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> NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

# Composition and Magnetic Characteristics of Plasma Electrolytic Oxide Coatings on Titanium

V. S. Rudnev<sup>*a*, *b*, \*, M. V. Adigamova<sup>*a*</sup>, I. A. Tkachenko<sup>*a*</sup>, K. I. Yanushkevich<sup>*c*</sup>, I. V. Lukiyanchuk<sup>*a*</sup>, and V. P. Morozova<sup>*a*</sup></sup>

<sup>a</sup>Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia <sup>b</sup>Far Eastern Federal University, Vladivostok, 690950 Russia <sup>c</sup>SSPA Scientific and Practical Materials Research Center of the Belarus National Academy of Sciences, Minsk, 220072 Belarus \*e-mail: rudnevvs@ich.dvo.ru Received April 14, 2016

Abstract—The results of studies of the composition and magnetic characteristics of coatings formed in different time periods on titanium in suspension electrolytes of compositions  $Na_3PO_4 + Na_2B_4O_7 + Na_2WO_4 + Fe_2(C_2O_4)_3$  (PBWFe, pH 7.8) and  $Na_2HPO_4 + Na_2B_4O_7 + Na_2WO_4 + Fe_2(C_2O_4)_3$  (P\*BWFe, pH 7.4), as well as the characteristics of coatings fabricated in filtrates of both electrolytes, are presented. PBWFe and P\*BWFe electrolytes contain colloid particles of iron hydroxides. Crystallites in pores of PBWFe coatings formed in different periods of time is equal to ~2.6, while in pores of P\*BWFe coatings it is equal to ~1.1. The samples with PBWFe coatings manifest ferromagnetic properties, while samples with P\*BWFe coatings and those obtained in filtrates of both electrolytes are paramagnetics. It was shown that, for PBWFe and P\*BWFe coatings formed in different time periods, the composition, thickness, and presence and composition of crystallites in pores, as well as magnetic and other controlled parameters, are fairly reproducible.

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#### 1. INTRODUCTION

Coatings on metals and alloys having specific magnetic characteristics may find application as protective means as well as in catalysis and medicine. We have recently shown that multicomponent Fe- and/or Cocontaining oxide coatings formed on titanium and aluminum in sol electrolytes by plasma electrolytic oxidation technique (PEO) manifested ferro- or ferrimagnetic properties [1-5]. Electrolytes were prepared through addition of Fe(III) oxalate and/or Co(II) acetate into the base alkaline electrolyte  $Na_3PO_4$  +  $Na_2B_4O_7 + Na_2WO_4$ , pH ~ 11 ("PBW electrolyte"). The processes of hydrolysis of transition-metal salts in an alkaline aqueous solution yield a sol containing colloid particles of these metals hydroxides [6-8]: here, the pH value decreases to 8-9. In an alkaline medium, particles are negatively charged [9]. Fe- and/or Cocontaining anodic-oxide coatings were formed in such electrolytes by the PEO method, i.e., at oxidation under the effect of an electric spark or arc discharges in the near-anodic area.

According to the available experimental data, the magnetism of the coatings is due to formation of micro- or nanocrystallites in channels of spark break-

downs (coating pores) during the PEO process [2-5], Fig. 1. Crystallites predominantly consist of the reduced metals contained in the electrolyte and the metal base. According to [3], the crystallites in the pores of coatings formed on titanium in the electrolyte PBW + 0.04 mol/L Fe2(C2O4)3 contain, at %: 74– 77 Fe, 8–13 Ti, 7–8 W, and 5–7 O (see points 1–3 in Fig. 1c). The oxide-coating matrix surrounding the pores contains about 7 at % of iron and up to 55 at % of oxygen (see point 4 in Figs. 1c–1e) [3].

As can be seen from literature sources, iron in an electrolyte with pH > 8 is present predominantly in the composition of colloid hydroxide particles, which sorb cations and anions of heavy metals contained in the solution [7, 8]. In our case, they can sorb tungsten anions and titanium ions that entered the electrolyte during the PEO. Iron concentrating in pores in the form of crystallites and the presence of tungsten and titanium in their composition are related to inclusion of colloid particles into the breakdown channels and their transformation under the effect of the conditions realized in these local areas (differences in pressure and temperature, water thermolysis etc.).

