C_2O_4)_3$, i.e., in the same concentration as in the impregnation solution. Introducing the salt resulted in the spontaneous formation of suspension containing colloid particles of ferric hydroxide.

The coatings of a thickness of 17 ± 2 μm were formed at effective current density 10 A/dm^2 during 10 min. Fig. 5 shows that conglomerates of crystallites consisting of individual crystal-like structures of a size of ~50 nm are within the coating pores. The coating elemental composition averaged over the surface area as to XSA and elemental compositions of nanocrystallites and surface site near the pore are given in Table 3. These data were obtained by concentrating the probe beam of electron microscopy accessory for energy-dispersive analysis within areas 1, 2 and 4, as shown in Fig. 5a and b. The crystallites in the pores are very different from the coating surface in composition. Such metals as iron, titanium

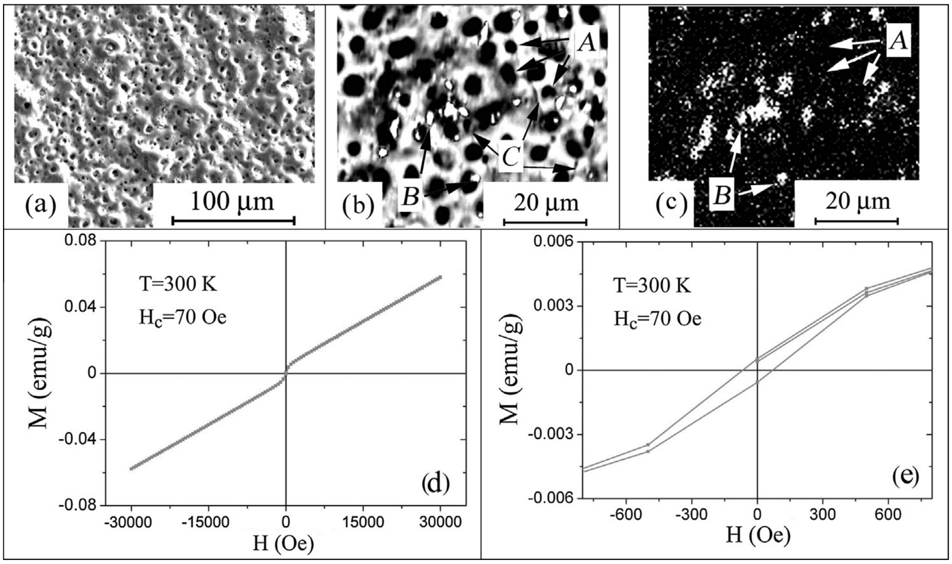

Fig. 3. SEM images of the surface: relief (a) and phase representation (b), iron distribution maps (c) and dependencies of the magnetic moment *M* on the external magnetic field strength *H* (d and e) for the samples with PEO coatings formed PBW-electrolyte (at i = 8 A/dm^2 during 5 min) and additionally impregnated in solution of 0.04 mol/L $Fe_2(C_2O_4)_3$ and annealed. On the images: A – pore, B – dispersed iron-containing particle, and C – cracks. The small fields are (e).

Table 2
Effect of coating formation conditions on coercive force H_c of the samples with coatings formed at i = 8 A/dm^2.

Formation conditions			H_c (Oe)
Electrolyte	PEO duration, (min)	Impregnation solution	
PBW	5	$Fe_2(C_2O_4)_3$	70[a]
		$Fe(NO_3)_3$	51[b]
PCa	5	$Fe_2(C_2O_4)_3$	20[a]
		$Fe(NO_3)_3$	54[b]
	10	$Fe_2(C_2O_4)_3$	44[b]
		$Fe(NO_3)_3$	51[a]

[a] Measurements at 300 K.
[b] At 340 K.

and tungsten are concentrated in the crystallites within the pores. Since oxygen amount is insufficient for oxide formation, the metals in the crystallites appear to be predominantly or partially in reduced oxidation level.

According to previously obtained experimental data [4,8,9] and a theoretical modeling of the causes of magnetism in such coatings [16,17] the crystals in the pores determine the magnetic characteristics of the coatings.

