
COLLOID CHEMISTRY
AND ELECTROCHEMISTRY

Structures and Magnetic Properties of Iron- and Cobalt-Containing Oxide Coatings on an Aluminum Alloy Formed in Electrolytes via Plasma Electrolytic Oxidation

V. S. Rudnev^{a,b}, V. P. Morozova^a, I. V. Lukiyanichuk^a, M. V. Adigamova^a,
I. A. Tkachenko^a, A. Yu. Ustinov^{a,b}, P. V. Kharitonovskii^a, and A. M. Frolov^b

^a Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia

^b Far East Federal University, Vladivostok, 690600 Russia

e-mail: rudnevvs@ich.dvo.ru

Received July 26, 2013

Abstract—The effect of the nature of the supporting electrolyte in the composition of electrolytic suspensions containing dispersed particles of Fe(III) and Co(II) hydroxides, and of anodic and bipolar anodic–cathodic polarization on features of the formation, composition, and magnetic characteristics of oxide coatings is studied. In all cases, iron and cobalt are incorporated into the coatings and are concentrated predominantly in pores. The pores of the coatings include particles consisting of the reduced metals, presumably surrounded by oxide or hydroxide shells. The electrolyte composition affects the concentration and ratio of the metals in the particles. A correlation is observed between the ferro- or ferrimagnetism of the coatings and the content and ratio of cobalt and iron in the pores.

Keywords: anodic oxidation, aluminum, spark discharges, electric arc, Fe and Co containing coatings, particles in the pores, ferromagnetics, ferrimagnetics.

DOI: 10.1134/S0036024414050264

INTRODUCTION

It was recently shown that Fe-, Co-, and/or Ni-containing oxide coatings on aluminum and titanium formed by one-stage plasma electrolytic oxidation (PEO) exhibit ferro- or ferrimagnetic properties [1–9]. PEO is the electrochemical anodic or alternating current anodic–cathodic oxidation of the metal and alloy surface in aqueous electrolytes at voltages that induce spark or arc discharges [10–17]. Under the effect of the electric discharges, the electrolyte components are involved in the formation of the coatings. They can participate in plasmachemical reactions in the discharge channel and are subjected to high temperatures in the vicinities of discharges. The coatings are formed due to both electrochemical oxidation on the surface regions free of discharges and the high-temperature interactions and transformations of the components of the electrolyte and support at the local sites of discharges. These features of the process allow us to form multicomponent coatings with certain physicochemical characteristics by introducing the appropriate precursors into the electrolytes.

PEO is traditionally used to prepare protective coatings on the surfaces of valve metals and alloys [10–14]. Application of the method to the formation of multicomponent oxide coating/metal systems, including those with certain catalytic, biocompatible, radiative, indicator, magnetic, and other characteris-

tics, has been studied in recent years [1–9, 15–21]. To form coatings with the ferromagnetic properties, solid micro- or nanoparticles of Fe⁰ [1], Fe₂O₃ [4], and Co⁰ [6] and complex ions EDTA–Fe³⁺ [7] are introduced as precursors into the electrolytes, thereby creating conditions for the formation of colloidal metal hydroxide particles inside them [2, 3, 5, 8, 9].

To form Fe-, Co-, and/or Ni-containing coatings on aluminum and titanium, we propose an alkaline electrolyte containing 0.066 mol/L Na₃PO₄ + 0.034 mol/L Na₂B₄O₇ + 0.06 mol/L Na₂WO₄ (PBW electrolyte). The introduction of Co(II), Ni(II), and/or Fe(III) acetates and oxalates into this electrolyte produced a suspension containing dispersed particles of hydroxides of the above metals [2, 3, 5, 8, 9]. The formed coatings displayed ferro- or ferrimagnetic properties. The metals are concentrated in the coating pores in the composition of crystallites 50–100 nm in size and joined in agglomerates. According to the existing data, iron and/or cobalt are found in the crystallite composition predominantly in the reduced state, and the presence of these particles in the pores determines the magnetic properties of the coatings [5, 8, 9].

The approach proposed in [2, 3, 5, 8, 9] requires no preliminarily prepared dispersed metallic or oxide powders and allows us to simultaneously introduce different metals from the electrolyte into the coating

composition. All experiments up to now have been performed with coatings formed by the anodic polarization of metallic samples in electrolytic suspensions containing dispersed (colloidal) particles of hydroxides of the above metals, and others formed by introducing acetates or oxalates of these metals into supporting aqueous PBW electrolyte. The aim of this work is to determine if the behavior established for the structures and magnetic characteristics of the coatings are observed when they are formed in electrolytic suspensions based on supporting alkaline electrolytes with different compositions and when both anodic and bipolar anodic–cathodic polarization are used.