Based on element-analysis data and taking into account the PEO process features and simulation



Fig. 1. Magnetization curves obtained at (a) 300 and (b) 10 K for titanium samples with PEO coatings formed in PBWFe electrolyte for 10 min at (a) different current densities and (b) i = 0.1 A/cm<sup>2</sup>; (c–e) SEM image of crystallites in pore at different magnifications [3].

results [10, 11], it was suggested [3] that crystallites consist of a metal core surrounded by an oxidehydroxide shell. The core contains the reduced ferromagnetic iron and paramagnetic titanium and tungsten. The presence of reduced iron in the coatings' composition was corroborated by the data of X-ray diffraction analysis and X-ray photoelectron spectroscopy [2–4].

For coatings on the aluminum alloy, one observes a correlation between changes in the coatings' magnetic characteristics and the value of atomic ratio n = Fe/ $\Sigma$ (W, Al) in crystallites [4].

The processes of hydrolysis of Fe(III) salts depend on many factors, including the pH value, iron-salt concentration, and background-solution (electrolyte) composition [6-8]. The present work describes the results of studies of the composition and magnetic characteristics of coatings formed within different periods of time on titanium in electrolytes of the compositions  $Na_2HPO_4 + Na_2B_4O_7 + Na_2WO_4 +$  $Fe_2(C_2O_4)_3$  and  $Na_3PO_4 + Na_2B_4O_7 + Na_2WO_4 +$  $Fe_2(C_2O_4)_3$  as well as the characteristics of coatings obtained in filtrates of both electrolytes. The objective of the present study was to reveal reproducibility of results, to obtain data on the effect of the pH value (or the nature of the applied phosphate) on the coatings' composition and morphology and the composition of crystallites in the coating pores, and to find the relation between the presence of iron-hydroxide colloid

particles in the electrolyte and the coatings' magnetic characteristics.

## 2. MATERIALS AND METHODS

## 2.1. Preparation of Electrolytes

To form PEO-coatings, two electrolytes were prepared (mol/L):  $0.14Na_2HPO_4 + 0.034Na_2B_4O_7 +$  $0.006 \text{Na}_2 \text{WO}_4 + 0.04 \text{Fe}_2(\text{C}_2 \text{O}_4)_3$  ("**P\*BWFe** electrolyte") and, as in [2, 3],  $0.066Na_3PO_4 + 0.034Na_2B_4O_7$  $+ 0.006 \text{Na}_2 \text{WO}_4 + 0.04 \text{Fe}_2(\text{C}_2 \text{O}_4)_3$  ("**PBWFe** electrolyte"). Each of the components of the base electrolytes was preliminarily dissolved in distilled water and, then, solutions were mixed at a preset ratio. The pH values of base P\*BW and PBW electrolytes were equal to 9.8 and 11.1, respectively. Base electrolytes were added with  $Fe_2(C_2O_4)_3$  solutions and held at stirring for at least 1 h. As a result, suspensions (sols) were formed. Insoluble compounds of iron, including hydroxides, oxyhydroxides, and, possibly, hydroxo salts, were present in the electrolyte in the forms of colloid and suspension. Here, the PBWFe electrolyte was of the brown color (pH 7.8), whereas the P\*BWFe electrolyte comprised a suspension of the light yellow-orange color (pH 7.4). Different pH values indicate to different degrees of hydrolysis of iron salts. Therefore, the ratio of Fe-containing components of different compositions (and different charge) in two electrolytes will be different.

## 2.2. Formation of Coatings

Coatings were formed on flat samples of titanium of VT1-0 technical grade of a size of  $2.2 \times 2.2 \times 0.1$  and  $0.7 \times 3 \times 0.1$  cm<sup>3</sup>. To standardize the surface prior to PEO, samples were polished in a mixture of concentrated acids HNO<sub>3</sub> : HF = 3 : 1 (by volume) at 70°C, washed with distilled water, and dried in air at 70°C.

Coatings on titanium anodes were formed in the galvanostatic mode with the effective current density of 10 A/dm<sup>2</sup> for 10 min. A computer-controlled TER4-100/460N thyristor device (Russia) operating in the unipolar mode served as a current source. The electrochemical cell comprised a vessel made of heat-resistant glass with the sample to be treated (anode) and a cathode made as a hollow coil from nickel alloy placed inside it. The electrolyte was stirred using a magnetic stirrer to maintain particles in the suspended state and cooled by feeding cold tap water through a hollow coil. The electrolyte temperature during the PEO process did not exceed 30°C.

