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Effect of Electrolyte Components on the Magnetic and Magnetoresistive Characteristics of Fe-Containing Plasma Electrolytic Oxide Coatings on Titanium

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Abstract—The effect replacing Na_3PO_4 with Na_2HPO_4 in aqueous phosphate–borate–tungstate electrolyte that additionally contains $Fe_2(C_2O_4)_3$ on the magnetic and magnetoresistive characteristics of oxide coating/titanium composites formed by means of plasma electrolytic oxidation (PEO) is investigated. It is established that PEO coatings with ferromagnetic characteristics form on titanium in an electrolyte containing Na_3PO_4 (pH ~ 11) upon adding iron(III) oxalate, while replacing Na_3PO_4 with Na_2HPO_4 and the respective drop in the pH of the base electrolyte down to 9.8 results in the formation of coatings with different magnetic characteristics. The correlation between changes in the values of the charge carriers' activation energy and the magnetic susceptibility is demonstrated for the latter. An increase in the electric resistance of coatings in a magnetic field is observed, and the type of the magnetic resistance temperature dependence is established.

Keywords: plasma electrolytic oxidation, titanium, oxide coating, magnetic characteristics

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INTRODUCTION

As we showed in [1–5], the Fe- and Co-containing oxide coatings that form on titanium or aluminum in suspension electrolytes via plasma electrolytic oxidation (referred to below as PEO) display ferro- or ferrimagnetic properties. Electrolytes were prepared by adding Fe(III) oxalate and/or Co(II) acetate to the base electrolyte $Na_3PO_4 + Na_2B_4O_7 + Na_2WO_4$, pH ~ 11 (PBW electrolyte). The hydrolysis of transition metals salts in an alkaline solution results in the spontaneous formation of a sol containing colloid particles of these metals' hydroxides, negatively charged in alkaline media [6, 7]. Anodic oxide coatings with ferromagnetic properties form on aluminum or titanium in such electrolytes through anodization under the effect of electric sparks or microarc discharges in the near–anode area (the PEO method [8–12]). According to the available data [1–5], a coating's ferromagnetism is determined by embedding Fe(III) and/or Co(II) hydroxide particles into them, with subsequent particle transformation under the impact of electric discharges.

Experimental results show that particles surrounded by oxide–hydroxide shells and containing predominantly ferromagnetic iron with paramagnetic titanium and tungsten form in a coating [2–5]. The presence of reduced metals in a coating's composition must be related to hydrogen emission as a result of water thermolysis in the electric breakdown channels [9] where such particles are formed. The presence of reduced iron in a coating's composition has been corroborated via X-ray diffraction analysis and X-ray photoelectron spectroscopy.

The aim of this work was to determine how a coating's characteristics change upon changing the conditions of the formation of colloid particles (their concentration, structure, and charge) in an electrolyte, e.g., as a result of changing the solution's pH. Data on the effect of replacing trisodium orthophosphate (Na_3PO_4) with disodium hydrogen phosphate (Na_2HPO_4) on the magnetic and magnetoresistive characteristics of oxide coating/titanium composites via PEO are presented.

EXPERIMENTAL

Coatings were obtained on flat samples of titanium of VT1–0 technical grade with sizes of 2.2 × 2.2 × 0.1

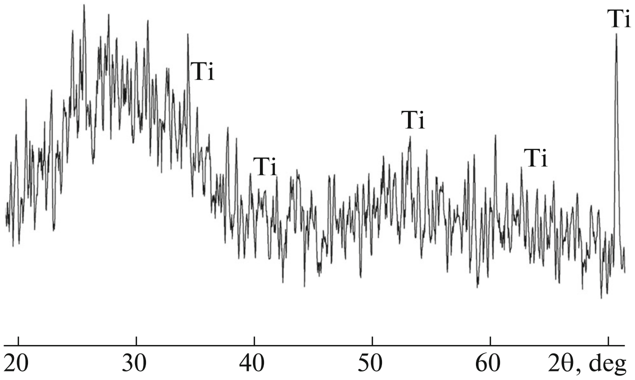

Fig. 1. XRD pattern of a coating in CuK_α radiation.

and 0.7 × 3 × 0.1 cm. For surface standardization prior to PEO, the samples were polished in a mixture of concentrated acids $HNO_3 : HF = 3 : 1$ (vol/vol) at 70°C, then washed with distilled water and dried at 70°C in air. A base electrolyte was prepared to form PEO coatings (mol/L): $0.14Na_2HPO_4 + 0.034Na_2B_4O_7 + 0.006Na_2WO_4$ (P*BW electrolyte, pH 9.8). Each of the components was preliminarily dissolved in distilled water and the solutions were mixed in preset ratios. An aqueous solution of $Fe_2(C_2O_4)_3$ was added to the base electrolyte and stirred for at least 1 h. When it was added, a suspension with a light yellow-orange color was formed (pH 7.4). The Fe(III) oxalate concentration in the electrolyte was 0.04 mol/L.

