

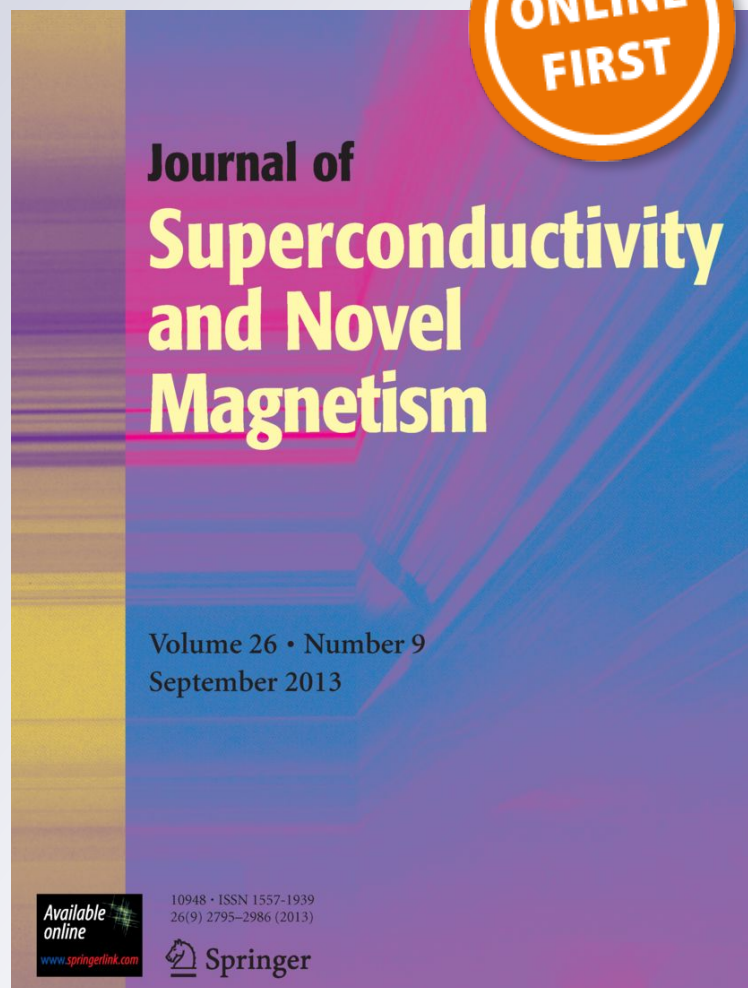
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Peculiarities of Magnetic States of Iron-Cobalt Coatings Formed on Aluminum by Plasma Electrolytic Oxidation

Petr Kharitonkii^{1,4} · Vladimir Rudnev^{2,3} · Elena Sergienko¹ · Kamil Gareev⁴ · Ivan Tkachenko² · Vera Morozova² · Irina Lukiyanchuk² · Maria Adigamova² · Anatoly Frolov³ · Alexander Ustinov^{2,3}

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Abstract Ferromagnetic oxide coatings were formed on aluminum alloy by the plasma-electrolytic oxidation technique in an electrolyte with colloidal particles of iron and cobalt hydroxides. Iron and cobalt are concentrated in the coating pores as a part of nanosized crystallites. The size of individual crystallites in the pores was ~50–100 nm. The deficit of oxygen to form oxides in crystallites shows that the metals in the crystallites are predominantly in a reduced state. It is also possible that the metal or oxide nuclei are surrounded by oxide-hydroxide shells. The coatings obtained within 5 min have a high coercive force $H_c = 1300$ Oe. A theoretical analysis of the magnetic properties of Fe-, Co-containing coatings has been performed using the model of clusters consisting of magnetostatically interacting particles. The theoretical value of the saturation magnetization and the experimental values of the coercive force can be explained with the presence of two phases in the nanoparticles: a large antiferromagnetic or ferromagnetic (hydroxides and/or oxides of iron and cobalt) and a small superparamagnetic (iron, cobalt, magnetite, maghemite).

