
NEW SUBSTANCES,
MATERIALS AND COATINGS

Compositions of Composite Polymer-Oxide Coatings on Aluminum from Pyrolytic Gas Chromatography Mass-Spectrometry Data

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Abstract—Data on the composition of the external polymer part of the composite polytetrafluoroethylene (PTFE) oxide coatings obtained on an aluminum substrate by plasma electrolytic oxidation (PEO) within a single stage are presented. The coatings were formed in an aqueous silicate electrolyte with addition of PTFE dispersed powder in a siloxane–acrylate emulsion. It has been established that the external polymer-like layer of the PTFE/PEO coatings does not represent a physical mixture of the siloxane–acrylate copolymer and PTFE particles, but is composed of fragments of them. A partial substitution of fluorine by hydrogen in fluorocarbons contained in the coatings has been revealed. The obtained data are crucial for expanding knowledge on the formation, structure, composition, and properties of the composite polymer-containing oxide coatings formed within a single stage by means of plasma electrolytic oxidation on the valve metal surface.

Keywords: plasma electrolytic oxidation, siloxane–acrylate emulsion, polytetrafluoroethylene powder, composite polytetrafluoroethylene/plasma electrolytic oxide coatings

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INTRODUCTION

Plasma electrolytic oxidation (PEO) consists in the formation of oxide layers on the surface of metals and alloys in electrolytes under conditions of spark- or microarc-discharge activation in the near-anode region [1–4]. Oxide PEO coatings are applied for protection from corrosion and mechanochemical wear of articles made of aluminum, titanium, and magnesium. PEO-coating modification by polytetrafluoroethylene allows improving practically important properties: hydrophobic, antifriction, wear resistance, and anti-corrosive [5–17].

Earlier, we suggested a single-stage method of producing PTFE/PEO coatings on aluminum and titanium by the addition of PTFE powder dispersed in an alkaline–silicate emulsion [11, 12]. Here, a preset amount of a fine PTFE powder was dispersed in 100 mL of a siloxane–acrylate emulsion. Due to adsorption of the emulsion micelles on the surface of the dispersed PTFE particles, the particles' wetting ability improved and, simultaneously, their surface was charged negatively. Upon introduction of the dispersion to the aqueous alkaline base electrolyte containing $\text{Na}_2\text{SiO}_3 + \text{NaOH}$, suspensions highly resistant to exfoliation were formed and the PEO process was implemented in them.

The PTFE/PEO coatings formed in the suggested suspension-emulsion electrolyte on the aluminum alloy oxide exhibited a layered structure [16, 17]. These coatings consisted of an oxide layer adjacent to metal of a thickness of $\sim 10 \mu\text{m}$ and an external polymer-like layer of a thickness of $\sim 70 \mu\text{m}$. The external-layer composition and thickness, as well as hydrophobic and wear-resistance properties of the coating, depended on the PTFE concentration in the electrolyte. The external polymer-like layer was constructed from the electrolyte components. For example, at contents of 100 mL of emulsion and 40 g of the PTFE powder per 1 liter of electrolyte, the external part of the coatings formed on aluminum alloy of total thickness of $\sim 40 \mu\text{m}$ contained, according to X-ray-spectral-microprobe analysis (analysis depth up to $5 \mu\text{m}$) (at %), 69.9C, 24.7O, 1.0F, 1.5Al, 2.9Si. At a powder concentration of 60 g/L, coatings of a thickness of $\sim 80 \mu\text{m}$ were obtained with an external layer containing (at %) 58.1C, 12.1O, 29.2F, 0.6Si.

In accordance with the electrolyte composition and the PEO-process specific features, one can suggest that the external part of the coatings contains not only the siloxane–acrylate copolymer and PTFE particles, but also the products of their destruction by spark and microarc electric charges during PEO. Dispersed PTFE particles were not observed on the sur-

face via the high-resolution scanning electron-microscopy method. The presence of the PTFE particles agglomerates was established only in pores on the surface and in cavities of the polymer-like layer internal part [16, 17]. Both PTFE particles and the siloxane-acrylate polymer must have been destroyed under the impact of electric discharges. The products of destruction, following the agglomeration, partial polymerization, or cross linking of various organic chains, units, or fragments, formed the external polymer-like layer.