Coatings on titanium anodes were formed in the galvanostatic mode with an effective current density of 10 A/dm^2 over 10 min. A computer-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 stable glass with a volume of 1 L, into which the sample to be treated (anode) and cathode (a hollow coil made of nickel alloy) were placed. The electrolyte was stirred using a magnetic stirrer, keeping the formed colloid particles in a suspended state. During the experiment, the electrolyte was cooled by feeding cold tap water through the hollow coil, so its temperature did not exceed 30°C. The thicknesses of the grown layers were determined using a VT-201 thickness gauge (Russia). To ensure accurate statistics, the coating thickness was measured 12 times from each side of a sample, and the obtained data were averaged. The pH of the solutions was determined using a Multitest IPL-102 pH-meter/ion meter (Russia).

Elemental composition data and surface images were obtained using a JXA 8100 X-ray spectral microanalyzer (Japan) additionally equipped with an INCA energy-dispersive (X-ray spectral) accessory (Great Britain). The averaged elemental composition was determined using the results from scanning five randomly selected surface areas of a square of ~250 μm^2 at a depth of 5 μm each. Gold was preliminarily sputtered on the coatings to prevent surface charging. X-ray diffraction (XRD) patterns were registered using a D8 ADVANCE X-ray diffractometer (Germany) with CuK_α-radiation. Magnetic measurements were performed at the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, using a SQUID MPMS 7 magnetometer (United States) at temperatures of 3 and 300 K. Samples were magnetized parallel to the direction of the magnetic field. For magnetization calculations, the measured magnetic moment was normalized on the mass of a sample with coating. The mass fraction of coatings in samples was ~(1–3)%.

The temperature dependences of specific magnetization $\sigma = f(T)$ and specific magnetic susceptibility $\chi = f(T)$ of PEO coatings on titanium of VT1–0 technical grade were also studied at the Laboratory of the Physics of Magnetic Materials, Scientific-Practical Materials Research Center, National Academy of Sciences of Belarus, on a certified setup using the ponderomotive method in an argon atmosphere. The setup enables us to study the above magnetic characteristics in the continuous mode (without sample reset, thermostat exchange, and so on) in the temperature range of ~(80–1400) K in a magnetic field with an induction of $B = 0.86$ T. The error in measuring the specific magnetization per mass unit of a sample is $\Delta\sigma \pm 0.005$ A m^2 kg^{-1}. For the magnetic susceptibility of a sample of known mass, it is $\Delta\chi \pm 1 \times 10^{-11}$ m^3 kg^{-1}.

A sample's electric resistance was measured using the four-probe method with a universal Agilent voltmeter without applying magnetic field and in a constant magnetic field of up to 8 kOe in the temperature range of 300–650 K, at Reshetnev Siberian State Aerospace University.

RESULTS AND DISCUSSION

Coatings of a thickness of 10 ± 2 μm were formed on our titanium samples. According to the results from microprobe analysis, the average elemental composition of the coating surfaces (depth of analysis, down to 5 μm, depending on a material's composition) was (at %): 16.4 C, 62.3 O, 1.3 Na, 7.6 P, 5.2 Ti, 6.6 Fe, and 0.6 W. According to X-ray diffraction analysis data, the crystal structure of the coatings under study was markedly amorphized (Fig. 1).

Our results from studying the specific magnetization of PEO coatings on samples of titanium of VT1–0 technical grade in a magnetic field with an induction of $B = 0.86$ T in the temperature range ~(80–850) K by means of ponderomotive method are shown in Fig. 2. The temperature dependences of the specific magnetic susceptibility and specific magnetization (insert, Fig. 2) of coating + technical grade titanium

