

APPLIED ELECTROCHEMISTRY
AND METAL CORROSION PROTECTION

Characteristics of Plasma-Electrolytic Oxide Coatings Formed on Aluminum and Titanium in Electrolytes with Siloxane Acrylate and Particles of Vanadium, Boron, and Aluminum Oxides

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Received March 30, 2018

Abstract—It is shown that aqueous suspension-emulsion electrolytes containing sodium silicate, siloxane-acrylate emulsion, and dispersed particles of oxides are promising for direct synthesis by the plasma-electrolytic oxidation method of coatings with multicomponent composition on titanium and aluminum. The formation processes, composition, and structure of the coatings were studied in electrolytes with 1–4- μm particles of V_2O_5 , B_2O_3 , or Al_2O_3 . The average content of metals and nonmetals of dispersed particles in the surface part of the coatings is ~1–2 at %. The coatings have a developed surface morphology and contain in the surface part up to 50–73 at % carbon.

DOI: 10.1134/S1070427218060101

The performance capabilities of the plasma-electrolytic oxidation (PEO) method are extensively studied in order to form oxide layers of required chemical composition, structure, and functional purpose on the surface of valve metals and alloys (Al, Ti, Zr, Mg, Nb, etc.) [1–4]. Spark and microarc electric discharges occurring in this method at the electrode/electrolyte interface make it possible to incorporate electrolyte components into a growing anodic oxide coating. In particular, the application for this purpose of suspension-electrolytes is studied: aqueous salt solutions with added dispersed particles of metals and nonmetals, including oxides, polymers, nanotubes, etc. [4–8]. In the general case, particles can be incorporated into coatings in the unchanged state, or enter, on being melted or degraded by electric discharges, into high-temperature interactions with matrix components. The built-in dispersed particles, or compounds formed on their basis strongly extend the range of characteristics and possible application fields of PEO coatings [4, 5].

To raise the stability of suspension-electrolytes, surfactants are additionally introduced [7, 8]. Simultaneously, the sorption of surfactants can impart a

required charge to the particle surface, which is important not only for the stability of electrolytes, but also in electrochemical processes.

It has been shown recently that the application of a siloxane-acrylate emulsion is effective for stabilization of polytetrafluoroethylene (PTFE) particles ~1 μm in size and graphite particles with size of ~50 μm in an aqueous silicate electrolyte [9–11]. The suggested suspension-emulsion electrolytes are stable in the course of time, dispersed particles bear a negative charge, and anodic PEO coatings formed on aluminum or titanium alloys contain in their composition PTFE or graphite.

Application of electrolytes with siloxane-acrylate emulsion added as emulsifier may be promising for formation by the PEO method of multicomponent coatings in electrolytes with dispersed particles of various polymers, as well as oxides, glasses, powder paints, and metals capable of adsorbing micelles of a siloxane-acrylate copolymer on their surface.

The goal of our study was to determine the composition and structure of PEO coatings formed on aluminum or titanium in a silicate electrolyte with addition of a

siloxane-acrylate emulsion and dispersed particles of V_2O_5 , B_2O_3 , or Al_2O_3 .

EXPERIMENTAL

The coatings were galvanostatically formed on $20 \times 20 \times 0.5$ mm samples of aluminum alloys (AMg5) and VT1-0 titanium at effective current density of 5 A dm^{-2} in the course of 10 min. A computer-controlled TEP-4/460H thyristor aggregate (Russia) operating in the unipolar mode was used as a current source. After the coatings were formed, the samples were washed with distilled water and dried in air.

The electrochemical treatment of the aluminum samples was performed in an electrolyte placed in a vessel made of heat-resistant glass. As a counter electrode served a hollow coil of a nickel alloy through which cold tap water was passed to cool the solution. The electrolyte temperature in the course of the treatment did not exceed 30°C .

The electrolyte was prepared from distilled water and commercial reagents of chemically pure brand: $Na_2SiO_3 \cdot 5H_2O$ and NaOH. As emulsifier served a KE 13-36 industrial siloxane-acrylate emulsion manufactured by Astrokhim OOO (Russia) (Fig. 1). Mechanically ground, with the subsequent separation into fraction, powders of the oxides V_2O_5 , Al_2O_3 , B_2O_3 were used, with the average particle size being $1\text{--}4 \mu\text{m}$.