Keywords Plasma electrolytic oxidation · Fe-, Co-containing coatings · Ferromagnetic properties · Nanocrystallites · Theoretical modeling

1 Introduction

The “ferromagnetic oxide coating/titanium” composites are of interest as absorbers of electromagnetic radiation, micro-transformers, and materials exhibiting specific biological properties when used as implants [1–6]. Recently, it has been shown that oxide coatings with ferro-, ferri-, or anti-ferromagnetic properties can be obtained by plasma electrolytic oxidation (PEO) [7–16] that is the electrochemical oxidation of the surface of the valve metal under spark and microarc electric discharges [17–20]. The following approaches were proposed to obtain PEO coatings with specific magnetic properties on the paramagnetic aluminum and titanium: (1) introduction of dispersed particles of Fe⁰, Co⁰ [7, 8], and iron oxides [9] into the electrolyte for oxidizing; (2) using electrolytes with complex ions, such as EDTA-Fe³⁺ [10, 11] or [FeP₆O₁₈]³⁻ [12]; and (3) application of slurry electrolytes (sols) for the introducing of iron subgroup metals into oxide coatings [12–16]. Aqueous slurry electrolytes were prepared by adding transition metal water-soluble salts to a basic alkaline electrolyte. In this case, the slurry solutions spontaneously precipitate colloidal particles of transition metal hydroxides because of hydrolysis processes. The coatings, in which the iron subgroup metals predominantly were concentrated in the pores and cracks, i.e., in the imperfections of the surface, were obtained in the slurry electrolytes [12]. Fe- and Fe-, Ni-containing coatings formed on aluminum alloy exhibit ferromagnetic properties with the coercive force value of 40–100 Oe at 300 K [13]. The residual magnetic moments

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for both types of coatings are quite stable, which corresponds to ferromagnetic ordering in the oxidized surface layer [12, 21].

Considering the uneven distribution of transition metals on the surface (their concentrating in the pores and cracks) and the slow change of the residual magnetic moment upon annealing the coated samples up to 770 K, one can be suggested the presence in the surface layer of individual islands (clusters) containing ferromagnetic particles in a state close to a single-domain state. For example, in the case of iron, it may be single-domain particles of magnetite or maghemite, including metals and impurities, such as Al and Ni [21, 22].

Theoretical modeling using the model for calculating the residual magnetization confirms the acceptability of these suggestions [21–23]. Calculations show that ferroparticles in clusters do not consist of the iron oxides in a pure form. Possibly, the particles are chemically heterogeneous multiphase systems.

Using a high-resolution scanning electron microscopy confirmed the presence of both nano- and micro-sized particles aggregated into clusters in the pores of coatings [14, 16] (Fig. 1). The composition of nano- and microcrystallites in the pores is markedly different from the average elemental composition of the coating surface [24].

For example, the crystallites of a size of ~ 50 nm in pores of the coatings (Fig. 1a, b) formed on titanium in the electrolyte containing 0.066 M $\text{Na}_3\text{PO}_4 + 0.034$ M $\text{Na}_2\text{B}_4\text{O}_7 + 0.006$ M $\text{Na}_2\text{WO}_4 + 0.04$ M $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ comprise (at.%) 5.3 O, 10.1 Ti, 76.9 Fe, and 7.6 W, while the average iron content in the coating composition is 6.5 at.% [14, 24].

A deficit of oxygen to form stoichiometric oxides allows one to suggest that the nano- and microcrystallites mostly contain reduced metal from electrolyte and substrate [14].

The whole set of the experimental and calculated data suggests that the magnetic characteristics of PEO coatings (their ferromagnetic, ferrimagnetic, or antiferromagnetic properties) are related to the size and composition of metal oxide crystallites in pores of the coatings. Based on the features of the PEO technique, one can assume that the particles consist of a core comprising a reduced metal surrounded by an oxide-hydroxide shell.

The formation of the crystallites in the coating pores is associated with involving the colloidal particles of transition metal hydroxides into the coating material from the slurry electrolytes during discharge phenomena [25]. At the same time, the coatings formed in electrolytes simultaneously containing colloid particles of hydroxides of different nature are poorly studied.

The purpose of this work is obtaining Fe-, Co-containing oxide coatings on aluminum alloy by PEO technique in electrolyte with colloidal particles of cobalt and iron hydroxides and investigation of their composition, structure, and magnetic properties.