EXPERIMENTAL

Planar samples of AMg5 aluminum alloy $2 \times 2 \times 0.1$ or $1 \times 0.5 \times 0.1$ cm in size were used. To remove the surface layers of metal oxides and standardize their surfaces, the samples were polished in a mixture of concentrated acids $\text{HNO}_3 : \text{H}_2\text{SO}_4 : \text{H}_3\text{PO}_4 = 1 : 2 : 4$ (vol/vol/vol) at $100\text{--}120^\circ\text{C}$ with exposure of 0.5 min prior to anodization. The polishings were performed five to six times, accompanied by washing with water between polishings until mirror surfaces were formed [22]. After chemical polishing, the samples were washed first with running water and then with distilled water and dried in air at 70°C .

Four supporting electrolyte solutions (mol/L) were prepared to obtain coatings containing both Fe and Co: $0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7 + 0.06 \text{ Na}_2\text{WO}_4$ (PBW electrolyte), $0.066 \text{ Na}_3\text{PO}_4 + 0.034 \text{ Na}_2\text{B}_4\text{O}_7$ (PB electrolyte), $0.1 \text{ Na}_2\text{B}_4\text{O}_7$ (B electrolyte), and $0.05 \text{ Na}_2\text{SiO}_3$ (Si electrolyte). As in [9], 0.04 mol/L Fe(III) and 0.04 mol/L Co(II) were additionally introduced into these supporting solutions. Iron(III) oxalate and cobalt(II) acetate were used. The following commercial reagents were used: $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (reagent grade) and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ (analytical grade).

The sequence of preparing the Fe- and Co-containing electrolytes was similar to the one described in [9]. Solutions with doubled concentrations of iron and cobalt were simultaneously prepared using distilled water. Each prepared solution was added to the selected supporting electrolyte. The obtained solutions were then poured in equal ratios and stirred for 1 h. The obtained Fe- and Co-containing electrolytes were dark suspensions (pH 7–8) with insoluble iron and cobalt compounds, including hydroxides, as colloids and suspensions. Depending on the type of the supporting solution, the working electrolytes were designated PBWFeCo (as in [9]), PBFeCo, BFeCo, and SiFeCo, respectively.

Our electrochemical cell for anodization consisted of a 1 L heat-resistant beaker, a coil-shaped cathode made from a hollow pipe of nickel alloy that simultaneously served as a cooler, and a magnetic stirrer. The

temperature of the electrolyte during the plasma electrolytic process did not exceed 35°C . A computer-controlled TER4-100/460N reversible thyristor unit served as the power source. When using the PBWFeCo, PBFeCo, and BFeCo electrolytes, the coatings were formed by anodic polarization of the samples in the galvanostatic regime. With the PBWFeCo and PBFeCo electrolytes, the process was conducted at effective current density $i = 0.1 \text{ A/cm}^2$ for 10 min. We chose $i = 0.3 \text{ A/cm}^2$ for the BFeCo electrolyte because qualitative coatings could not be obtained at a lower current density. The time of formation was reduced to 5 min, since the final voltage drops substantially at longer durations of the process because of the predominant dissolution of the formed coating. Bipolar anodic–cathodic polarization was used to produce coatings in the SiFeCo electrolyte: the effective densities of the anodic and cathodic currents were $i_A = i_C = \pm 0.1 \text{ A/cm}^2$, pulse duration was $\tau_A = \tau_C = 0.02 \text{ s}$, and the times of formation were 5 and 10 min. The coatings were obtained on two samples, each of which acted alternately as an anode or cathode. The coating thickness was measured with a VT-201 eddy-current thickness gauge (Russia).

X-ray diffraction analyses of the samples with the coatings were performed on a D8 ADVANCE X-ray diffractometer (Germany) using CuK_α radiation. The signal was accumulated for 10 s. The EVA search program with the PDF-2 database was used to decode the obtained spectra.

Data on the elemental composition of the coatings at the depth to $2\text{--}5 \mu\text{m}$ and images of the surface were obtained using a JXA 8100 X-ray spectral microanalyzer (Japan) with an INCA energy dispersive attachment (Great Britain). The data on the elemental composition were obtained by scanning at least three surface areas $300 \times 300 \mu\text{m}$ in size at different coating sites. The resulting data were then averaged. A high-resolution Hitachi S5500 scanning electron microscope (SEM) (Japan) with a Thermo Scientific attachment for energy dispersive analysis (United States) was used to obtain information about the distribution of elements over particular morphological aggregates. In both cases, gold was sputtered on the coatings prior to analysis to prevent surface charging.