The suspension-emulsion electrolytes were prepared in two stages. Initially, 100 mL of a siloxane-acrylate emulsion was mixed with a prescribed amount of a powder. A high-speed (13 000 rpm) mechanical stirrer was used to agitate the mixture for 10 min. The resulting mixture was combined with 900 mL of an already prepared aqueous solution containing $10.6 \text{ g } Na_2SiO_3 \cdot 5H_2O + 2 \text{ g } NaOH$. The following powder concentrations were used (g L^{-1}): $2 V_2O_5$, $5 Al_2O_3$, $10 B_2O_3$. The concentrations were found experimentally in each case. As the choosing criterion served the absence of a visually visible stratification of the electrolyte during 24 h of observation.

The thickness of the coatings was measured with a VT-201 thickness meter (Russia).

High-resolution surface images were obtained with a Hitachi S-55009 electron scanning microscope (Japan). The Thermo Scientific attachment (United States) to the microscope for energy-dispersive spectroscopy was used to determine the elemental composition of separate surface areas. The depth of analysis was $\sim 1 \mu\text{m}$.

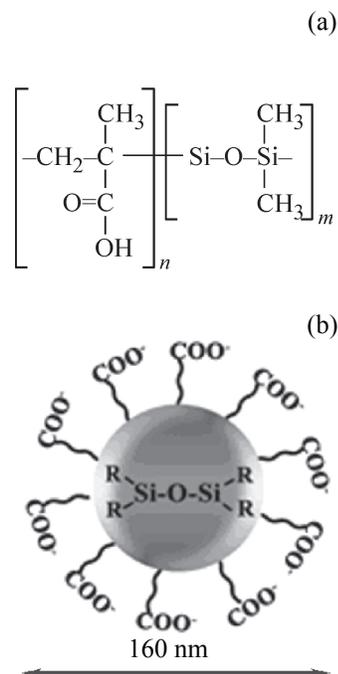


Fig. 1. (a) Structural formula of KE 13-36 siloxane-acrylate emulsion manufactured by Astrokhim OOO and (b) structure of an emulsion micelle in water.

The averaged elemental composition of the surface layer of the coatings (analysis of a $\sim 2\text{-}\mu\text{m}$ -thick layer) was determined on a JXA-8100 Electron Probe Microanalyzer electron-probe X-ray fluorescence microanalyzer (Japan). The content of an element was determined as the average of five measurements obtained at different parts of coatings in scanning of $300 \times 200 \mu\text{m}$ sample pads.

The composition of boron-containing coatings ($\sim 3\text{-nm}$ layer) was determined by X-ray photoelectron spectroscopy (XPS). The XPS spectra were measured in a Specs ultrahigh-vacuum installation (Germany) with a 150-mm electrostatic semispherical analyzer.

X-ray diffraction patterns were obtained on a D8 ADVANCE X-ray diffractometer (Germany) with $\text{CuK}\alpha$ radiation. The X-ray diffraction (XRD) analysis was made with an EVA search program with PDF-2 database.

The incorporation of vanadium and boron oxides from suspension-emulsion electrolytes was examined when PEO coatings were formed on an aluminum alloy. Figure 2 shows how the voltage across the electrodes depends on the PEO process duration. The final values of the electrode voltages upon completion of the process were used to obtain the series starting electrolyte < starting + emulsion < starting + emulsion + $V_2O_5 \approx$ starting + emulsion + B_2O_5 . As the electrolyte

Thickness and elemental composition of coating according the results of X-ray fluorescence microanalysis

Electrolyte	Thickness and elemental composition of coatings, at %								
	h , μm	C	O	Al	Si	Na	V	B	Ti
Starting (true) solution	4	40.3	40.5	15.8	2.7	0.7	–	–	–
Starting + emulsion	9	44.8	38.4	12.5	3.7	0.6	–	–	–
Starting +emulsion + V_2O_5	54	64.6	25.5	0.4	6.4	0.5	2.6	–	–
Starting ^a +emulsion + B_2O_3	20	50.5	34.5	7.1	6.2	0.5	–	1.2	–
Starting ^b +emulsion + Al_2O_3	52	73.1	24.5	0.7	1.4	0.2	–	–	0.1

^a The elemental composition was measured by X-ray photoelectron spectroscopy

^b The coating was formed on titanium.

composition becomes more complex and a transition occurs from a true solution to a solution with addition of an emulsion and further to a suspension-emulsion, the electrical resistance of the system grows. Simultaneously, the coating thickness increases in electrolytes with dispersed particles (see the table). It can be assumed that the electrical resistance of the system is associated both with the increase in the coating thickness due to the incorporation of the electrolyte components and with the presence in solution of bulky siloxane-acrylate micelles (Fig. 1) and also comparatively low-mobile dispersed particles with sorbed micelles. Micelles not only can be adsorbed on oxide particles, but also can bind silicate polymers, with the concentration of current carriers and their mobility in solution thereby lowered.