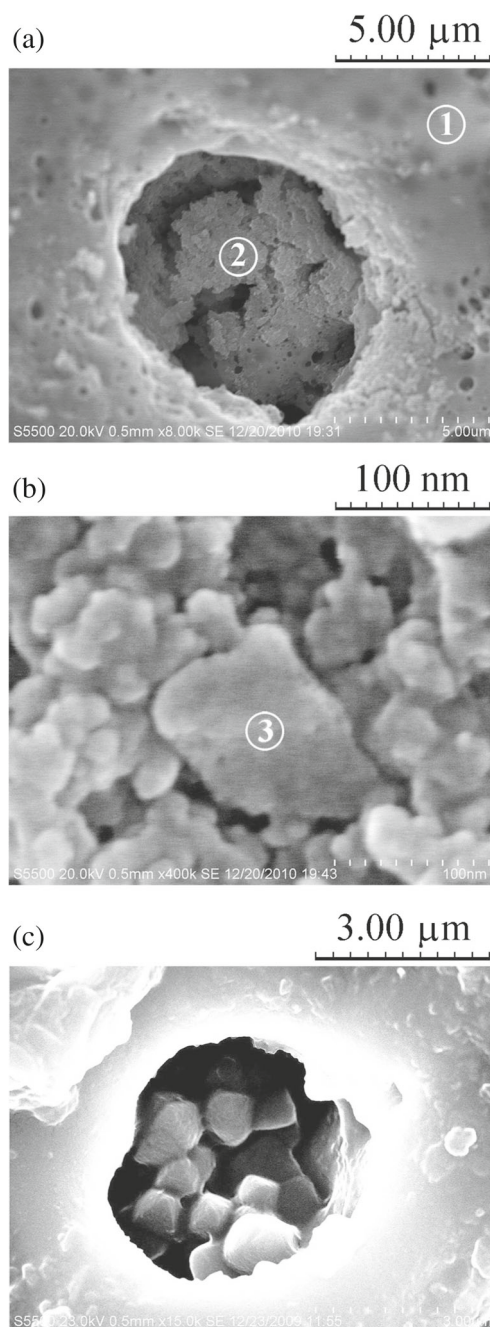


Fig. 1 The examples of clusters of particles in the pores of PEO coatings having ferromagnetic properties: **a, b** nano-sized particles in pores of the coatings on titanium and **c** micro-sized crystallites in the pores of coatings on aluminum

2 Experimental

2.1 Materials

The PEO layers were formed on the samples of AMg5 aluminum alloy (4.8–5.8% Mg, 0.50.8 % Mn, 0.02–0.01% Ti, and the balance Al). Planar samples of $2 \times 2 \times 0.1$ or $1 \times 0.5 \times 0.1$ cm in size were used.

To standardize pre-coating sample surfaces, they were chemically polished to high luster (surface finish classes 8–9) in a mixture of concentrated acids $\text{H}_3\text{PO}_4:\text{H}_2\text{SO}_4:\text{HNO}_3 = 4:2:1$ (by volume) at 110–120 °C. Then the samples were washed with distilled water and dried by air at 70 °C.

We used aqueous electrolyte (mol/L) $0.066\text{Na}_3\text{PO}_4 + 0.034\text{Na}_2\text{B}_4\text{O}_7 + 0.006\text{Na}_2\text{WO}_4$ (PBW-electrolyte) into which iron(III) oxalate and Co(II) acetate were added (PBWFeCo-electrolyte) to form Fe + Co-containing coatings on aluminum alloy. The Fe(III) and Co(II) concentrations were each equal to 0.04 mol/L. Fe(III) oxalate and Co(II) acetate were used, along with the following commercially available reagents: $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ of chemically pure grade and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ of analytical grade. At the preliminary stage, the PBWFe and PBWCo electrolytes were prepared in water with doubled concentrations of iron and cobalt salts, respectively, then mixed in equal ratios and stirred for 1 h. The obtained electrolyte was a dark suspension (pH 8–9) with insoluble compounds of iron and cobalt, including hydroxides, in colloid forms.

The electrochemical cell for anodization consisted of a vessel with a volume of 1 L made of thermally stable glass; a cathode in the form of a coiled hollow pipe of nickel alloy, through which cold tap water was fed to make a cooler; and a magnetic stirrer for electrolyte stirring. A PC-controlled TER4-100/460N thyristor (Russia) working in the unipolar mode was used as the power source. The coatings were formed via the anodic polarization of aluminum samples of AlMg5 alloys in the galvanostatic mode with an effective current density of 10 A/dm² over periods of 5, 10, and 20 min. The electrolyte temperature during the plasma electrolytic process did not exceed 35 °C.

2.2 Coating characterization

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

The thickness of the coatings was measured using an eddy-current thickness gage VT-201 (Russia).

The element composition and coating surface images were obtained using an electron probe micro-analyzer JXA 8100 (Japan) with an INCA energy spectrum analyzer (UK) (hereinafter referred to as XSA). The averaged element composition was determined on the basis of the results of scanning three to five surface parts of an area of ~250 μm² 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 (EDA), we determined the element composition of individual coating parts by focusing the probe beam at the site radius of 1 to 10 nm. In both cases, gold was preliminarily sputtered on films to prevent the surface charging.

The samples' magnetization (M) in magnetic moment units was measured on a Quantum Design SQUID MPMS XL magnetometer at temperatures of 300 down to 2 K. During the measurements, the sample plane was placed parallel to the direction of the magnetic field. The M values were normalized for the sample weight (coating + metal). Note that the coating proportion in the samples was of 1–3 wt%. The M dependences (emu/g) on H (Oe) were recorded at temperatures 300 and 2 K and in fields of up to 30 kOe.

