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Formation of Oxide Layers Modified with Polytetrafluoroethylene or Graphite on Aluminum and Titanium Alloys by Plasma Electrolytic Oxidation

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Abstract—For one-stage formation of coatings containing polytetrafluoroethylene or graphite, it was proposed to use $\text{Na}_2\text{SiO}_3 + \text{NaOH}$ aqueous electrolyte containing siloxane–acrylate emulsion and dispersed powders of polytetrafluoroethylene or graphite. The phase and elemental composition and surface morphology of the formed coatings were determined. It was shown that the introduction of polytetrafluoroethylene markedly increases the hydrophobic and wear-resistant properties of coatings.

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Introduction of polytetrafluoroethylene (PTFE) or graphite into oxide coatings formed on aluminum and titanium alloys by plasma electrolytic oxidation (PEO), which is also known as microarc oxidation (MAO), leads to an increase in their protective properties [1–4]. Polymers and graphite are introduced into electrolytes [1–3] or applied to the surface of preliminarily formed oxide coatings by tribological or deposition methods [4, 5]. In the presence of the above additives, homogeneity of aqueous electrolytes becomes unstable. As in template synthesis [6], the use of electrolyte emulsions, in which dispersed particles of polymers, graphite, and other solid compounds are stabilized in the micelles of the emulsifiers, is the possible way to solve the above problem.

We studied the regularities of formation of PEO coatings on aluminum and titanium in aqueous electrolytes in the presence of dispersed PTFE or graphite particles and a siloxane–acrylate emulsion in the base electrolyte.

Polymer- and graphite-containing oxide layers were formed on $20 \times 20 \times 0.5$ -mm samples made of AMg5 aluminum and VT1-0 titanium alloys. Sample preparation prior to oxidation, electrochemical cell, power source,

and determination of phase and elemental composition and coating thickness were similar to those described previously [7]. The oxide coatings were deposited in the galvanostatic mode at a current density of 0.05 A cm^{-2} for 20 min. The base electrolyte of composition $10.6 \text{ g L}^{-1} \text{ Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O} + 2 \text{ g L}^{-1} \text{ NaOH}$ was prepared from distilled water and chemically pure grade commercial reagents. Electrolyte composition was similar to that described in [8]. As emulsifier was used KE 13-36 commercial siloxane–acrylate emulsion produced at an Astrohim Limited Responsibility Company, Russia (Fig. 1). We used inequigranular PTFE powder of the Forum brand (Russia), grain size of main fraction about $1 \mu\text{m}$. Dispersed graphite particles with average sizes less than $50 \mu\text{m}$ were obtained from graphite rods by grinding and following separation of coarser particles by sieving (sieve mesh $50 \times 50 \mu\text{m}$).

Working electrolytes were prepared in two stages. First, 100 mL of siloxane–acrylate emulsion was mixed with 50 g of PTFE powder or 10 g of graphite. The mixture was thoroughly stirred with a magnetic stirrer for at least 30 min till wetting of powder particles with the

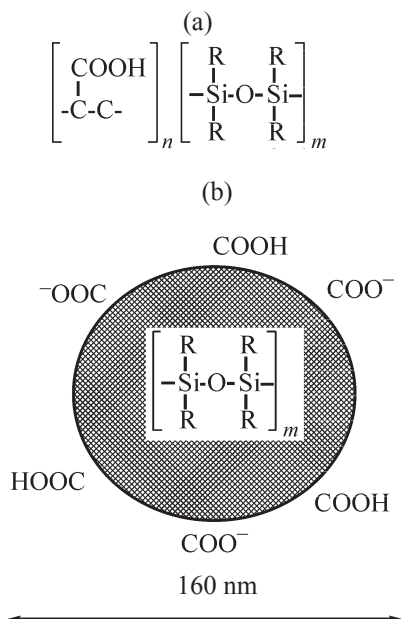


Fig. 1. (a) The structural formula of the KE 13-36 siloxane-acrylate emulsion produced at an Astrokhim LRC and (b) the structure of the micelle of an aqueous emulsion.

emulsion was complete. Second, the resulting mixtures were introduced into the prepared aqueous solution of the base electrolyte. The prepared electrolyte was a complex emulsion-suspension system containing dispersed particles of solid PTFE or graphite in the “shell” of a siloxane-acrylate emulsion, which prevented formation of coarse agglomerates and imparted a negative charge to the surface. Electrolytes were stable with time at least within 1 month of observation, and no separation of emulsion-suspension was virtually observed. In the course of the coating formation, the electrolytes were mixed with a mechanical stirrer. The coated samples were washed with distilled water and dried in air.