## 2.3. Determination of the Thickness, Element and Phase Composition of Coatings and Pore Structure

The layer thickness was determined using a VT-201 thickness meter (Russia). There were 12 measurements for each sample side, and the obtained data were averaged.

The data on element composition and surface images were obtained using a JXA 8100 X-ray spectral analyzer (Japan) equipped with an INCA energy-dispersive (X-ray spectral) accessory (United Kingdom). The averaged element composition was determined from the results of scanning five random surface areas of a size of  $\sim 250 \ \mu m^2$  each at a depth of up to 5  $\mu m$ . The coating surface and the pore structure were also studied using a Hitachi S5500 high-resolution scanning electron microscope (Japan). Using a Thermo Scientific microscope accessory for energy-dispersive analysis (United States), the element composition of individual coating areas, including pore bottoms and formations inside pores, were determined. In both cases, gold was sputtered on coatings prior to measurements to prevent the surface contamination.

X-ray images were registered using a D8 ADVANCE X-ray diffractometer (Germany) in  $CuK_{\alpha}$  radiation (hereinafter referred to as XRD). During the XRD analysis, the EVA search program with the PDF-2 database was used.

## 2.4. Study of Magnetic Characteristics

Magnetic measurements were performed using a SQUID MPMS 7 magnetometer (United States) at temperatures in the range 3–300 K. Samples were magnetized in parallel to the magnetic-field direction. For the magnetization calculation, the magnetic

moment was normalized on the mass of the sample with coating. The mass fraction of coatings in samples was  $\sim 1-3\%$ .

For the sample obtained in the P\*BWFe electrolyte, the magnetic susceptibility was measured by the ponderomotive method in the Laboratory of Physics of Magnetic Materials of the SSPA Scientific and Practical Materials Research Center of the Belarus National Academy of Sciences. For the measurement, samples were placed into quartz ampoules. The equipment certified at the Belarus State Institute of Metrology enables one to study magnetic characteristics in the continuous mode (without sample reinstallation, thermostat exchange, etc.) in the temperature range of  $\sim$ 80–1400 K in the magnetic field of an induction of B = 0.86 T. The error of measurement of the specific magnetization divided into the mass of the sample to be measured was equal to  $\Delta \sigma \pm 0.005$  A m<sup>2</sup> kg<sup>-1</sup>, while that of the magnetic susceptibility of a sample of the known mass was  $\Delta \chi \pm 1 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1}$ .

## 3. RESULTS AND DISCUSSION

## 3.1. Electrode-Voltage Behavior in Formation of Coatings

Figure 2 shows the data on changes in electrode voltage over time U = f(t) in formation of coatings in the electrolytes: PBW (curve 1), PBWFe and its filtrate (curves 2 and 3), and P\*BWFe and its filtrate (curves 4 and 5). Addition of Fe(III) oxalate into the base PBW electrolyte results in a decrease of electrode voltage U at certain moment t. For example, upon the process completion (10 min of treatment), the average for a series of two to four samples, final voltages  $U_f$  in the cell were equal to 230, 163, and 109 V for PBW, P\*BWFe, and PBWFe electrolytes, respectively (see Table 1). The thicknesses of the obtained coatings were equal to 28 ± 3, 14 ± 2, and 11 ± 1 µm.

In general, during anodization (including PEO), the current passing through the anode has three main components [12, 13]:

$$i = i_{\rm i} + i_{\rm e} + i_{\rm d}$$

where  $i_i$  is the ionic current related to ionic transfer and coating growth,  $i_e$  is the current related to the electron transfer, and  $i_d$  is the current related to dissolution of the growing oxide. During galvanostatic formation, the decrease of the U value at the t and of the coating thickness in formation in electrolytes similar in composition are related, first of all, to the increase of the contribution of dissolution processes to that of formation of coatings.

In our case, the addition of  $Fe_2(C_2O_4)_3$  into base alkaline electrolytes and formation of iron hydroxide colloid particles yield the release of oxalate ions having an etching effect on the growing oxide, which results in the voltage decrease.