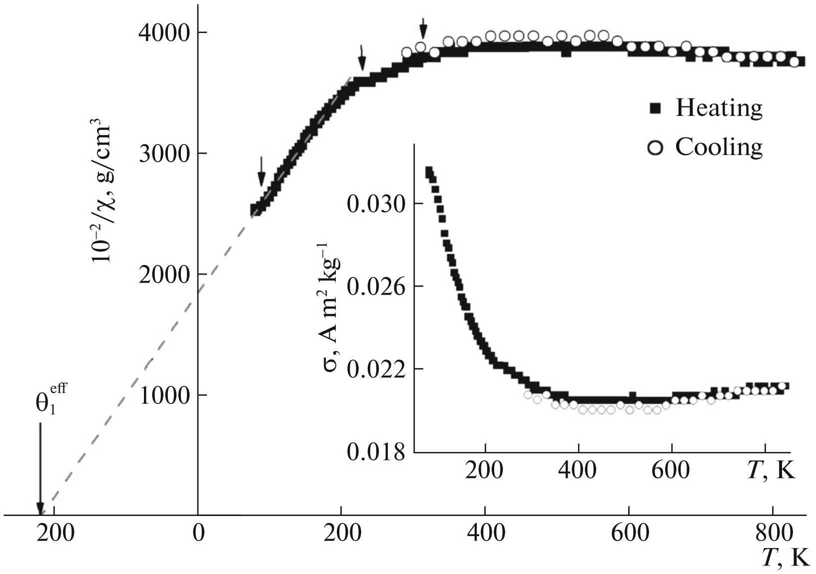

Fig. 2. Specific susceptibility of PEO coatings on samples of titanium of VT1–0 technical grade in a magnetic field with an induction of $B = 0.86$ T in the temperature range of $\sim$(80–850) K.

composites obtained in the heating and cooling modes are virtually identical. The latter demonstrated the stability of the coatings' magnetic properties in the temperature range of $\sim$300 K $\le T \le$ 850 K.

In the temperature range of $\sim$300 K $\le T \le$ 850 K, changes in the magnetic susceptibility were negligible. This showed that in the specified temperature range, the coating + technical grade titanium composite displayed properties of a Pauli paramagnetic ($\chi \approx$ const). Below $\sim$300 K, the $10^{-2}/\chi = f(T)$ dependence resulted in several magnetic phase transformations with changes in the spin state. Extrapolating part of the $10^{-2}/\chi = f(T)$ dependence in the temperature range of 100 K $\le T \le$ 200 K to the temperature axis takes us to the negative area, while $\theta_{\text{eff}} \approx |-220|$ K. The negative value of the Curie–Weiss temperature is due to antiferromagnetic ordering in the range of low temperatures.

Figure 3 shows the field dependences of magnetization obtained using a SQUID MPMS 7 magnetometer at two temperatures: 300 and 3 K. As follows from the $M = f(H)$ dependences, magnetization grows linearly at room temperature, along with the increase in field intensity. This corroborates our conclusion as to the paramagnetic behavior of the sample under study above 300 K, made on the basis of the magnetization temperature's dependence. The temperature falling to 3 K changes the character of the dependence of magnetization on the field intensity and its increase. The increase in magnetization along with the rise in the intensity of the external magnetic field could indicate that the coating under study contained particles with superparamagnetic properties.

Electrical resistance was measured in the temperature range of 300–650 K in an argon atmosphere (Fig. 4a). Around 430 K, we observed an increase in the temperature of activation, from 0.1 up to 0.4 eV (the insert in Fig. 4a). At this temperature, the magnetic susceptibility had a minimum and gradually grew along with the temperature increase (Fig. 2). Both of these effects can be explained by the increase in the electron concentrations at the bottom of the conduction band. In a magnetic field of 2 kOe, the resistance grew by 2%; in a field of 8 kOe, it doubled (Fig. 4a). Upon heating, the magnetoresistive effect fell

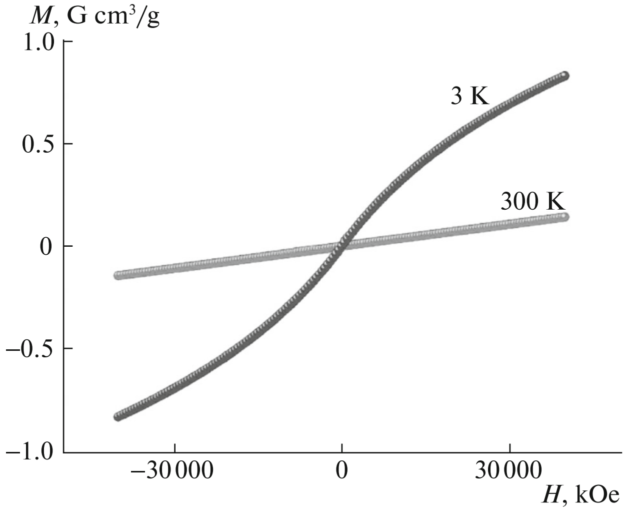

Fig. 3. Field dependences of magnetization at 3 and 300 K, obtained using a SQUID MPMS magnetometer.