The magnetization of the samples with the coatings was measured on a SQUID MPMS XL magnetometer (Quantum Design, Germany). When measuring, the plane of the sample was parallel to the direction of the magnetic field. The dependences of sample magnetization M (emu/g) on the strength of external magnetic field H (Oe) were detected at temperatures 300 or 340 K in fields lower than 30 kOe. The values of M were calculated with allowance for the total weight of the samples.

RESULTS AND DISCUSSION

The dependences of the change in voltage on the electrodes vs. the times required to prepare the coat-

ings in our electrolytes are shown in Fig. 1. PBW electrolyte was proposed for the PEO formation of protective decorative coatings on the aluminum and titanium alloys [23]. The voltage on the electrodes (U) increases monotonically during galvanostatic buildup in this electrolyte on AMg-type alloys [23, 24]. As can be seen from curve 1 in Fig. 1a, U ceases to grow at buildup times of more than 300 s upon adding cobalt acetate and iron oxalate to the electrolyte. This is likely due to the etching action of acetate and oxalate ions on aluminum and its oxide and thus to an increased contribution from the dissolution currents to coating formation. This is confirmed by a notable drop in U (curve 2, Fig. 1a) for the PBFeCo electrolyte, which contains no sodium tungstate and is a passivator of aluminum and its alloys, and by the growth of a secondary layer on the coating (Fig. 2b). The latter is characteristic of moving from electrolytes in which coatings are formed to those in which formation is impossible because of dissolution [25].

The same effect is observed during the formation of coatings in borate electrolyte, where the growth of the PEO coatings was possible under the experimental conditions only at enhanced current densities and within times no longer than 5 min (BFeCo electrolyte, Figs. 1c and 2c). In the SiFeCo electrolyte, the secondary coating likely grows for the same reasons and covers the whole surface in 10 min (Figs. 2d and 2e). Since two identical samples were placed in the cell, connected to different poles of the current source, and alternately polarized (anodically and cathodically) for anodic–cathodic formation, the behavior of the voltage in the anodic and cathodic periods was symmetrical (Fig. 1b).

As can be seen from the data in Fig. 2a, the surface of the coating obtained in PBWFeCo electrolyte has alternating elevations, depressions, and pores (break-down channels). Two layers are observed on the surfaces of coatings obtained in PBFeCo and BFeCo electrolytes and formed within 5 min in the SiFeCo electrolyte (Figs. 2b–2d). The coating surface obtained within 10 min in the same electrolyte is evidently the surface of a secondary layer and also contains melted elevations, depressions, and pores.

The thicknesses and elemental compositions of the surface areas (2–5 μm) averaged over the surfaces of the coatings are given in Table 1. It can be seen that both parameters depend on the electrolyte composition and conditions of formation. Note that iron and cobalt are incorporated into the coatings in all cases. In other words, the application of electrolytic suspensions based on supporting electrolytes with different compositions and anodic or bipolar anodic–cathodic conditions of formation yield the same qualitative result. The nature of the electrolyte and possibly the conditions of formation affect the quantitative content of metals in the coatings. If iron and cobalt are introduced into the electrolytes in a molar ratio of 1 : 1, they are found in approximately the same ratio in the coat-

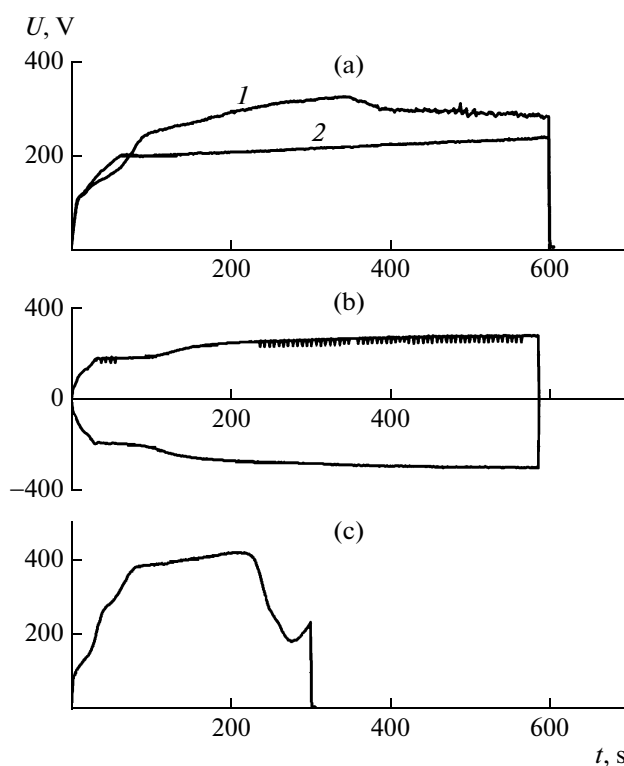


Fig. 1. Effect of electrolyte composition on changes in electrode voltage with the time of formation. Electrolytes: (a, curve 1) PBWFeCo, (a, curve 2) PBFeCo, (b) SiFeCo, and (c) BFeCo. (a, c) Anodic and (b) bipolar anodic–cathodic regimes.