**Fig. 2.** Effect of electrolyte composition on changes in electrode voltage on the formation time. Electrolytes: PBW (curve 1), PBWFe (curve 2), filtrate of PBWFe electrolyte (curve 3), P\*BWFe (curve 4), and filtrate of P\*BWFe electrolyte (curve 5).

According to [7, 8], when pH > 8, virtually the whole amount of iron in aqueous solutions is present in the composition of hydroxides. The increase of the etching effect in the PBWFe electrolytes, as compared to the P\*BWFe electrolyte, can be explained by the fact that on more alkaline PBWFe electrolyte virtually the whole amount of iron is present in the composition of colloid particles, so that the concentration of oxalate ions is higher.

In addition to  $Fe(OH)_3$  particles, more soluble

forms, for example,  $Fe(OH)_2^+$  cations, are known to be present at pH values ~6 in solutions with iron concentration similar to the one used in the present study [7]. The presence of such forms in the P\*BWFe electrolyte is indirectly corroborated by their color. The suspension in the PBWFe electrolyte has a deep brown color (according to [8], the color of  $Fe(OH)_3$  is red-brown), while in the P\*BWFe electrolyte it is light yelloworange. Evidently, the P\*BWFe electrolyte with lower pH contains smaller quantities of different iron hydroxo salts, including those with  $Fe(OH)_2^+$  cations, than the PBWFe electrolyte. The latter affects the concentration of oxalate ions, the etching effect, and, finally, the coating thickness, and the U=f(t) function changes.

Removal of colloid and dispersed particles from solutions insignificantly modifies the behavior of U = f(t) dependences over time (Fig. 2). Note that both the U = f(t) dependences themselves and the values of the final formation voltage ( $U_f$ ) are fairly reproduced at formation of coatings within different periods of time (Table 1).

## 3.2. Coatings' Element and Phase Compositions and Morphology

Table 1 shows the results of determination of the final formation voltage and thickness and element composition of the coating surface part at a depth of up to 5  $\mu$ m formed in PBWFe and P\*BWFe electrolytes (from data of X-ray microprobe spectral analysis). In each case, the composition was determined on several randomly selected surface areas and averaged. The results of measurements for coatings formed in both electrolytes and filtrates in different periods of time are presented. Figure 3 shows the data of X-ray diffraction analysis for these layers, and Fig. 4 shows their surface morphology.

Analysis of the data of the Table 1 and Figs. 3 and 4 demonstrates that the coatings obtained within different periods of time for each electrolyte are virtually identical in terms of element composition and similar in the final formation voltage value, phase composition, and surface structure. Therefore, for each of the studied electrolytes, these parameters are fairly reproducible under the same conditions.

Electrolyte				PBWFe	P*BWFe				
pH		7.8				8.3	7.	7.9	
date, month, year		2010	2012	04.2014	11.2014	filtrate 11.2014	10.2013	11.2014	filtrate 11.2014
$U_j$	, V	113.3	90.5	126.1	106.1	141.2	158.6	167.5	153.8
<i>h</i> , μm		9 ± 1	$12 \pm 1$	11 ± 1	$10 \pm 1$	$7 \pm 1$	$14 \pm 2$	$14 \pm 1$	$8\pm 2$
Element composition, at %	С	$18.6\pm0.6$	$15.2 \pm 1$	$7.9 \pm 1$	$12.3\pm1$	$10.9\pm1.2$	$16.4 \pm 1$	$13.3 \pm 5$	$10.3\pm1.1$
	0	$61.3\pm0.6$	$59.7 \pm 1$	$69.9\pm0.7$	$64.4\pm0.7$	$67.7 \pm 1$	$62.3\pm1$	$65.9\pm3.5$	$67.5\pm0.7$
	Na	$1.8\pm0.1$	$2.2\pm0.2$	$1.5\pm0.1$	$1.1\pm0.2$	$0.7\pm0.1$	$1.3\pm0.1$	$1.6\pm0.1$	$1.0\pm0.1$
	Р	$6.4\pm0.1$	$7.0\pm0.2$	$6.1\pm0.2$	$6.0\pm0.2$	$2.1\pm0.1$	$7.6\pm0.2$	$6.8\pm0.5$	$4.0\pm0.1$
	Ti	$3.0\pm0.1$	$5.8\pm0.2$	$8.2\pm0.2$	$6.6\pm0.1$	$16.8\pm0.5$	$5.2\pm0.2$	$7.4\pm0.6$	$15.5\pm0.2$
	Fe	$8.1\pm0.1$	$9.0\pm0.2$	$5.2\pm0.1$	$7.9\pm0.2$	$0.8\pm0.1$	$6.6\pm0.2$	$4.4\pm0.3$	$1.2\pm0.1$
	W	$0.8\pm0.1$	$1.1 \pm 0.1$	$1.2\pm0.1$	$1.7\pm0.1$	$1.5\pm0.1$	$0.6\pm0.1$	$0.6\pm0.1$	$0.6\pm0.1$