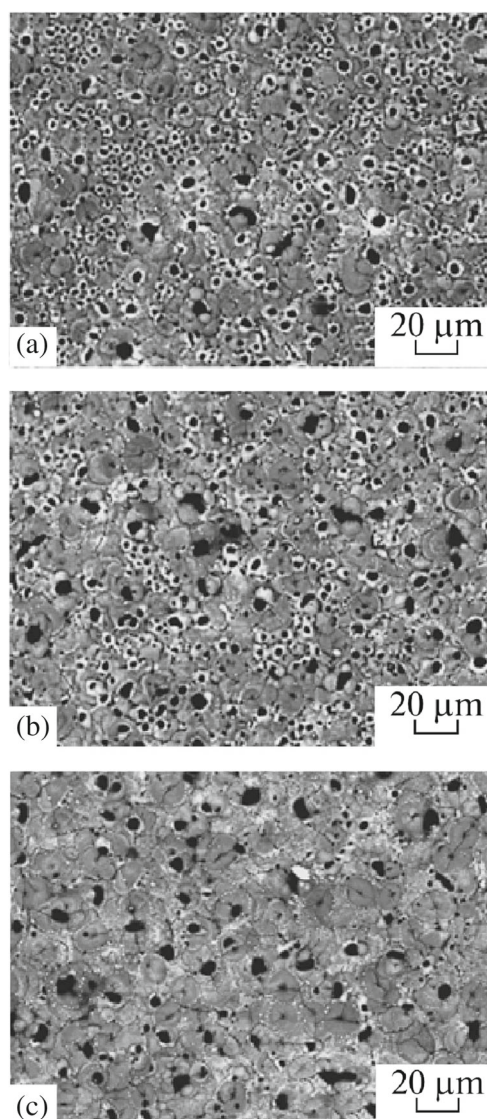


Fig. 2 Morphology of coating surface, phase representations. Black spots are pore openings. Coatings were formed in PBWFeCo electrolyte within **a** 5, **b** 10, and **c** 20 min

Table 1 Effect of processing on thickness of oxide coatings and value of coercive force H_c

Electrolyte	Processing time (min)	Thickness (μm)	Elemental composition (at %)							H_c (Oe)	
			C	O	Al	P	Fe	Co	W	$T = 300\text{ K}$	$T = 2\text{ K}$
PBWFeCo	5	11.5 ± 2	12.1	58.9	23.6	0.5	1.9	1.9	0.2	-21/100	-1300/1300
	10	12.7 ± 2	9.0	60.2	25.3	0.5	1.9	2.2	0.2	-113/113	-260/260
	20	16.7 ± 1	13.4	56.4	24.8	0.6	1.8	1.5	0.2	-110/113	-252/251
PBWFe, $C_{\text{Fe(III)}} = 0.03\text{ mol/L}$	10	13.0 ± 2	25.0	50.0	25.0	1.0	5.0		1.0	174	263 (10 K)

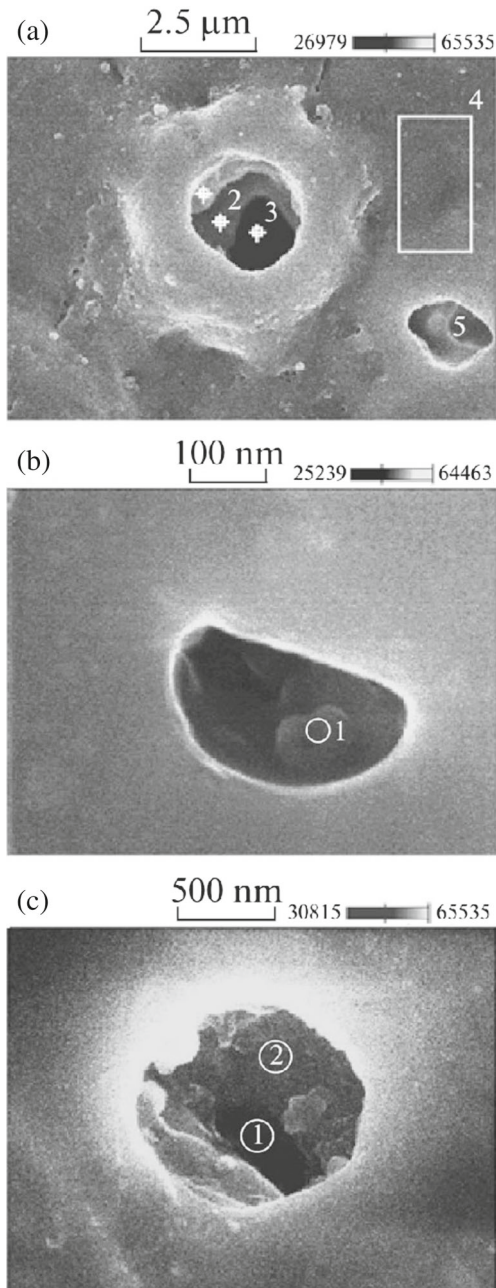


Fig. 3 Pore openings with crystallites. Coatings were formed in PBWFeCo electrolyte within **a** 5, **b** 10, and **c** 20 min