The composite PTFE/PEO coatings fabricated in [11, 12, 14–17] exhibited hydrophobic properties (the limiting wetting angle reaching up to 105°), increased the wear resistance of the coatings, and, after annealing in air at 200°C , demonstrated fair anticorrosive properties. Thus, one can state that the produced materials are promising for application as protective and hydrophobic coatings. In view of this, it is important to determine the composition of these coatings in order to understand their structure, to identify their area of application areas, and possibly, to improve the fabrication process.

To identify polymers, including the PTFE, pyrolytic gas chromatographic mass spectrometry (Py-GC/MS) is extensively used. This method enables one to perform, within a single analysis and in real time, thermal decomposition of a polymer, to separate the pyrolysis products into individual components, and to determine the structure of each of them.

The objective of the present study was to obtain data on the composition of the external part of the composite polymer-like PTFE/PEO coatings formed on aluminum in an alkaline-silicate electrolyte with an addition of the PTFE powder dispersed in the siloxane-acrylate emulsion by the method of pyrolytic gas chromatography mass spectrometry.

MATERIALS AND METHODS

The PTFE/PEO coatings were formed in the aqueous suspension-emulsion electrolyte (latex) according to the technique described in [11, 12, 14–17]. The electrolyte contained $10.6\text{ g/L Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O} + 2\text{ g/L NaOH} + 100\text{ mL emulsion} + 60\text{ g/L PTFE powder}$. The following materials were used: polytetrafluoroethylene powder of the Forum brand (Russia) with the majority of particles having a size of $\sim 1\text{ }\mu\text{m}$ and a commercial KE 13–36 siloxane-acrylate emulsion (JSC Astrokhim, Russia). Sixty grams of the powder was preliminarily dispersed in 100 mL of emulsion. The obtained dispersion was mixed with 900 mL of an aqueous silicate-base electrolyte. Coatings were formed by means of emulsion-suspension electrodeposition on the aluminum alloy of AMg5 grade under a current density of 0.05 A/cm^2 for 20 min. Features of the cell for coating formation via the PEO method; the source of current; the emulsion composition; the

thickness, morphology, phase, and elemental composition of the coatings; and the effect of the annealing temperature in air on these parameters were described in detail in [11, 12, 14–17].

The solid residue of the emulsion was obtained by evaporating water from 10 mL of the emulsion in air at 80°C for 10 h. The solid residue of the dispersion—60 g of PTFE powder in 100 mL of emulsion—was obtained by a similar method.

A Double Shot Pyrolyzer PY-2020iD (Japan) connected to a Shimadzu GCMS QP-2010 gas chromatograph mass spectrometer (Japan) was used in the present study. Adjustments of the chromatograph and mass spectrometer were conducted under standardized conditions according to the F-Search All-in-One, Ver. 3.10, catalogue for the polymer identification. The pyrolysis temperature (500°C) was determined in accordance with earlier studies [18, 19]. Separation of the pyrolysis products was performed using an Ultra ALLOY-5 column (length 30 m, inner diameter 0.25 mm, film thickness of the phase $0.25\text{ }\mu\text{m}$), with the carrier gas being helium, the gas flow 1 mL/min , and the flow splitter 1 : 50. Temperature programming of the column started at 40°C (holding time 3 min), and then there was a temperature increase at a rate of 20°C/min up to 320°C (holding time 8 min). The mass range (m/z) was 29–800, the temperature of the mass-spectrometer-detector (MSD) interface was 280°C , the temperature of the ionic source was 250°C , and the voltage on the detector was 1 kV.