High-resolution images of the surface were obtained on a HITACHI S-55009 electron scanning microscope (Japan) equipped with a Thermo Scientific energy dispersive analyzer (USA). The elemental composition within coating plateaus and local areas with the diameter up to 50 nm was determined. The depth of the analysis did not exceed 1 μm .

The wear-resistance properties of the coatings were determined on an end friction laboratory installation [9]. Onto a coating, a cylindrical indenter made of R6M5 high-speed steel (diameter 2–3 mm) dropped down. The indenter was pressed into the sample under the load

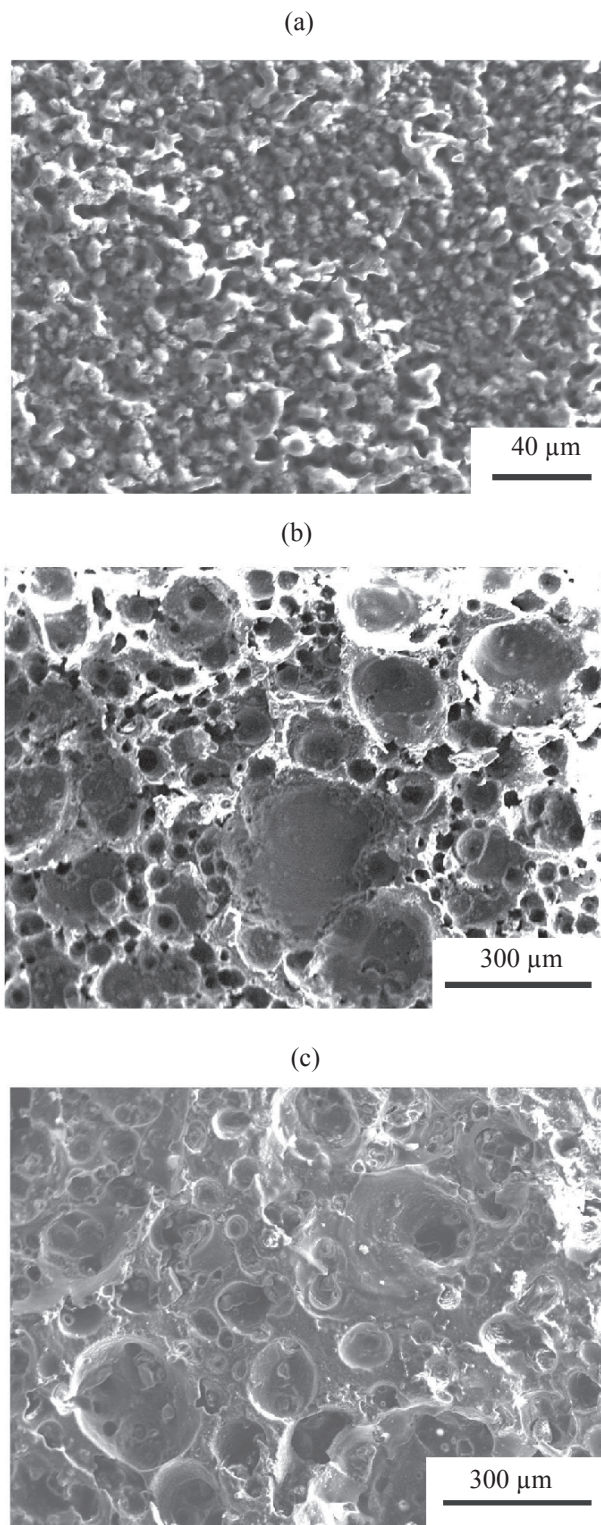


Fig. 2. Surface morphology of the coatings formed in (a) base electrolyte and (b, c) base electrolyte containing 100 mL L⁻¹ of emulsion + 50 g L⁻¹ of PTFE powder. Alloy: (a, b) AMg5 aluminum and (c) VT1-0 titanium.