3 Results and Discussion

3.1 Surface Morphology

Figure 2 shows the surface morphology of the coating formed in PBWFeCo-electrolyte within 5, 10, and 20 min. Obviously, the pore size increases with the processing time.

3.2 Elemental and Phase Composition of Coatings

As to XRD analysis, all coated samples contain $\gamma\text{-Al}_2\text{O}_3$. Elemental coating composition is given in Table 1. Independently of processing time, the coatings' compositions are about the same. The coatings contain ~ 2 at% Fe and 2 at% Co.

3.3 Pore Structure and Crystallite Composition

Figure 3 shows the pore openings. There are crystallites in the pores. According to energy dispersive analysis, the elemental composition of the crystallites is presented in Table 2. The comparison of data in Tables 1 and 2 graphically represented in Fig. 4 shows that the iron and cobalt are concentrated in the pores within the crystallites. We should mention that the size of individual crystallites in the pores was $\sim 50\text{--}100\text{ nm}$ (Fig. 3). The deficit of oxygen to form oxides in crystallites shows that the metals in the crystallites were predominantly in a reduced state, in agreement with the conclusions drawn in [12, 14]. It is possible that the metal nuclei are surrounded by oxide-hydroxide shells. The proposed reasons for metal reduction in electric breakdown channels call for the existence of a reducing atmosphere of,

Table 2 Composition (at.%) of crystallites in the pores of the coatings formed on aluminum alloy in the PBWFeCo electrolyte

Processing time (min)	O	Al	Fe	Co
5	13.7	22.1	25.6	38.7
10	12.1	13.1	29.3	45.6
20	18.3	26.6	29.3	24.8

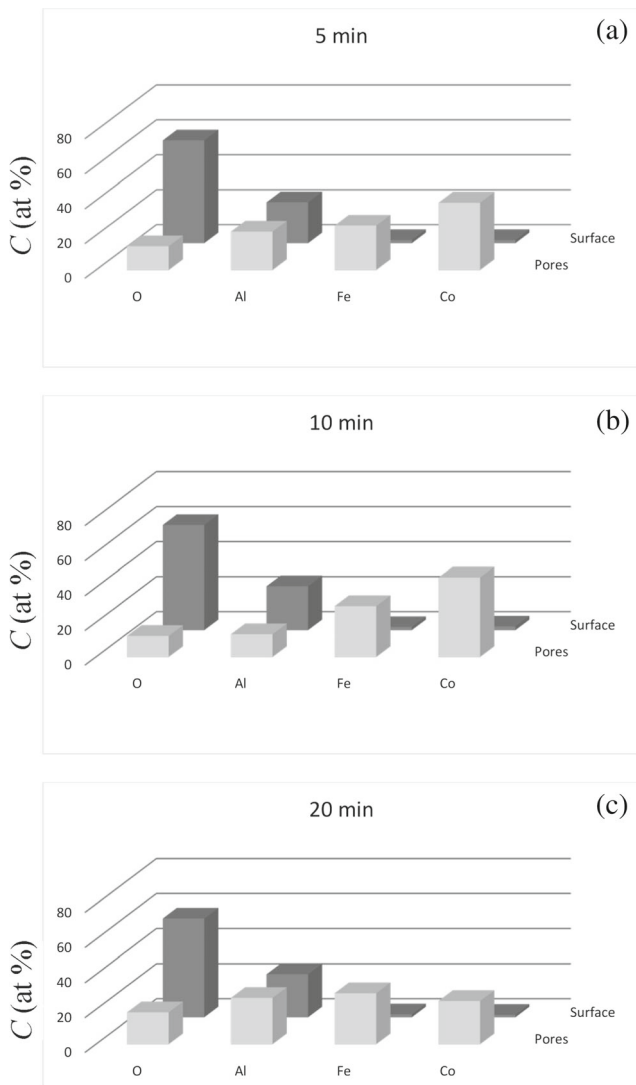


Fig. 4 Comparison of the composition of pores and surface of the coatings formed within 5 (a), 10 (b), and 20 min (c)

e.g., hydrogen, due to the thermolysis of water under the effect of elevated temperatures.