Samples of the PTFE/PEO-coating/Al, emulsion solid residue, or the PTFE dispersion solid residue in emulsion were placed in the pyrolyzer in a form of fragments of sizes of $1 \times 1 \times 1\text{ mm}^3$.

RESULTS AND DISCUSSION

Figure 1 shows a scanning-electron-microscopy (SEM) image of the PTFE powder (Fig. 1a), the structural diagram of the siloxane-acrylate copolymer (Fig. 1b), the general appearance of the emulsion solid residue (Fig. 1c), and an image of the PTFE/PEO-coating surface (Fig. 1d).

Figure 2 shows chromatograms of the investigated PTFE powder (Fig. 2a), the solid residue of the siloxane-acrylate copolymer (Fig. 2b), and the PTFE/PEO coating (Fig. 2c). Chromatograms were obtained upon pyrolysis of the samples at 500°C .

Chromatograms of the dispersed PTFE powder of the Forum brand were studied in detail earlier in [18, 19]. According to the data provided in [18, 19], the PTFE powder represented a mixture of perfluorocarbons—homologs of PTFE with a number of carbon atoms in chain from C5 to C70. The mass spectra of perfluorocarbons showed two series of ions—for saturated and unsaturated components—while the spectra themselves were not distinguishable for compounds with different numbers of carbon atoms in the chain.