Table 1. Final formation voltage, thickness, and element composition of coatings obtained in different periods of time

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Removal of the colloid precipitate from electrolytes results, in both cases, in a noticeable decrease of the layers' thicknesses and changes in their morphologies. Coatings become more compact and crystallized, the pore radius decreases, and elevated molten formations are absent. These changes evidently related to the absence of incorporation of colloid particles of hydroxide or hydroxo compounds of iron into coatings, what affects the thickness and mechanism of the formation of coatings.

## *3.3. Averaged Data on Coatings' Compositions and Pore Structures*

Figure 5 shows pores in coatings formed in PBWFe and P\*BWFe electrolytes and their filtrates. One can see that pores of the coatings obtained in PBWFe and P\*BWFe electrolytes contain so-called "plugs" composed of nano- and microcrystallites. Qualitative analysis demonstrates that the number of crystallites in pores of coatings formed in the P\*BWFe electrolyte is smaller than in PBWFe (see Figs. 5a, 5c). In addition, crystallites are not present in all the pores on the surface of coatings formed in the P\*BWFe electrolyte. Crystallites are absent in pores of coatings obtained in filtrates of these electrolytes (see Fig. 5b). The latter directly corroborates that crystallites are formed in pores only under the condition of the presence of hydroxide colloid particles or hydroxo compounds of iron in the electrolyte bulk. Evidently, the process occurs due to transfer of colloid particles into pores and their subsequent transformation under the effect of electric discharges in accordance with conditions realized in the pore.

Table 2 presents the averaged element composition of coatings formed in different periods of time in the studied electrolytes (Table 1) and the averaged (on five to seven individual pores) data on the element composition of crystallites and bottom and walls of pores, in which crystallites are absent (for coatings obtained in filtrates), and the surface adjacent to pores. The examples of the analyzed areas on pores (circles) and on the surface around pores (rectangles) are shown in Fig. 5.

According to the data of the X-ray microprobe spectral analysis, the main difference in the composition of the surface layer of a thickness of up to 5  $\mu$ m for four examined coatings is in the contents of iron and titanium. The largest titanium content characterizes coatings formed in electrolytes upon the removal of iron-containing particles. At the same time, such coatings contain iron in trace quantities.

The composition of crystallites in coatings pores differs substantially. Crystallites in pores of PBWFe coatings contain more than 60 at % of iron. Aside from iron, they are characterized with rather large titanium content (>20 at %). Crystallites in pores of P\*BWFe coatings contain half the amount of iron and 1.5 times the amount of titanium (>30 at %). In pores of coat-



**Fig. 3.** X-ray images of coatings obtained in (a) PBWFe and (b) P\*BWFe electrolytes. The coatings were obtained in (month, year): (1) 2010, (2) November 2014, (3) October 2013, (5) November 2014, (3, 6) X-ray images of coatings formed in filtrates of electrolytes 2 and 5, respectively.

ings formed in the filtrate, one observes large contents of titanium (>76 at %) and trace quantities of iron ( $\sim$ 2 at %). Note that all pores are characterized by a decreased content of phosphorus as compared to that on the surface. Evidently, under the effect of electric discharges, phosphorus leaves the pore in the composition of volatile compounds.

The element composition of the surface around the pore is a transitional one between that of pores and includes formations and the average element composition of the coating bulk.

The differences described above are related to different ionic compositions of electrolytes and different concentrations of colloid particles in PBWFe and P\*BWFe electrolytes as well as their absence in the filtrate.