3.4 Magnetic Properties

Examples of the magnetization curves of the samples are shown in Fig. 5, and data on the coercive force are given in Table 1. As can be seen from the data shown in Table 1 and Fig. 5, all of the coatings formed on aluminum alloy in PBWFeCo electrolyte were magnetically active. At low temperatures (2 K), the samples formed in this electrolyte manifest typically ferromagnetic properties. At room temperatures, upon an increase in the external magnetic field intensity, magnetization diminishes i.e., the samples become ferrimagnetics.

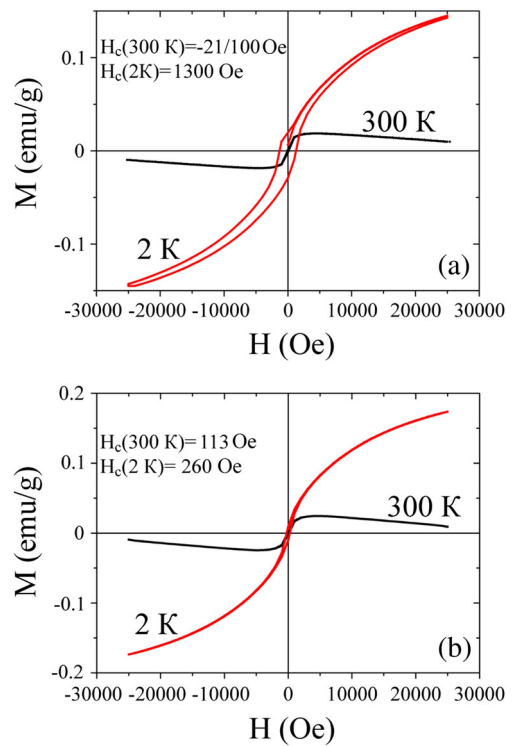


Fig. 5 Magnetization curves for aluminum samples with PEO coatings formed in PBWFeCo electrolyte within a 5 and b 10 min

We should mention that ferromagnetic behavior was observed earlier for coatings with iron compounds formed on titanium and aluminum in PBWFe electrolyte [12–14] at both room temperature and $T \leq 10$ K. Introducing Co into coatings with iron compounds thus affects the exchange interactions in magnetically active particles and (eventually) the mechanism for the emergence of magnetism.

The coercive force value $H_c = 1300$ Oe at 2 K for coatings formed within 5 min in PBWFeCo electrolyte (Table 1) is anomalously high. Apparently, a high H_c value must be related to the single-domain state of magnetic particles in the coatings at such temperatures. On the other hand, the H_c values measured at 2 K for coatings formed by PEO in PBWFeCo electrolyte within 10–20 min lie in the range of 217–260 Oe (i.e., substantially lower). These facts can be associated with different sizes of crystallites in the pores of the coatings obtained within 5 min and those formed within a greater processing time. As can be seen from Fig. 2, with an increase in processing time, electric spark and then more powerful arc discharges form defect-rich (from the physical standpoint) coatings with larger pores. Apparently, the sizes of the crystallites in the pores increase accordingly. They become multi-domain with roughly the same H_c value. The size and structural features of the crystallites in pores of small geometric size can be responsible for the noticeable asymmetry in the H_c value measured at 300 K for coatings formed within 5 min (Table 1).

3.5 Theoretical Modeling

A residual magnetization calculation model can be used to describe the magnetic properties of the samples of oxide coatings containing Fe + Co. The model considers clusters of dipole-dipole interacting chemically in homogenous small particles [22]. Clusterized particles provide ferromagnetic properties of the coatings and have a mean size of about 10–100 nm; therefore the particles are single domain or superparamagnetic. At a sufficiently high concentration of superparamagnetic particles in clusters, the sample may have a residual magnetization [23].

Let us examine the ensemble (cluster) of identical single-axis chaotically distributed particles which have saturation magnetization I_s . Assume that α and β are the relative number of magnetic moments oriented towards or against external field H accordingly. Then $\zeta = \alpha - \beta = I/(\eta I_s)$ is the ensemble's magnetization, where η is the volumetric concentration of iron oxide particles in the specimen. The equation for ζ is

$$\zeta = 1 - 2 \int_{-\infty}^{-x_0} \varphi(x) dx, \tag{1}$$

where $x_0 = \frac{H_0 + H + \langle Hi \rangle}{\sigma}$, H_0 is the magnetic reversal critical field of the particle, and $\langle Hi \rangle$ and σ are an average and mean-square values of random fields of dipole-dipole particles' interaction accordingly. In the approaching of the local field, the density of distribution $\phi(x)$ can be gotten with the modified moment's method [26]. On integrating (1) taking into account decomposition into Gram-Charlier series of $\phi(x)$, we get an expression for ζ :

$$\zeta = \operatorname{erf} \left(\frac{x_0}{\sqrt{2}} \right) - \varphi_u(x_0) \times \left[\frac{\gamma_1}{3} H_2(x_0) - \frac{\gamma_2}{12} H_3(x_0) - \frac{\gamma_1^2}{36} H_5(x_0) \right]. \tag{2}$$