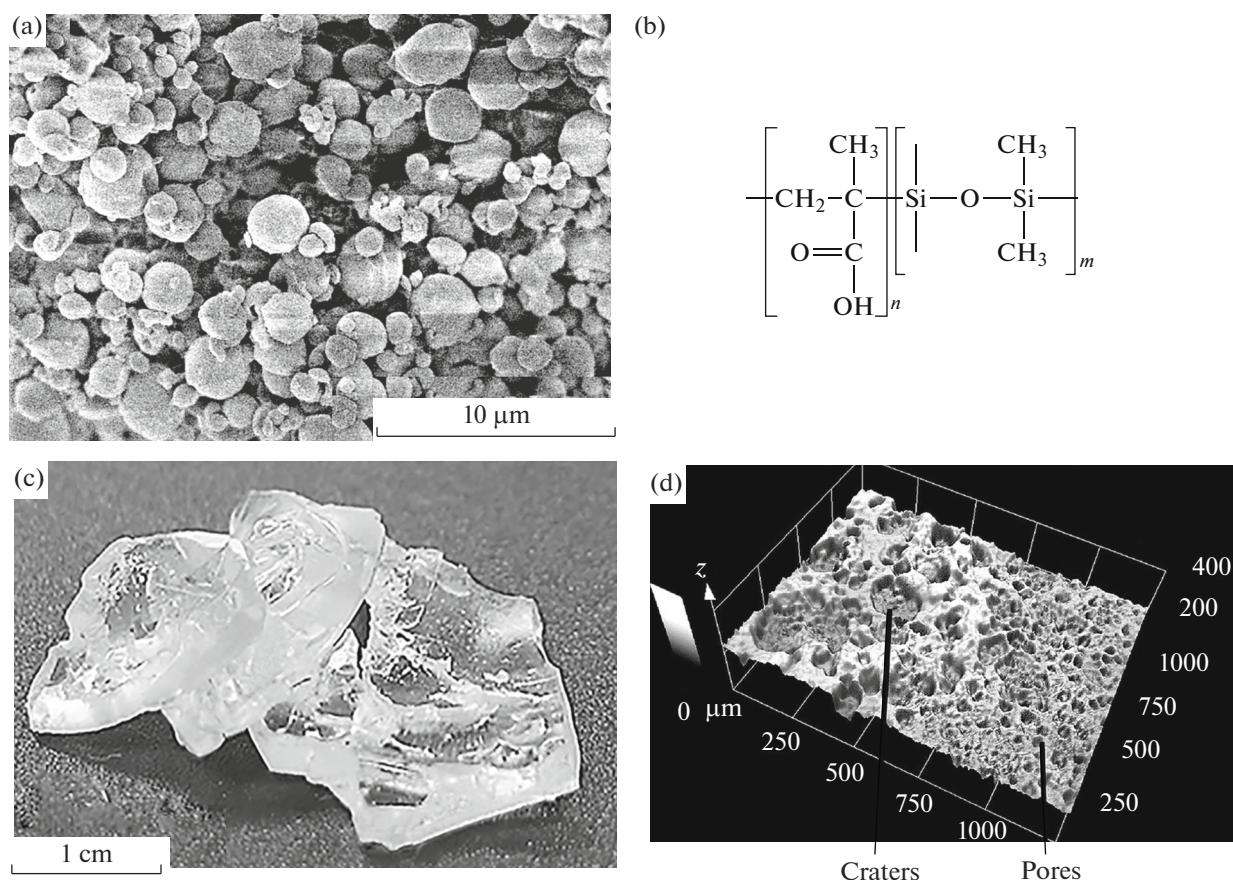


Fig. 1. (a) SEM image of the PTFE powder, (b) structural formula of the siloxane–acrylate copolymer, (c) general appearance of the emulsion solid deposit, and (d) image of the investigated PTFE/PEO-coating surface.

For the saturated components, the most intense ion appeared to be the one with m/z (ion mass to its charge ratio) equal to 69 (CF_3^+), while for unsaturated fluorocarbons it was that with m/z of 131 (C_3F_5^+) (Fig. 3a). Intense ions for the “alkane” series are those with m/z 69, 119, 169, and 219 and for “alkene” series with m/z of 131, 181, 231, 281, and greater. The mass difference for the main ions of these two series comprised 50 units, which equaled the mass value of the CF_2 group.

Upon pyrolysis, a solid residue of the siloxane–acrylate emulsion decomposed into acrylic esters of varied fragments length (Fig. 2b). Peak 1 corresponded to the methyl-ester acrylate, peak 2 to the isobutyl-ester acrylate, and peak 3 to the butyl-ester acrylate. Peaks located to the left from peak 1 and not marked by numbers corresponded to air, including carbon dioxide, presumably dissolved in the siloxane–acrylate-emulsion solid residue. Peaks 4–10 appeared to be unidentifiable using the available catalogues of mass spectra, just like smaller peaks that were not marked on the chromatogram.

Figure 2c shows the chromatogram of the PTFE/PEO coating. The general appearance of the chromatogram is quite similar to that of the siloxane–acrylate-emulsion solid residue (Fig. 2b), peaks 1–3 corresponded to carbon dioxide and air, presumably contained in pores of the coating. Peaks 4–6 represented products of the emulsion decomposition: 4, methylmethacrylate; 5, isobutylmethacrylate; and 6, butylmethacrylate. Peaks 7–15 were impossible to deconvolute using the available catalogs. A general chromatogram of the PTFE/PEO coating (Fig. 2c) does not contain a characteristic large number of peaks of saturated and unsaturated fluorocarbons as in Fig. 2a. This is related to the fact that peaks of the siloxane–acryl-emulsion solid residues overlap the fluorocarbon peaks and conceal them.

On the PTFE/PEO chromatogram, we identified peaks of the components corresponding to the solid residue of the siloxane–acryl emulsion, as well as the fluorocarbon peaks. The main ions on the fluorocarbons mass spectra appeared to be those with m/z 69, 100, 131, 169, 181, 219, 231, and 269. Besides the peaks typical for the fluorocarbons’ mass spectra, peaks of an evident fluorocarbon nature were observed, but the