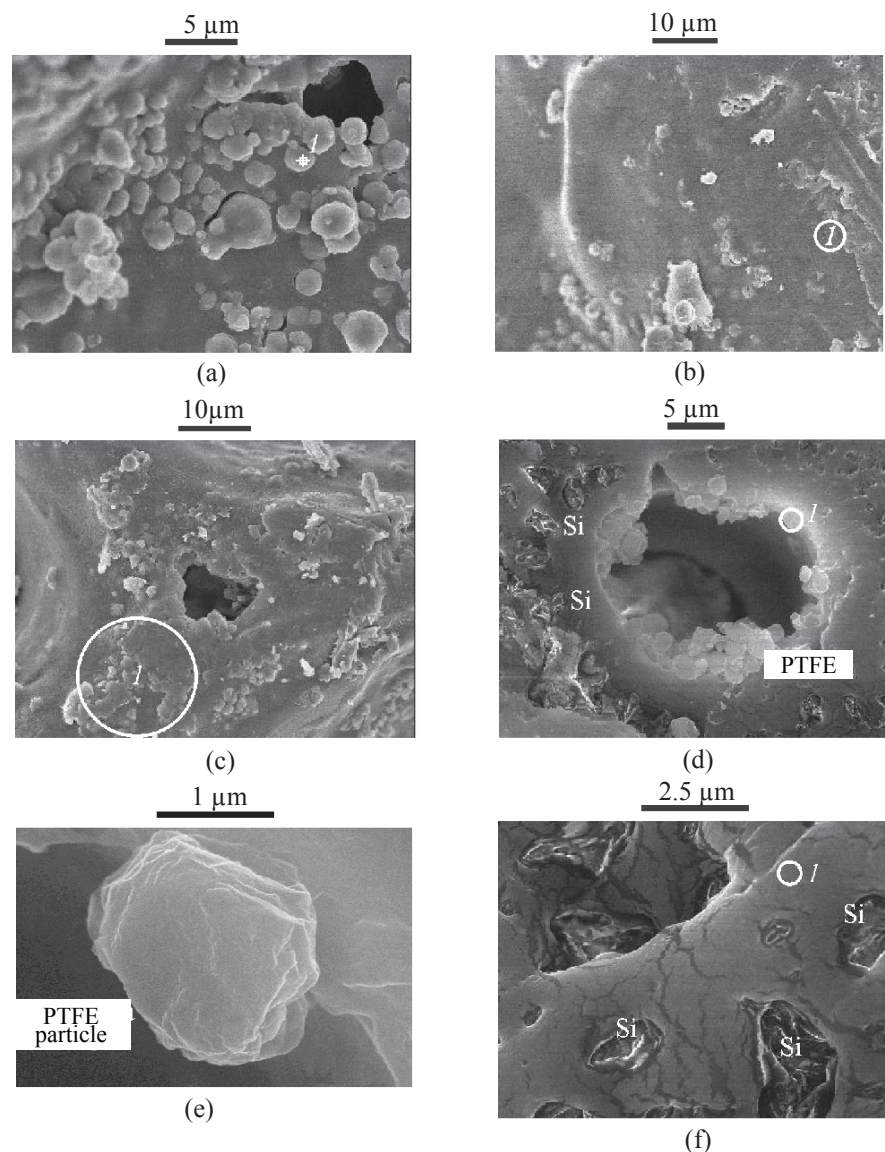


Fig. 3. Surface morphology of the coatings formed on AMg5 aluminum alloy in an electrolyte containing $\text{Na}_2\text{SiO}_3 + \text{NaOH} + 100 \text{ mL L}^{-1}$ of emulsion + 50 g L^{-1} of PTFE powder at $i = 0.05 \text{ A cm}^{-2}$ for $\tau = 20 \text{ min}$. (a–c) PTFE particles and products formed by emulsion decomposition on the surface, (d, e) PTFE particles in a pore, and (d, f) silicon particles in the pore periphery.