**Fig. 4.** Microphotographs of coatings obtained in (a, b) PBWFe and (d, e) P\*BWFe electrolytes, in filtrates of (c) PBWFe and (f) P\*BWFe electrolytes. Coatings were obtained in (a) 2010, (d) 2013, and (b, c, e, f) November 2014.



Fig. 5. SEM images of pores in coatings obtained in (a) PBWFe electrolyte, (b) its filtrate, and (c) P\*BWFe electrolyte. 1 and 2 are examples of analyzed areas of pores and surface, respectively.

As in earlier-studied cases [2-4], low oxygen concentrations were registered in pores, which provides grounds to conclude that reduced metals are predominantly concentrated on the pore bottom and walls, as well as in crystallites. The complete or partial reduction of metals in anodic coatings can be explained as follows. As was demonstrated in [14-16], the gas emitted on the anode during PEO consisted of hydrogen by 90 mol %. According to these works' data, the temperature in discharge cannels exceeded 3000 K, which initiates thermochemical reactions of water decomposition. Most probably, the conditions for reduction of metals transferred into the breakdown areas in the compositions of ions, salts, and colloid particles or present in the composition of the already-formed oxides are created in the vapor-gas atmosphere in the spark electric-discharge channel at an increased hydrogen concentration. Note that the presence of crystallites in pores of some coatings was also demonstrated in a number of works [17-19].

## 3.4 Coatings' Magnetic Characteristics

Both the behavior of magnetization curves and the determined values of the coercive force (at room and helium temperatures) are rather satisfactorily reproducible for any type of coating, independently of the time period of its formation.

The magnetism of coatings formed in the PBWFe electrolyte is of a complex character, that can be seen from the dependencies of the magnetic moment on the strength of external magnetic field (Figs. 6a, 6b). Most probably, these samples are characterized by superposition of a few types of magnetism, such as paramagnetism, ferromagnetism, and superparamagnetism. For instance, at 300 K, the presence of a small coercive force, the absence of saturation, and a linear dependence of magnetization on the imposed field above 1000 Oe indicate that these materials consist of ferro- and paramagnetic phases. The temperature decrease down to 3 K results in an increase of the coercive force values and the deviation of the magnetiza-

Flactrolyta	Object	Averaged element analysis, at %							
Electrolyte	Object	С	0	Na	Р	Ti	Fe	W	
PBWFe	Surface*	13.5	63.8	1.7	6.4	5.9	7.6	1.2	
	Surface	23.5	48.1	1.6	4.8	5.1	16.3	0.3	
	Crystallites in pore	-	14.0	—	1.4	23.3	61.3	_	
Filtrate PBWFe	Surface*	10.9	67.7	0.7	2.1	16.8	0.8	1.5	
	Surface	33.3	38.9	0.9	1.4	21.8	1.3	2.4	
	Pore bottom	5.0	10.0	0.2	0.6	76.0	1.9	6.3	
P*BWFe	Surface*	14.9	64.1	1.5	7.2	6.3	5.5	0.6	
	Surface	14.9	56.5	2.7	7.7	11.2	5.9	1.1	
	Crystallites in pore	3.1	24.7	0.8	3.6	31.8	34.7	1.3	

**Table 2.** Averaged data on the element composition of coatings obtained in different periods of time and the composition of crystallites on pore bottom and walls (when crystallites are absent)

\* From the data of X-ray microprobe spectral analysis; all other cases, from the data of scanning electron microscopy (SEM).

tion-field dependence from linearity in the range of high fields, which is evidence of the increase of the contribution of the ferromagnetic component and the emergence of phases with properties different from paramagnetism and ferromagnetism, for example, phases with superparamagnetic properties.

Coatings obtained in both P\*BWFe electrolytes and filtrates of both electrolytes manifest a behavior similar to that of paramagnetics at room temperature. At 3 K, the appearance of the magnetization-field dependences differs from the linear one, which must be related to the emergence of contribution from particles characterized with superparamagnetic properties. Such particles may form not only in pores, but also in the coating oxide bulk.

The ferromagnetic properties of coatings formed in the PBWFe electrolyte are determined by the presence of crystallites with increased iron content in their pores (see Table 2). The removal of colloid particles from such an electrolyte yielding the absence of crystallites in pores (see Fig. 5b) is accompanied by a loss of ferromagnetic properties in samples (see Fig. 6c).