ings for PBWFeCo and PBFeCo electrolytes only. Cobalt predominates in the composition of coatings formed in BFeCo electrolyte, while coatings formed in the SiFeCo electrolyte mostly contain iron. It is likely that features of the hydrolysis of the iron and cobalt salts introduced into the electrolytes differed in composition, and the initial values of the pH affected the quantitative content of these metals in the coatings. One feature of the elemental composition is the notable content of carbon in the coatings, which could be due to both the incorporation of carbon from the electrolyte during the formation of the coatings and the contamination of the surfaces with this element when manipulating the samples. According to the X-ray diffraction data (Table 1), reduced metals Fe^0 and Co^0 were found in the coating composition in a number of cases.

All of the prepared samples exhibit either ferromagnetic (Fig. 3a, curves 2–4) or ferrimagnetic (Fig. 3a, curve 1) characteristics. The samples can be arranged in the following order according to the magnetization in the region of strong external fields ($H > 5000$ Oe): SiFeCo > PBFeCo > BFeCo > PBWFeCo. This order correlates with the average iron content in the analyzed surface layer of the coatings. The higher the iron content (Table 1), the higher the magnetization of the sample in strong fields (Fig. 3a).

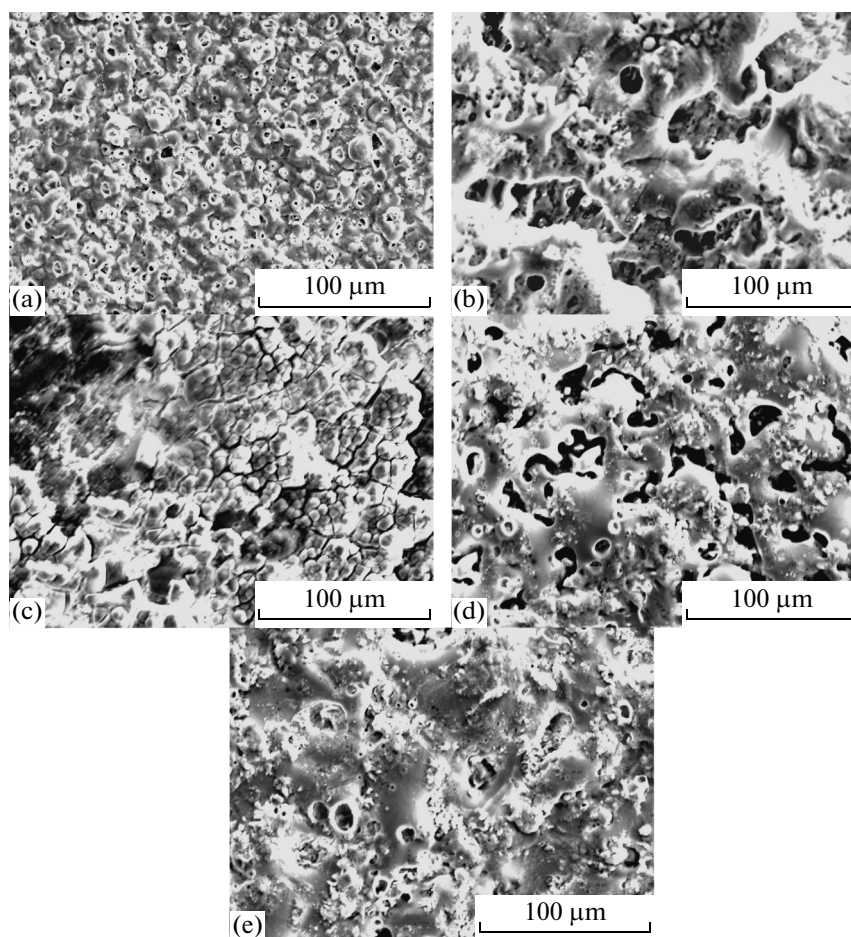


Fig. 2. Surface morphology of the coatings formed in electrolytes: (a) PBWFeCo, (b) PBFeCo, (c) BFeCo, (d) SiFeCo, 5 min; (e) SiFeCo, 10 min. (a–c) Anodic and (d, e) bipolar anodic–cathodic regimes.