Changing the composition and state of the electrolyte noticeably affects the morphology of PEO coatings (Fig. 3). The surface of the coatings formed in a silicate-

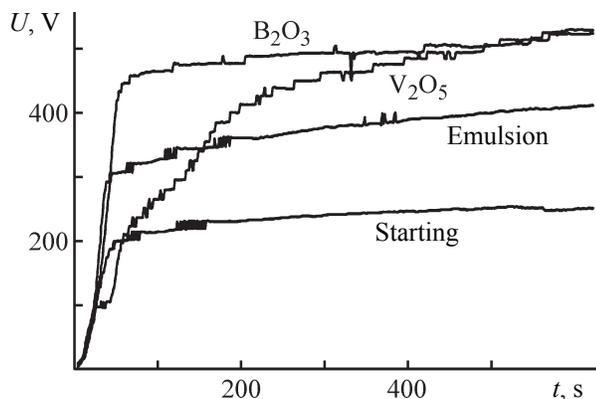


Fig. 2. Effect of the electrolyte composition on the dependence of the voltage U across the electrodes on time t in the course of PEO of aluminum alloy AMg5.

alkaline electrolyte looks as alternating elevations and depressions (Fig. 3a). When the emulsion is introduced, the geometric dimensions of elevations and depressions grow (Fig. 3b). Similar changes have also been observed for coatings on the aluminum alloys upon introduction of a siloxane-acrylate emulsion into the silicate electrolyte [10]. The influence exerted by the emulsion on the surface morphology is similar to the effect of anion-active surfactants [12, 13]. An additional introduction of dispersed oxide particles into electrolytes with emulsion makes this effect even more pronounced (Figs. 3c and 3d). The latter may be due both to the incorporation of bulky particles, which is also a reason for the steep rise in the coating thickness on passing from an electrolyte with emulsion to the suspension-emulsion electrolyte, and also to the increase in the formation voltage in a transition of this kind (Fig. 2) and, consequently, to the occurrence of more powerful electric discharges.

As follows from the data in the table, introduction of an emulsion into the starting electrolyte in the absence of dispersed particles results in that the thickness of the coatings grows and their content of carbon and silicon increases. The latter may be due to the penetration into coatings of the emulsion and products of its destruction under electric discharges. The presence of noticeable amounts of carbon in the surface of coatings formed in the starting silicate electrolyte has been noted previously [14, 15]. Presumably, this results from the presence of carbonates in the alkaline solution due to the absorption of atmospheric carbon dioxide by the solution.

Additional introduction into the electrolyte, together with the emulsion, of dispersed V_2O_5 and B_2O_3 particles results in a noticeable rise in the content in the surface layer of carbon (up to 50–65 at %), silicon (up to 6.2–

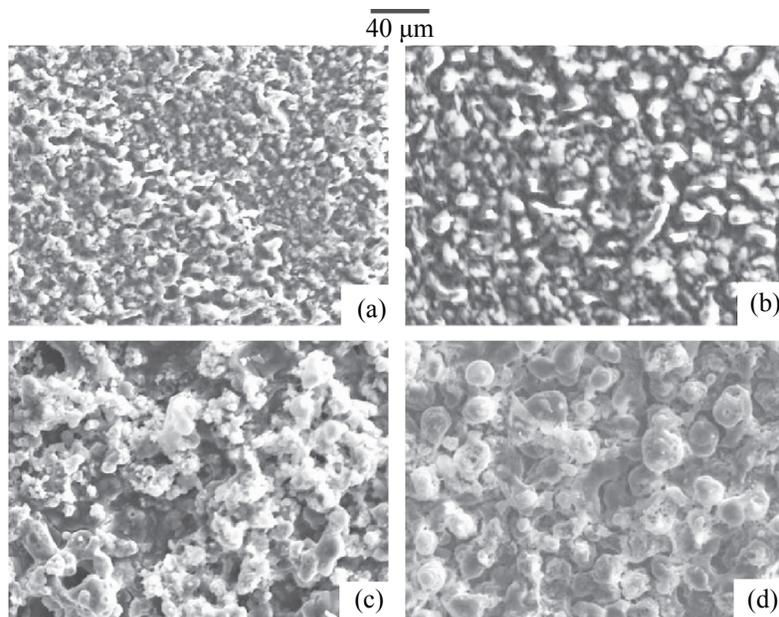


Fig. 3. Effect of the electrolyte composition on the surface morphology of coatings on the aluminum alloy. Electrolyte: (a) starting, (b) starting + emulsion, (c) starting + emulsion + V_2O_5 , (d) starting + emulsion + B_2O_3 .