6.3 MPa m^{-2} . Under the action of an electric motor the coated sample performed reciprocate motion under the indenter with a step of 1 cm at a rate $7.30 \text{ times min}^{-1}$. The time, at which the electrical resistance of the indenter/coating contact sharply decreased, was fixed as abrasion time.

The contact angle coating/distilled water was measured by a “sitting” drops method [10].

Surface morphology of the coatings formed on AMg5 aluminum and VT1-0 titanium alloys in a base electrolyte and in the presence of the emulsion (100 mL g^{-1}) and PTFE powder (50 g L^{-1}) in it is demonstrated in Fig. 2.

The coating obtained in a base electrolyte has rather heterogeneous surface in the form of alternating rises, cavities, and pores (Fig. 2a), whereas that formed in the electrolyte containing emulsion and PTFE powder has cellular fused surface (Fig. 2b, c). The coatings thickness is $h = 48 \text{ μm}$ on aluminum and $h = 104 \text{ μm}$ on titanium.

Figure 3 demonstrates coating areas filled with PTFE particles and products formed by emulsion decomposition. Formations on the surface are spherical and contain carbon in an amount of 100 at % (see Fig. 3a, point I). A fairly uniform section of the coating is demonstrated in Fig. 3b. The composition within plateau I of this section

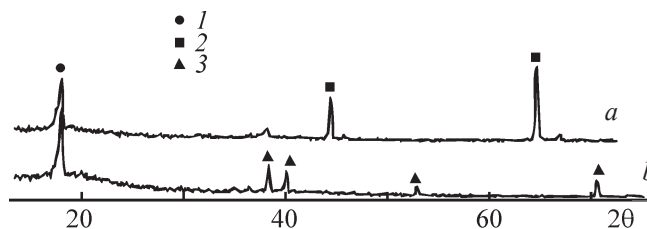


Fig. 4. X-Ray diffraction patterns of the coatings formed in an electrolyte containing $\text{Na}_2\text{SiO}_3 + \text{NaOH} + 100 \text{ mL L}^{-1}$ emulsion + 50 g L^{-1} PTFE powder. (2θ) Bragg angle (deg); the same for Fig. 6. Reflection: (1) PTFE, (2) Al, (3) Ti. Alloy: (a) AMg5 aluminum and (b) VT1-0 titanium.

is closer to that of PTFE (at %): C 78.9 and 21.1 F. The plateau *I* in Fig. 3c has the composition: C 47.4, 28.9 O, 13.8 F, and 9.6 Si. The PTFE particles are concentrated in pores and cracks of the coating (Fig. 3d) and silicon particles, probably a product formed by emulsion decomposition, around the pores. A PTFE particle and silicon-containing areas are shown at higher magnification in Figs. 3e, 3f.

Thus, the surface composition is rather complex; both PTFE and particles consisting of carbon and silicon, i.e., products formed in thermal decomposition and thermal transformations of electrolyte components are present.

According to the X-ray microprobe analysis of the $300 \times 200\text{-nm}$ parts of the coating obtained in the electrolyte of composition $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O} + \text{NaOH} + 50 \text{ g L}^{-1}$ PTFE + 100 mL L^{-1} siloxane–acrylate emulsion, the elemental composition of a surface layer of the coating to a depth of about $2.5 \mu\text{m}$ is (at%) : 65.1 C, 18.9 O, 15.2 F, 0.1 Al, and 0.8 Si for AMg5 aluminum alloy and 70.2 C, 20.8 O, 8.2 F, 0.1 Ti, 0.6 Si for VT1-0 titanium alloy.

The above results show that the surface layer of the coatings mainly consists of PTFE and products of its

decomposition under the action of electric discharges, since aluminum, titanium, and silicon contents in it are minimal. Incorporation of PTFE into the coating is also directly confirmed by the X-ray phase analysis (Fig. 4). In the diffraction patterns of the coatings formed on aluminum and titanium alloys, PTFE reflections are determined starting from the PTFE concentration in the electrolyte 40 g L^{-1} and larger. The presence of PTFE phase is also confirmed by the value of the angle of contact of the coatings with the water, which for the PTFE concentration in the electrolyte exceeding 50 g L^{-1} is close to the value for Teflon ($\theta = 105^\circ$).