Here, γ_1 is asymmetry and γ_2 is the distribution function excess, $H_n(x_0)$ is Hermite polynomials, $\operatorname{erf} \left(\frac{x_0}{\sqrt{2}} \right)$ is the error function integral, and $\varphi_u(x_0)$ is the density of distribution by an average equal to zero and dispersion equal to one.

Let us solve the inverse problem (1) and estimate the saturation magnetization of the samples. The highest value of the residual magnetic moment of the samples per unit mass (~ 0.03 emu/g) was observed at the temperature 2 K. The obtained calculated saturation magnetization was about 1.5–6.5 emu/cm³. The scatter can be due to the fact that a volume concentration of clusters in the samples is known and quite small, and the concentration of particles in the cluster is not determined precisely but is probably about 0.1–0.3.

In order to explain such a small magnetization value, let us consider a two-phase particle (Fig. 6). Then, a mean saturation magnetization of a particle

$$I_s = pq[(1 - \varepsilon)M_1 + \varepsilon M_2], \tag{3}$$

where M_1 and M_2 are spontaneous magnetization of the phases. Therefore, the obtained saturation magnetization value can be explained with the presence of two phases in the nanoparticles: a large antiferromagnetic or ferrimagnetic (hydroxides and/or oxides of iron and cobalt) and a small superparamagnetic (iron, cobalt, magnetite, maghemite).

Let us consider the model of two-phase particles proposed in [27]. The model of the two-phase particle with an infinitely thin boundary is shown in Fig. 6. A cuboid of $a \times pa \times qa$ size (a , a characteristic size of the order of the single-domain size; p and q , elongations on axes y and z , respectively) divided by the boundary parallel to the plane (xz) into two phases of widths $p(1 - \varepsilon)$ and $p\varepsilon$. Each phase is a crystallographically uniaxial ferromagnet with easy axis parallel to one of the coordinate axes, the spontaneous magnetization M_1 and M_2 and the crystallographic anisotropy constant of K_{11} and K_{12} . The phases are considered uniformly magnetized, and the direction of magnetization vectors in them is given by the spherical angles θ and ϕ .

If we neglect the magnetoelastic effects so the magnetic energy of the grain consists of three parts (the energy

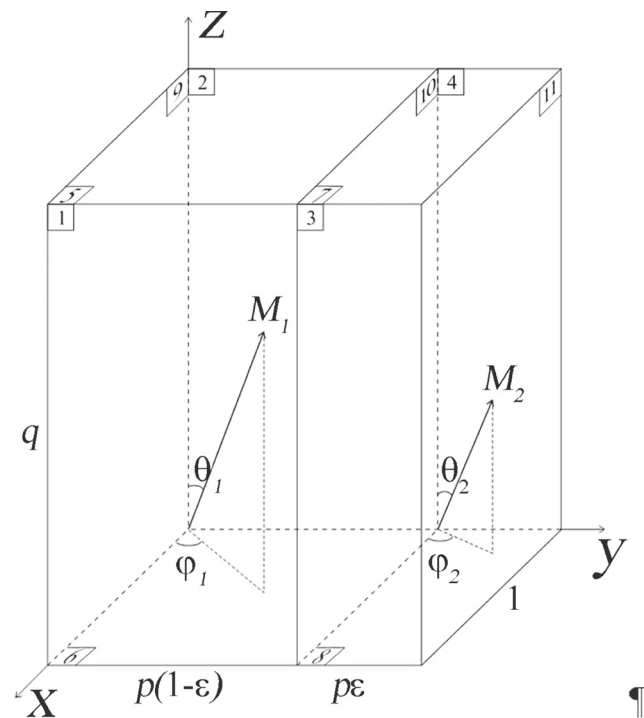


Fig. 6 The model of the two-phase ferromagnetic particle

crystallographic anisotropy, the magnetostatic energy, and the Zeeman energy):

$$E = E_0 + qa^3 \left\{ \left[M_1^2 (N_{1x} - N_{1z}) + K_{11} (1 - \varepsilon) \right] \sin^2 \theta_1 + \left[M_2^2 (N_{2x} - N_{2z}) + K_{12}\varepsilon \right] \sin^2 \theta_2 + M_1 M_2 N_{3x} \times \sin \theta_1 \sin \theta_2 + M_1 M_2 N_{3z} \cos \theta_1 \cos \theta_2 - H M_1 (1 - \varepsilon) \cos \theta_1 - H M_2 \varepsilon \cos \theta_2 \right\} \quad (4)$$

Here, E_0 is a part of energy which does not depend on the angles, N_i is demagnetizing factors for a two-phase cuboid [28], $\varphi_1 = \varphi_2 = 0$, $p = 1$.