The coercive force of the samples measured at room temperature (Table 1, Fig. 3) diminishes in the order $\text{PBFeCo} > \text{PBWFeCo} > \text{BFeCo} > \text{SiFeCo}$. It is difficult to correlate the value of coercive force with the average contents of iron and cobalt in the coatings or with their ratio. In coatings studied earlier [5, 8, 9] with ferro- or ferrimagnetic characteristics formed in PBWFe and PBWFeCo electrolytic suspensions, iron and cobalt were concentrated in the coating pores, where they existed in the composition of nanosized crystallites joined into agglomerates. These crystallites were evidently particles of the reduced metals encapsulated in oxide shells. The results from experiments [5, 8, 9] and simulations [26] suggest that the magnetic characteristics of the coatings were determined predominantly by the composition and structure of the iron- and cobalt-containing crystallites in the coating pores, and by the behavior of exchange interactions in them.

It follows from microscopic studies of the pore orifices in the investigated coatings that most of them contained agglomerates of crystallites (Fig. 4), as in [5, 8, 9]. The compositions of the agglomerates or the bottom of the pores were examined using the microscope's energy dispersive attachment, and randomly

chosen pores found in both the primary and secondary layers were studied. The elemental composition of the agglomerates and structures on the pore bottoms, averaged for three or more pores, is given in Table 2.

The surface areas for which the elemental composition of the structures in the pores and surfaces of coatings formed in SiFeCo electrolyte within 10 min in the anodic–cathodic regime are shown as an example in Fig. 4a. The elemental compositions (at %) determined for the surface areas are presented below:

Surface area 1, elevation near pore:

3.6 C, 47.2 O, 2.4 Na, 0.4 Mg, 3.9 Al, 18.2 Si, 23.3 Fe, 1.1 Co.

Surface area 2, elevation near pore:

9.6 C, 45.2 O, 1.7 Na, 3.8 Al, 15.1 Si, 22.2 Fe, 2.5 Co.

Surface area 3, structures in pore (agglomerate of crystallites):

6.8 O, 2.3 Si, 86.4 Fe, 4.5 Co.

Surface area 4, structures in pore (pore bottom):

15.6 O, 4.7 Si, 76.8 Fe, 3.2 Co.

Surface area 5, structures in pore (pore bottom):

15.8 O, 4.4 Si, 69.7 Fe, 10.0 Co.

Table 1. Thickness (d), composition, and coercive force (H_c) of coatings formed in different electrolytes

Parameters of coating		PBWF _{Fe} Co, A	PBF _{Fe} Co, A	BFeCo, A	SiFeCo, 5 min, AC	SiFeCo, 10 min, AC
d , μm		12 ± 2	39 ± 3	29 ± 3	13 ± 3	25 ± 2
H_c , Oe		113*	177	89	39	31
Phase composition		FeO, ?W ^o	$\gamma\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, ?Fe ⁰ , ?Co ⁰	no data	?Fe ⁰ , ?SiO ₂	?Fe ⁰ , ?SiO ₂
Elemental composition according to X-ray diffraction data, at %	C	9.0	32.6	24.7	17.6	21.1
	O	60.2	47.7	52.6	57.6	55.6
	Na	—	1.6	—	0.5	0.6
	Mg	1.1	0.3	0.5	—	—
	Al	25.3	6.0	9.4	2.5	1.7
	Si	—	—	—	10.8	10.5
	P	0.5	3.5	—	—	—
	Fe	1.9	4.6	2.2	10.6	10.1
	Co	2.2	3.8	10.7	0.4	0.6
	W	0.2	—	—	—	—

Note: The value of H_c for PBWF_{Fe}Co was measured at 300 K; in other cases, H_c was measured at 340 K. A denotes the anodic regime, AC is the bipolar anodic–cathodic regime, and ? means that the phase is possible (weak reflections).

Table 2. Elemental composition (at %) of agglomerates and structures on the pore bottom, averaged for three or more pores

Element	PBWF _{Fe} Co, A	PBF _{Fe} Co, A	BFeCo, A	SiFeCo, 5 min, AC	SiFeCo, 10 min, AC
C	—	—	2.4	0.8	0.2
O	12.0	2.7	3.7	7.2	11.7
Al	13.1	0.5	8.0	—	0.1
Si	—	—	—	4.1	3.3
P	—	0.7	—	—	—
Fe	29.3	46.4	65.1	85.6	78.8
Co	45.6	49.6	20.83	2.4	5.9

For notes, see Table 1.