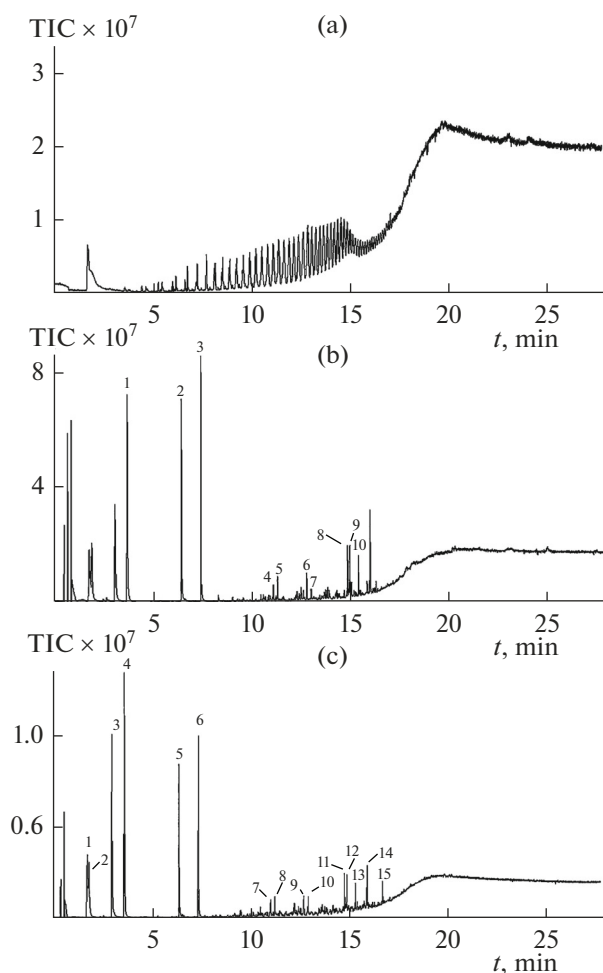


Fig. 2. Chromatograms of (a) the dispersed PTFE powder, (b) the emulsion solid residue, and (c) the PTFE/PEO coating.

113 ion dominated in these mass spectra. This ion with the mass to charge ratio of 113 was absent in the PTFE-powder mass spectra, as well as in that of the siloxane-acryl-emulsion solid residue. The intensity of this ion peak (Fig. 3b) indicates that it is present to some extent in the PTFE/PEO coating.

A fragment of the chain with the m/z 113 ion corresponded to the $C_3F_4H^+$ group. It was suggested that upon formation of the PEO coating, a fluorine atom was substituted by hydrogen atom in certain unsaturated fluorocarbons. The energy necessary for this kind of replacement was provided by spark and microarc discharges in the anode region during PEO. In addition, hydrogen (including ionized hydrogen) was present in the discharge channels due to water electrolysis and thermolysis. Such a substitution corroborated an insignificant decrease of the electrolyte acidity after PEO.

To verify that PEO has an effect on the formation of the compound containing the ion with m/z 113, a solid residue of the PTFE particles dispersion in the siloxane-acrylate-emulsion (60 g of powder in 100 mL of emulsion) was investigated by means of pyrolytic gas chromatography mass spectrometry. The chromatogram of the dispersion solid residue differed significantly from that of the PTFE/PEO coating (Fig. 4). The group containing the ion with m/z 113 is typical only for the composite coating. On the other hand, comparison of the chromatograms showed that a PTFE/PEO-coating polymer-like layer evaporable at 500°C did not correspond to a mechanical mixture of the PTFE dispersed powder and the siloxane-acrylate-emulsion solid residue.

Upon PTFE/PEO-coating pyrolysis at 500°C, fluorocarbon peaks were almost indistinguishable in the chromatogram because of a large amount of emulsion components (Fig. 3c). However, it was possible to identify the ions typical for fluorocarbons upon a detailed examination of the mass spectra, whereas, according to the X-ray spectral analysis (XSA) provided earlier in [16, 17], such coatings contained up to 29 at % of fluorine, i.e., a rather substantial amount of fluorocarbons. On the other hand, as was shown in [16], the polymer-like part of the PTFE/PEO coating at 200°C transformed into a viscous flow state and filled up pores and cavities, while at 300–400°C it sublimated. This means that, at varied pyrolysis, temperatures various components can sublimate. To explicate thus, we performed coating pyrolysis at 100, 200, 300, and 400°C.