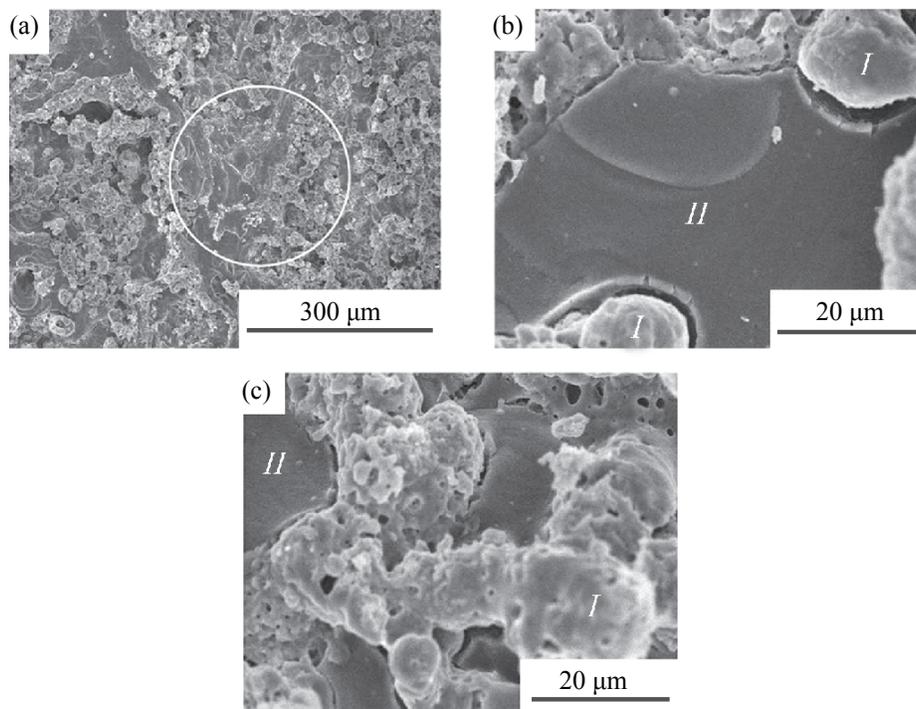


Fig. 4. (a) Scanning-electron-microscopic surface images of a coating formed in the suspension-emulsion electrolyte with vanadium oxide and (b, c) separate fragments of the surface. *I* and *II* are the characteristic surface fragments.

6.4 at %), with a simultaneous decrease in the amount of aluminum (to 0.4–7.1 at %). The surface-average contents of boron and vanadium are, respectively, 1.2 and 2.6 at %, i.e., the surface parts of the coatings are predominantly composed of the electrolyte components.

The data obtained on a scanning electron microscope with an energy-dispersive attachment demonstrate that the composition and surface profile of vanadium-containing coatings are nonuniform, fragmentary (Fig. 4). The surface has areas of two kinds, *I* and *II*. According to the

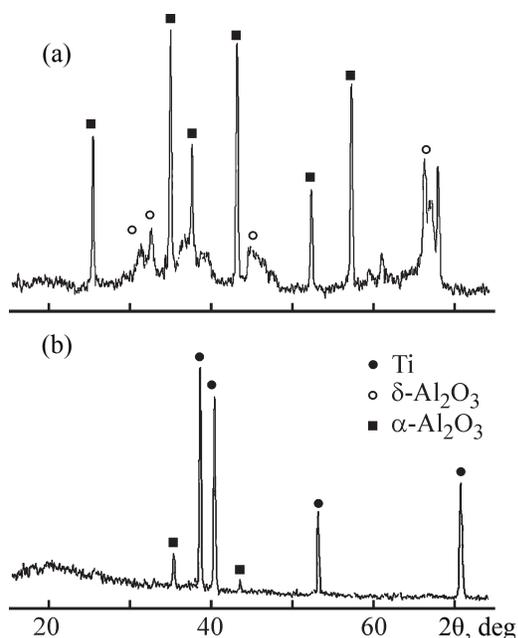


Fig. 5. X-ray diffraction patterns of (a) Al_2O_3 and (b) sample with Al-containing coating on titanium. (2θ) Bragg angle.

results of the energy-dispersive analysis, the compositions of these areas are the following (at %) (data averaged over four areas under study):

I contains C 50.9, O 34.9, Si 9.3, V 4.1;

II contains C 85.7, O 11.8, Si 2, V 0.2.