The data presented above and those of Table 2 show that the composition of the structures in the pores differed sharply from the average composition of the surfaces (Table 1). The main difference was a sharp rise in the content of iron and cobalt, i.e., the metals of the electrolyte. The pores either contained carbon, sodium, magnesium, and aluminum, or their amount was considerably smaller than on the surface. The oxygen content was several times lower. The oxygen deficit meant that the metals in the composition of the structures in the pore existed predominantly in the reduced state, which is consistent with the X-ray diffraction data (Table 1). The carbon and hydrogen in the pores during and after the decay of the electric discharge could have been the metals' reducing agents. The ridges adjacent to each pore were intermediate between the pores and surfaces of the coatings in elemental composition.

The main qualitative features of the structure and elemental composition of the pores (concentrated metals of the electrolyte, agglomerates, and a sharply reduced oxygen content) were thus common for the coatings studied in this work and in [5, 8, 9]. The nature of the supporting electrolyte affected the quantitative content and the ratio of cobalt and iron in the pores. For example, the cobalt content was higher in the PBWF_{Fe}Co electrolyte, the contents of iron and cobalt were approximately equal for the PBF_{Fe}Co coatings, and the iron content was notably higher for the BFeCo and SiFeCo coatings.

Our results suggest that iron and cobalt are concentrated in the pores and are in the composition of nano- or micro-sized particles consisting of the reduced metals surrounded by oxide or hydroxide shells for the coatings formed in both PBWF_{Fe} and PBWF_{Fe}Co electrolytes in [5, 8, 9] and those studied in this work.

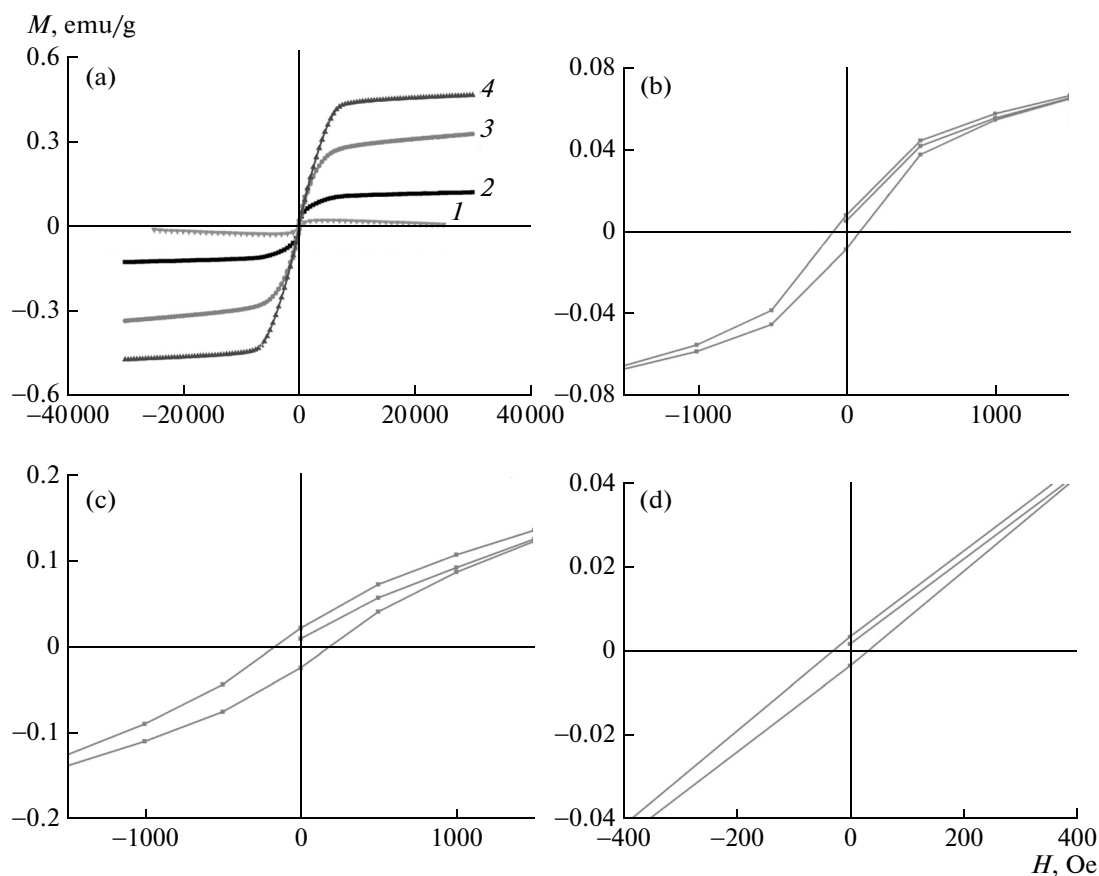


Fig. 3. Magnetization of samples (M) vs. strength of the external magnetic field (H). (a) The coatings were formed in electrolytes PBWFeCo, BFeCo, PBFeco, and SiFeCo (10 min), respectively (curves 1, 2, 3, and 4). (b–d) Regions of low fields for BFeCo, PBFeco, and SiFeCo, respectively: (b–d) $T = 340$ K; $H_c =$ (b) 89, (c) 177, and (d) 31 Oe.