To sum up, both the combination of PEO with impregnation followed by annealing and the one-stage PEO in slurry electrolytes enables one to obtain the coatings with ferromagnetic characteristics. The composites formed have different surface structure. Modifying the coatings by impregnation with subsequent annealing

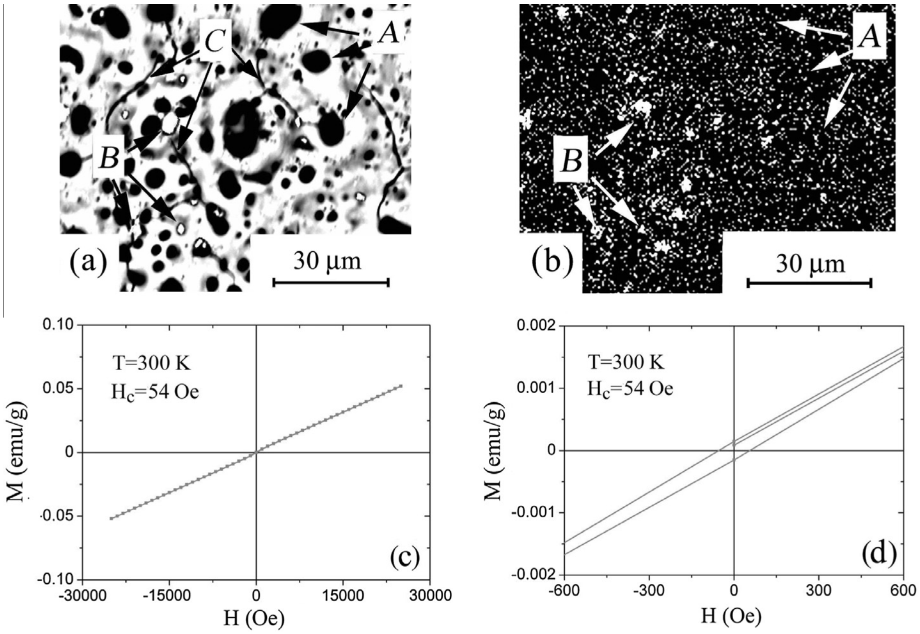

Fig. 4. General view of the surface, phase representation (a), iron distribution maps (b) and dependencies of the magnetic moment *M* on the external magnetic field strength *H* (c and d) for the samples with PEO coatings formed in PCa-electrolyte (at i = 8A/dm^2 for 10 min) and additionally impregnated in solution of 1 mol/L $Fe(NO_3)_3$ and annealed. On the images: A – pore, B – dispersed iron-containing particle, and C – cracks. The small fields are (d).

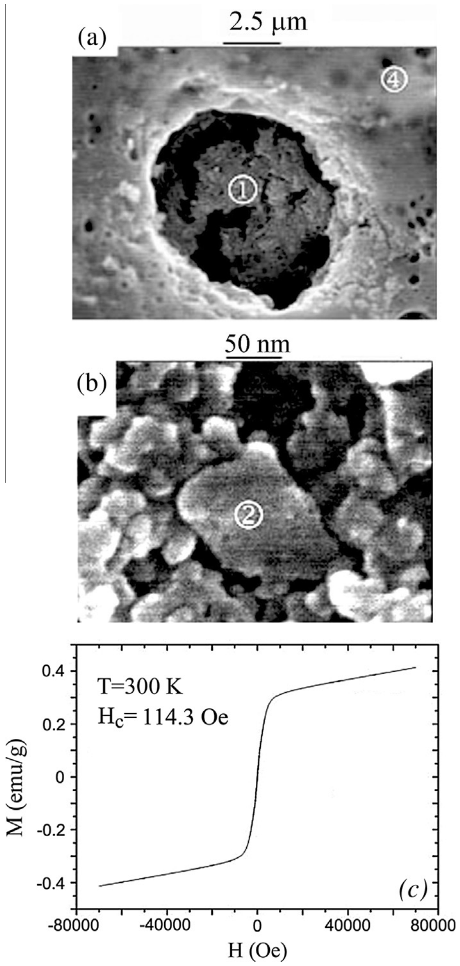

Fig. 5. Conglomerates of nanocrystallites (a and b) in pores and magnetization curve $M = f(H)$ (c) for the samples with coatings obtained by one-stage PEO technique in PBWFe-electrolyte at i = 10 A/dm^2 for 10 min.

results in the concentration of iron in dispersed particles of 1–10 μm fixed on a surface around the pores. Upon one-stage formation in Fe-containing slurry electrolyte iron and other metals from electrolyte are concentrated within the pores in the composition of the crystallites incorporated into conglomerates. Moreover, in crystallites the part of the metals is present in the reduced state. Fe-containing disperse particles on the surface and nanoparticles conglomerates in the pores determine magnetic properties of the coatings.