Areas *II* are mostly constituted by carbon and, possibly, by products of destruction of free emulsion unbound to oxide particles. Areas *I* contain, in addition to carbon, noticeable amounts of oxygen, silicon, and up to 4 at % vanadium. Presumably, these are products of thermal transformation of oxide particles–emulsion micelles–silica conglomerates under the action of electric discharges.

The joint presence of vanadium and silicon in type-I areas confirms the assumption that oxide particles adsorb from the electrolyte, together with micelles, also silicate. It is noteworthy that areas simultaneously containing zirconium and silicon have been observed previously in coatings formed by the PEO method in a silicate electrolyte with dispersed ZrO_2 particles [16]. That is these elements were also jointly deposited on separate parts of the coatings being formed.

The elemental composition of the coatings, determined with the energy-dispersive attachment of the scanning

electron microscope and averaged over a large area (circle in Fig. 4a) is the following (at %): C 65, O 25, Si 6, and V 3. This result is in good agreement with the data furnished by microprobe analysis (see the table).

The thus formed coatings containing vanadium compounds in their surface part may be of interest for being tested as catalysts.

As already noted, the surface morphologies of the coatings formed in electrolytes with a siloxane-acrylate emulsion and dispersed particles of vanadium and boron oxides are on the whole similar (Fig. 3). In both cases, fragments protruding over planar parts are present on the surface. However, the surface of boron-containing coatings looks more flowed, apparently due to the low melting point of boron oxide. Coatings of this kind may be dense and low-porous and be of interest for tests as protective coatings with anticorrosion properties.

Similar patterns in the composition and structure of coatings were also observed in PEO of titanium. In this case, the treatment was performed in a suspension-emulsion electrolyte with added dispersed particles of aluminum oxide (see the table).

According to the results of an XRD analysis, the material of V- and B-containing coatings on the aluminum alloy is X-ray amorphous, i.e., crystalline particles introduced into the coatings are melted or destructed under the action of electric discharges and the resulting temperatures, with amorphous products subsequently formed. Figure 5 shows an X-ray diffraction pattern of a coating formed on titanium in an electrolyte with Al_2O_3 particles. The particles introduced have the following phase compositions: δ and α -phases of aluminum oxide. The diffraction pattern of the coating has peaks of the α -phase (corundum), i.e., high-melting corundum particles are incorporated into coating partly in that state in which they were introduced into the electrolyte.

CONCLUSIONS

Using the siloxane-acrylate emulsion as emulsifier is promising for stabilization of dispersed oxide particles about 1 μm in size in an aqueous alkaline electrolyte for plasma-electrolytic oxidation (PEO). Coatings formed on aluminum and titanium in an electrolyte of this kind with dispersed particles of vanadium, boron, or aluminum oxides by the PEO method contain vanadium, boron, or aluminum oxides.

The particles or their material is incorporated into coatings formed by the PEO method in electrolytes of this kind, with the surface architecture and composition noticeably changed. The surface morphology becomes more developed. Under the experimental conditions, the average content of metals and nonmetals of dispersed particles in the surface part of the coatings is about 1–2.5 at %. The V-containing coatings studied in more detail have a fragmented structure of their surface part. Parts mostly composed of carbon alternate with those containing vanadium and silicon in addition to carbon.

On the whole, the experimental data obtained in the study demonstrate that use of suspension-emulsion electrolytes is promising for incorporation of dispersed particles and polymers of varied nature into coatings formed by PEO.

The strategy suggested in the study provides a possibility in principle of forming coatings of prescribed complex composition via simultaneous introduction into the suspension-emulsion electrolyte of several dispersed particles of varied nature, e.g., polymers + oxides etc. Coatings of this kind may be of interest, depending on the nature of particles being introduced, their relative amounts, composition, and structure, for application as catalysts, magnetic materials, etc.

ACKNOWLEDGMENTS

The study was supported in part by the “Far East” program (grant no. 18-3-034).

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