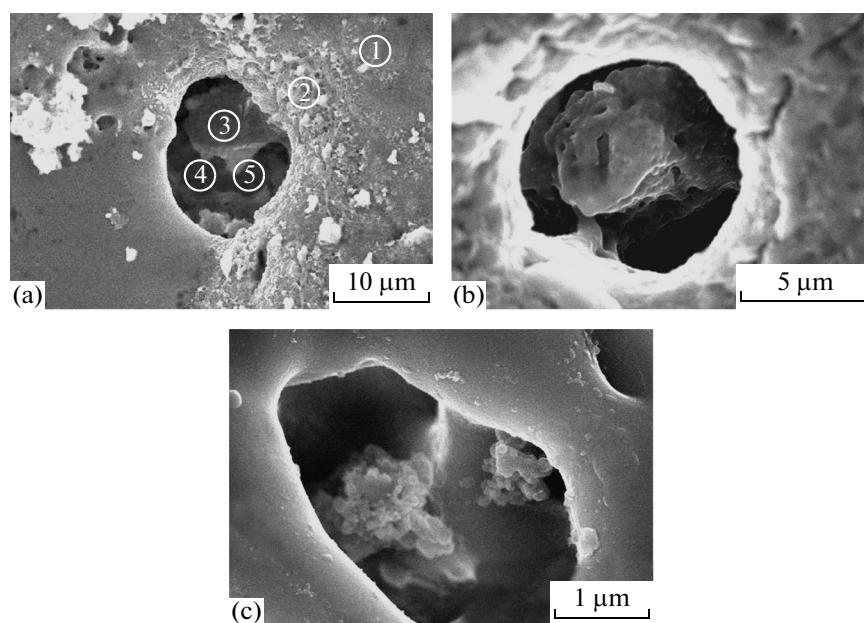


Fig. 4. SEM images of pore orifices in the coatings formed in the electrolytes: (a) SiFeCo, 10 min; (b) PBFeco; and (c) PBWFeCo. The surface areas for which the elemental compositions were determined are indicated by circles in Fig. 4a.

Agglomerates of these particles in the pores likely determined the magnetic characteristics of the coatings. The concentration, ratio, and distribution of the metals probably determined the behavior of exchange interactions in the particles and thus the magnetic characteristics of the coatings as a whole. With an excess of cobalt, for example, the formed coatings displayed ferrimagnetic properties (PBWFeCo electrolyte, Table 2, Fig. 3a, curve 1). As the relative content of iron increased, the coatings exhibited ferromagnetic properties, the coercive force simultaneously fell, while the magnetization in the region of strong external fields grew (Fig. 3a). Note that the ratios and contents of cobalt and iron in the pores correlate, on the whole, with the average content of these elements in the coatings obtained from the X-ray diffraction data (Tables 1 and 2). This and the maps of iron distribution obtained earlier for PBWFe coatings [5, 8] indicate the electrolyte metals concentrated predominantly in the pores and defect sites of the coatings.

CONCLUSIONS

Common features are observed for PEO coatings on aluminum alloys formed in the galvanostatic regime under both anodic and bipolar anodic–cathodic conditions in electrolytic suspensions of different compositions with dispersed (colloidal) particles of iron and cobalt hydroxides. Iron and cobalt are incorporated into the coatings and are concentrated predominantly in pores. The pores of the coatings include structures containing these metals in certain ratios. The coatings exhibit ferro- and ferrimagnetic properties. Correlation is observed between the ferro- or ferrimagnetism of the coatings and the contents and ratios of cobalt and iron in the pores. The higher the iron content, the more pronounced the ferromagnetic properties. The amounts of iron and cobalt and their ratio in the pores and the entire coating depend on the nature of the supporting alkaline electrolyte on which the electrolytic suspension is based. Along with earlier data [5, 8, 9], our results suggest that there are iron and cobalt in the coating pores in compositions of nano- or microparticles encapsulated in oxide or hydroxide shells and joined into agglomerates.