4. Discussion

The fact established in [4,8,9] of concentrating the metals from electrolyte at the bottom and walls of pores and in the structured valleys penetrated by small pores upon the formation of the coatings by PEO technique in slurry electrolytes with colloidal particles of metal hydroxides is not previously noted and discussed in the literature. Meanwhile, this fact is important not only for understanding the properties of the coatings, but also for the development of the knowledge about the mechanisms of oxide coating formation under electric discharges. The metals concentrating in pores and their presence in the reduced state must be common properties of PEO-coatings. For instance, similar facts were observed at obtaining iron-containing PEO-coatings in electrolytes with soluble complexes of iron with ethylenediamine tetra-acetate [Fe(III)EDTA]$^-$, i.e. in true solutions [7]. Varying the composition of slurry electrolytes and the parameters of formation enables one to change within wide limits not only the average composition, thickness, structure and morphology of the coatings but also, apparently, the composition of micro- and nanoparticles in the pores [4,8,9]. For example [8], using electrolyte containing hydroxides of Fe(III) and Co(II) favors obtaining conglomerates of particles simultaneously containing both metals in pores of the coatings.

In the suspension electrolyte containing 0.04 mol/L $Fe_2(C_2O_4)_3$ that is the same concentration as in impregnation solution we obtained coatings with average iron content ~8 at.% and coercive force 100–114 Oe at 300 K. Upon the combination of PEO in the PBW electrolyte with subsequent impregnation in solution of 0.04 mol/L $Fe_2(C_2O_4)_3$ and annealing, the average iron content in the coatings was less than 1 at.% and coercive force was 50–70 Oe, see Table 2. In other words, here both the concentration of iron and the value of the coercive force were much lower. However, it is possible that both H_c value and total iron content on the surface can be increased by the methods combination, for instance, through repeating impregnation-annealing operations or changes in impregnation solutions salinities.

The coatings formed by both methods and the structural components of the surfaces contain significant amounts of carbon. As shown in [18,19] its content decreases in lower layers of PEO coatings. Elevated concentrations of carbon on the surface can be related to both the surface contamination due to handling samples and building up carbon under electric discharges. Acetate ions present in the electrolyte or carbon dioxide adsorbed from the air by alkaline solution can serve as a source of carbon [18,19].

According to the structure namely localization of magnetic elements in disperse particles at the surface, the PEO coatings modified by impregnation followed by annealing seem to be similar to the coatings obtained by PEO in slurry electrolytes with solid iron particles [1] or by mechanically rubbing metal nanoparticles onto the surfaces [6].

5. Conclusions

To sum up, the combination of the methods of PEO and impregnation with subsequent annealing enables one to form coatings with ferromagnetic characteristics. Unlike the coatings formed under similar conditions by a one-stage PEO method, in which iron is concentrated in the pores, upon combination of PEO and impregnation with subsequent annealing, iron is present in the composition of localized dispersed particles distributed over the surface. This fact, on the one hand, can determine lower adhesion of iron-containing particles and, on the other hand, as was demonstrated earlier at obtaining catalytically active systems by a combination

Table 3
The element composition of surface, nanocrystallites and areas around the pores for the coatings on titanium formed by one-stage PEO technique in PBWFe-electrolyte.

Morphological structure	Example	Element composition (at.%)						
		C	O	Na	P	Ti	Fe	W
Coating surface	–	11.3	67.2	1.3	6.5	5.5	7.2	1.0
Areas around the pores	Site 4 in Fig. 5a	27.6	57.7	5.5	3.2	3.1	4.4	0.4
Nanocrystallites in pores	Sites 1 and 2 in Fig. 5a and b	7.2	19.2	1.7	2.2	13.5	51.0	5.2

of methods, opens the possibility to embed different metals into the composition of dispersed particles. As compared to direct obtaining of active coatings by the PEO method, a disadvantage of the above approach consists in its multistage character. In the meantime, both approaches can be applied to obtain magnetically active systems 'coating/valve metal'. The combination of methods PEO + impregnation + annealing can be applied to impart specific magnetic characteristics to different functional PEO-coatings including protective or bioactive ones. As was shown in the present work, we can use PEO in electrolyte with calcium polyphosphate complexes to obtain the coatings that are promising for biomedical application [15] and post-impregnation with next annealing to impart them specific magnetic properties.

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