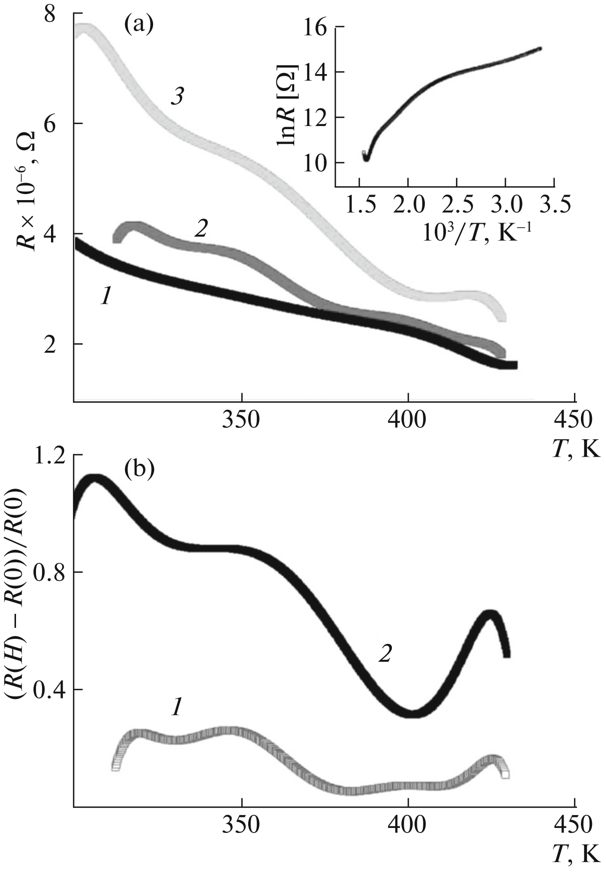

Fig. 4. (a) Dependence of the electric resistance of PEO coatings on samples of titanium of VT1–0 technical grade in magnetic fields of H = (*1*) 0, (*2*) 2, and (*3*) 8 kOe. (b) Dependence of magnetoresistance ($(R(H) - R(0))/R(0)$) in magnetic fields of H = (*1*) 2, and (*2*) 8 kOe on temperature. The insert shows the dependence of the logarithm of electric resistance on the inverse temperature.

($(R(H) - R(0))/R(0)$), passed through a low minimum, reached its maximum at $T = 425$ K, and asymptotically disappeared with a further temperature increase (Fig. 4b).

The effect of magnetoresistance in PEO coatings on samples of titanium of VT1–0 technical grade is explained by the heterogeneity and dispersion in the function of the carrier mobility distribution. Multiple electron scattering in regions with low mobility in heterogeneous semiconductors results in induced disorder: free carriers are frozen in channels with high mobility at some specific temperature. A high mobility channel must be present in the subsurface layer and is not connected to the impurity subband, since its mobility is much higher than that of the bulk channel. The disorder-induced magnetoresistance [13] depends on temperature and is not symmetric relative to the imposed magnetic field.

CONCLUSIONS

Our studies of the magnetic and electric properties of coatings formed in alkaline phosphate–borate–tungstate sol electrolytes with colloid hydroxo-compounds of iron(III) on titanium surfaces by means of PEO established their dependence on the solution pH and/or sodium phosphate structure (basic/acidic). PEO coatings with ferromagnetic characteristics formed on titanium in an electrolyte based on sodium orthophosphate (Na_3PO_4) (PBW; pH ~ 11) upon adding iron(III) oxalate [1–4]. Replacing the sodium orthophosphate with disodium hydrogen phosphate (Na_2HPO_4) and reducing the initial electrolyte pH from 11 to 9.8 result in the formation of a coating with a complex composition that contains phases with different magnetic characteristics. According to our results, the synthesized coatings were characterized by fairly high electric resistance. A correlation between changes in the value of charge carriers' activation energy and the magnetic susceptibility was observed. An increase in the electric resistance in a magnetic field was observed, and the magnetoresistance temperature dependence was investigated.

Our results show that the temperature and external magnetic fields strongly affect the magnetic and electric components of the properties of oxide coatings on titanium. By changing the pH and/or type of phosphate, we can control the magnetic and electric characteristics of multicomponent oxide coatings formed on titanium by means of PEO using alkaline sol phosphate–borate–tungstate electrolytes with colloid hydroxo-compounds of iron(III).

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