In this case, the four equilibrium states of magnetic moments of phases are possible [27]: (1) $\theta_1 = 0$, $\theta_2 = 0$; (1) $\theta_1 = \pi$, $\theta_2 = \pi$; (3) $\theta_1 = 0$, $\theta_2 = \pi$; and (2) $\theta_1 = \pi$, $\theta_2 = 0$. Consequently, the ensemble consists of four types of particles:

$$\begin{aligned} H_{23} &= H_{k1} + H_{N1} - H_{2N3}, & H_{24} &= H_{k2} + H_{N2} - H_{1N3}, \\ H_{41} &= H_{k1} + H_{N1} + H_{2N3}, & H_{31} &= H_{k2} + H_{N2} + H_{1N3}, \end{aligned} \quad (5)$$

where H_{lm} is critical l to m states transition fields for a particle,

$$\begin{aligned} H_{k1} &= 2K_{11}/M_1, & H_{k2} &= 2K_{12}/M_2, & H_{N1} &= 2M_1(N_{1x} - N_{1z})/(1 - \varepsilon), \\ H_{N2} &= 2M_2(N_{2x} - N_{2z})/\varepsilon, & H_{1N3} &= M_1 N_{3z}/\varepsilon, & H_{2N3} &= M_{12} N_{3z}/(1 - \varepsilon). \end{aligned}$$

The probability of particles being in equilibrium states is proportional to $\exp(-E/kT)$. It is clear that most of the particles are in the third and fourth states, i.e., when the magnetic moments of phases are opposite to each other. If their form is close to cubic, $H_{N1} = H_{N2} = 0$. Then, the transition to the first state with the magnetic moments of the phase aligned with the external field is mainly determined by the critical fields H_{41} и H_{31} . The crystallographic anisotropy makes the largest contribution to these fields. The H_{31}/H_{41} ratio is much greater than 1, i.e., a magnetically weak phase ($M_1 \ll M_2$) has a higher coercivity (most likely due to the presence of cobalt). Thus, a magnetically strong phase occupies a significantly smaller volume ($\varepsilon \ll 1 - \varepsilon$) but this phase is superparamagnetic and is stabilized by a highly coercive magnetically weak phase. In addition, let us notice that some asymmetry of the hysteresis loop is probably related to the phenomenon of the exchange or unidirectional anisotropy of cobalt oxide [29, 30]. Adding this energy to (2) ($E_a = -\delta k_d \cos \theta$ where δ is the thickness of the antiferromagnetic layer and k_d is its exchange anisotropy constant), therefore, $\delta \ll \varepsilon$. Typically, the thickness of the antiferromagnetic layer is small. It should be noted that temperature behavior (Table 1) is opposite to the usually observed during unidirectional anisotropy [29, 30]. Therefore, our suggestion requires additional research.

4 Conclusion

Using the slurry electrolytes containing colloidal particles of iron and cobalt hydroxides, alumina coatings modified by iron and cobalt were formed on aluminum alloy by the plasma electrolytic oxidation technique. In the pores of the coatings, the crystallites were found in which the concentration of iron and cobalt is significantly higher than their average concentration in coating composition. The deficit of oxygen to form oxides in crystallites shows that the metals in the crystallites were predominantly in a reduced state. Crystallite formation is the result of spark and microarc electrical discharges implemented during PEO. The coatings formed manifest ferromagnetic properties. The coatings formed within 5 min are characterized by abnormally high values of the coercive force at 2 K. The results obtained in this study and previously allow one to suggest that the ferromagnetic properties of the coatings are due to the presence of iron- and cobalt-containing nanocrystallites in the pores. Theoretical analysis of magnetic properties of Fe-, Co-containing coatings allows one to make the following conclusion: the hysteresis characteristics of the coatings under study (low value of residual magnetic moment, high or abnormally high coercivity under certain conditions, the asymmetry of the magnetization curves) can be explained by the presence of antiferromagnetic and superparamagnetic phases in the nanoparticles and enough strong magnetostatic interaction both between the particles and between the phases.

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