Crystallites are also contained in pores of the P\*BWFe coatings, but the coatings themselves do not manifest ferromagnetic characteristics. One of the reasons for this may be changes in the iron/titanium atomic ratio in crystallites. If in the case of crystallites in pores of the PBWFe coatings this ratio is ~2.6, for those in pores of the P\*BWFe coatings it is just ~1.1. Note that the Fe/Ti ratio for bottom and walls of samples with coatings formed in filtrates is equal to ~0.025.

To reveal the reasons of magnetic characteristics features for samples with P\*BWFe coatings, additional studies by the ponderomotive method were performed (see Fig. 7).

The temperature dependences of the specific magnetic susceptibility and specific magnetization (insert) of the "coating + technical grade titanium" composite obtained in heating and cooling modes are virtually identical, which allows concluding that the coating magnetic characteristics are stable in the temperature range ~100 K  $\leq T \leq 850$  K.

In the temperature range  $\sim 300 \text{ K} \leq T \leq 850 \text{ K}$ , changes in the specific magnetic susceptibility are insignificant. In this temperature range, the "coating + technical-grade titanium" composite manifests the properties of a Pauli paramagnetic ( $\chi \approx \text{const}$ ). Below ~300 K, the  $10^{-2}/\chi = f(T)$  dependence exhibits the presence of several magnetic phase transitions with spin state changes. Extrapolation of part of the  $10^{-2}/\chi =$ f(T) dependence in the temperature range 100 K  $\leq T \leq$ 200 K to the temperature axis falls into the negative range, while the value  $\theta_{eff} \approx |-220|$  K. The negative value of the Curie-Weiss temperature indicates antiferromagnetic ordering of magnetic moments in the temperature range 100 K  $\leq T \leq$  200 K. Manifestation of the effect of the paramagnetic state at temperatures above 300 K is also corroborated by the M = f(H) magnetization dependences of the coating of the composition under study (Fig. 6d).

## 4. CONCLUSIONS

Coatings formed on titanium by the PEO in the suspension electrolyte  $Na_3PO_4 + Na_2B_4O_7 + Na_2WO_4 + Fe_2(C_2O_4)_3$  contain iron-titanium crystallites with an average Fe/Ti ratio of ~2.6 in pores and manifest ferromagnetic properties. Substitution of  $Na_3PO_4$  by  $Na_2HPO_4$  in the electrolyte is accompanied by a decrease of the pH value and changes in the suspension electrolyte color. Coatings formed in such an electrolyte also contain crystallites in pores, but with



**Fig. 6.** Magnetization curves for samples with coatings formed in (a, b) PBWFe electrolyte and (c) its filtrate and (d, e) in the P\*BWFe electrolyte and (f) its filtrate. Coatings were obtained in (a) 2010, (b) November 2014, (d) October 2013, and (e) November 2014.

an Fe/Ti ratio of  $\sim$ 1.1, and manifest paramagnetic properties at room temperature. Qualitative analysis demonstrates that, in this case, the crystallite concentration is lower. Crystallites were not found in pores of coatings formed upon removal of colloid and suspended particles from electrolytes, while the coatings themselves are paramagnetics at room temperature. The latter serves as a direct corroboration of the relation between the presence of crystallites of specific composition in coatings pores, the presence of iron hydroxide particles in the electrolyte bulk, and the coatings' magnetic characteristics. At helium temperatures, all the coatings are characterized with the absence of saturation on magnetization-field dependences. The latter must be related to the presence of superparamagnetic particles in all coatings.

Thus, substitution of sodium orthophosphate by sodium hydrophosphate in the studied system results



Fig. 7. Results of studies of the specific magnetization and magnetic susceptibility of PEO coatings formed on samples of technical-grade titanium (VT1-0) in the magnetic field of the induction B = 0.86 T in the temperature range  $\sim 80-850$  K. Coatings were formed in 2013 in the P\*BWFe electrolyte.

in changes in pH and conditions of hydrolysis of iron(III) oxalate, which enables one to change the element composition of crystallites in pores and, as a result, to modify the coatings magnetic characteristics. Comparison of the parameters of coatings obtained in different periods of time under identical conditions demonstrates good reproducibility of results, taking into consideration the experiment's multifactorial character.

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