The presence of PTFE particles on the surface of the obtained hybrid coatings and, apparently, inside them increases their wear resistance. Indeed, at the PTFE concentration 30 g L^{-1} and above the abrasion time, including that per unit thickness, increases by several orders of magnitude (see the table).

The method suggested is promising for the formation of wear-resistant hybrid coatings containing another than polytetrafluoroethylene compounds. The method was applied for formation of graphite-containing coatings on titanium. To do this, emulsion and 10 g L^{-1} of dispersed graphite particles were introduced into a silicate electrolyte. Coatings with a thickness of $56 \mu\text{m}$ were formed. A general view of the coating and some of its sections are shown in Fig. 5 at different magnifications. The surface consists of black, relatively dense areas with heterogeneous “island-like” structures on them (Fig. 5a). The black dense areas consist of alternating pores and rises around them (Figs. 5b, 5c at larger magnification). The rises (Figs. 5b, 5c, plateau *I*) consist entirely of carbon (100 at % C). A white formation on the black area has the composition (at. %): C 53.5, 40.8 O, and 5.8 Si (plateau 3 in Fig. 5b). The pores are filled (closed) with a material whose composition was not determined in this series of the experiments (Fig. 5c).

The island formations (Fig. 5d, plateau *I*) consist of the following elements (at. %): 64.7 O, 2.6 Si, and 28.6 Ti,

Influence of concentration of PTFE powder in electrolyte on the wear resistance of the coatings formed on AMg5 alloy

Coating no.	Concentration of PTFE particles in electrolyte, g L^{-1}	Wear time
1	0 (Initial)	~1 s
2	10	~1 s
3	20	~1 s
4	30	137 s
5	40	4 h 25 min
6	50	More than 10 h
7	60	More than 10 h