The obtained data show that electrolytic suspensions of different compositions having the conditions for the formation of dispersed particles of hydroxides of the corresponding metals can be used for the formation of PEO coatings with certain magnetic characteristics on the surfaces of valve metals. PEO coatings can be formed for both anodic and alternating current anodic–cathodic polarizations.

REFERENCES

1. F. Y. Jin, H. H. Tong, J. Li, et al., *Surf. Coat. Technol.* **201**, 292 (2006).
2. V. S. Rudnev, A. Yu. Ustinov, I. V. Lukiyanichuk, et al., *Dokl. Phys. Chem.* **428**, 189 (2009).
3. V. S. Rudnev, A. Yu. Ustinov, I. V. Lukiyanichuk, et al., *Fizikkokhim. Poverkhn. Zashch. Mater.* **46**, 494 (2010).
4. A. Jagminas, R. Ragalevicius, K. Mazeika, et al., *J. Solid State Electrochem.* **14**, 271 (2010).
5. V. S. Rudnev, I. V. Lukiyanichuk, M. V. Adigamova, et al., *Korroziya: Mater. Zashch.*, No. 12, 33 (2011).
6. S. V. Gnedenkov, S. L. Sinebryukhov, I. A. Tkachenko, et al., *Perspekt. Mater.*, No. 5, 55 (2011).
7. A. B. Rogov, O. P. Terleeva, I. V. Mironov, and A. I. Slonova, *Appl. Surf. Sci.* **258**, 2761 (2012).
8. V. S. Rudnev, M. V. Adigamova, I. V. Lukiyanichuk, et al., *Prot. Met. Phys. Chem. Surf.* **48**, 543 (2012).
9. V. S. Rudnev, V. P. Morozova, I. V. Lukiyanichuk, et al., *Russ. J. Phys. Chem. A* **87**, 1052 (2013).
10. G. A. Markov, O. P. Terleeva, and E. K. Shulepko, *Trudy Mosk. Inst. Neftekhim. Gaz. Promyshl. Gubkina*, No. 185, 54 (1985).
11. P. Kurze, W. Krysmann, and H. G. Schneider, *Cryst. Res. Technol.* **21**, 1603 (1986).
12. V. I. Chernenko, L. A. Snezhko, and I. I. Papanova, *Formation of Coatings by Anode-Spark Electrolysis* (Khimiya, Leningrad, 1991) [in Russian].
13. V. V. Bakovets, O. V. Polyakov, and I. P. Dolgovesova, *Plasma-Electrolytic Anodic Metal Processing* (Nauka, Novosibirsk, 1991) [in Russian].
14. A. L. Yerokhin, X. Nie, A. Leyland, et al., *Surf. Coat. Technol.* **122**, 73 (1999).
15. V. S. Rudnev, *Prot. Metals* **44**, 263 (2008).
16. F. C. Walsh, C. T. J. Low, R. J. K. Wood, et al., *Trans. Inst. Metal Finish.* **87** (3), 122 (2009).
17. B. L. Jiang and Y. M. Wang, in *Surface Engineering of Light Alloys*, Ed. by Hanshan Dong (Woodhead, Oxford, Cambridge, New Delhi, 2010), pp. 110–154.
18. O. P. Terleeva, Yu. P. Sharkeev, A. I. Slonova, et al., *Surf. Coat. Technol.* **205**, 1723 (2010).
19. Z. W. Wang, Y. M. Wang, Y. Liu, et al., *Curr. Appl. Phys.* **11**, 1405 (2011).
20. F. Patcas and W. Krysmann, *Appl. Catal. A: Gen.* **16**, 240 (2007).
21. G. I. Marinina, M. S. Vasilyeva, A. S. Lapina, et al., *J. Electroan. Chem.* **689**, 262 (2013).
22. A. M. Yampol'skii, *Etching of Metals* (Metallurgiya, Moscow, 1980) [in Russian].
23. V. S. Rudnev, P. S. Gordienko, A. G. Kurnosova, and T. I. Orlova, RF Patent No. 2061107, *Byull. Izobret.* No. 15 (1996).
24. V. S. Rudnev, T. P. Yarovaya, A. E. Lysenko, et al., *Korroziya: Mater. Zashch.*, No. 5, 38 (2007).
25. V. S. Rudnev, P. S. Gordienko, A. G. Kurnosova, et al., *Elektrokhimiya* **27**, 224 (1991).
25. P. V. Kharitonovskii, A. M. Frolov, V. S. Rudnev, et al., *Bull. Russ. Acad. Sci.: Phys.* **74**, 1404 (2010).
26. V. Rudnev, A. Ustinov, I. Lukiyanichuk, et al., *Solid State Phenom.* **168–169**, 289 (2011).

Translated by E. Yablonskaya