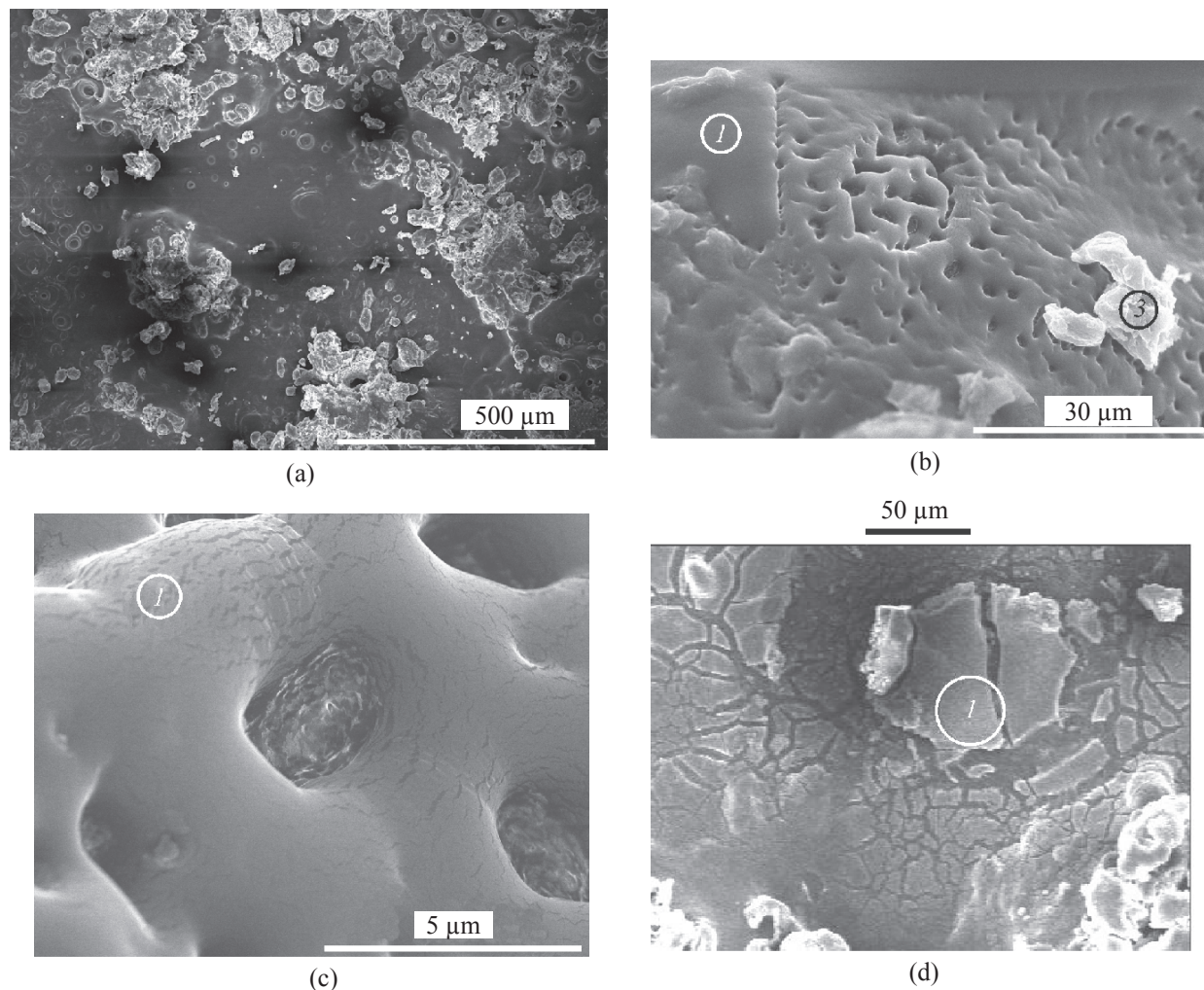


Fig. 5. Coatings formed on titanium in a base electrolyte containing emulsion and 10 g L^{-1} of dispersed graphite powder. (a) General view and (b–d) some coating areas at different magnifications.

i.e., they are titanium oxides with the impurity of silicon oxides. The X-ray phase analysis of the coatings revealed titanium and graphite (Fig. 6).

Thus, coatings with a surface layer richer in polytetrafluoroethylene and graphite may be formed by the direct plasma electrolytic oxidation in electrolytes containing a siloxane-acrylate emulsion and dispersed PTFE or graphite powders. The introduction of polytetrafluoroethylene strongly increases the wear-resistant properties of the coatings.

Graphite-containing coatings can possess electrical conductivity along the plane and have low friction coefficient. Both types of the formed coatings can have protective properties in chlorine-containing media.

The proposed method is promising for one-stage formation of graphite-containing coatings, wear-resistant

hybrid coatings containing polytetrafluoroethylene and, apparently, other polymers, and presumably, of coatings containing oxides, glass, highly dispersed metal particles, pigments, and other particles and compounds, which can enter the micelles of the siloxane-acrylate emulsion. Prob-

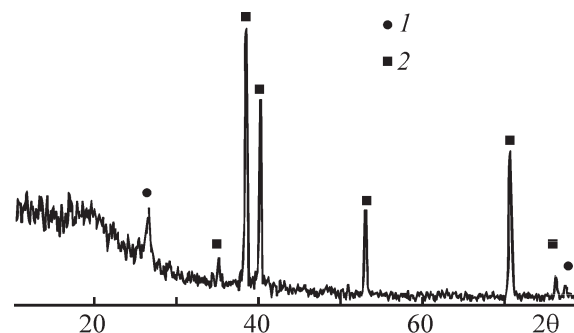


Fig. 6. X-Ray diffraction pattern for the graphite-containing coating on titanium. Reflection: (1) graphite and (2) titanium.

ably, the methods of template synthesis [6] can be used for controllable introduction into coatings of required compounds and formation of hybrid or composite coatings with desired composition and properties.

CONCLUSIONS

Coatings with a surface layer containing polytetrafluoroethylene, graphite, and products formed by their decomposition and thermal transformations may be formed in a silicate aqueous electrolyte in the presence of siloxane-acrylate emulsion and dispersed powder of polytetrafluoroethylene or graphite.

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