Figure 5 shows chromatograms of the PTFE/PEO coatings obtained at pyrolysis temperatures of 100 and 200°C. Upon pyrolysis at 100°C, only the products of destruction of the siloxane-acrylate-emulsion solid deposit were observed: peaks 1–6, 8, 10, and 12–14 corresponded to carbohydrates; peak 7, to diphenylamine; peak 9, to 2,6-ditretbutyl-1,4-benzeneodiol; and peak 11, to siloxanes (Fig. 5a). At a pyrolysis temperature of 200°C, a general appearance of the chromatogram changed abruptly: the spectrum structure typical for fluorocarbons was observed (compare Figs. 2a, 5b, 5c). Peaks 1–6, 10, and 11 on the spectrum correspond to fluorocarbons and peaks 7–9 to fluorocarbons, in which the fluorine atom is substituted by a hydrogen atom. The peaks 12, 13, 16, and 17 were impossible to identify.

The chromatograms obtained upon pyrolysis at 300 and 400°C contained many peaks corresponding as to different products of destruction of the siloxane-acrylate emulsion as to high-temperature fractions of fluorocarbons. The absence of numerous peaks in the chromatogram of the PTFE/PEO coating obtained upon pyrolysis of the entire polymer-like layer at 500°C (Fig. 3a) must be related the fact that fluorocarbon peaks were concealed by the peaks of the siloxane-acrylate-emulsion solid residue.

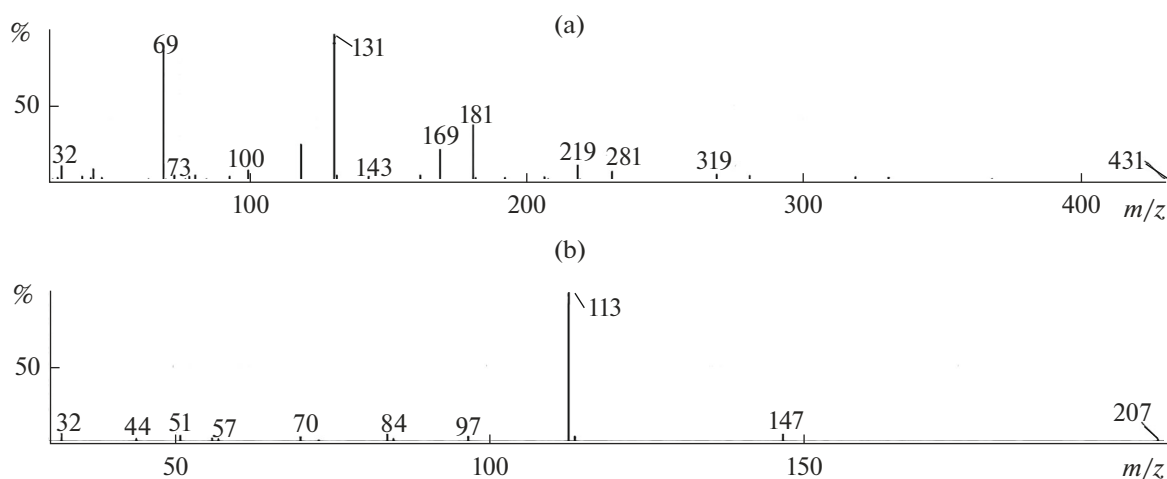


Fig. 3. Typical mass spectrum of a perfluorocarbon homolog of PTFE (a) and (b) that of the compound containing $C_3F_4H^+$ in the PTFE/PEO coating.

As seen from the above, the external polymer-like-layer batch does not represent a mechanical mixture of the PTFE particles and the siloxane–acrylate copolymers. According to the pyrolytic gas chromatography mass-spectrometry data, this layer contains fragments of both PTFE and siloxane–acrylate emulsion. Moreover, a partial substitution of fluorine by hydrogen in fluorocarbons was observed.

According to the data of [11, 12, 14–17] and the present study, the PTFE/PEO coatings formed in the suspension-emulsion electrolyte containing more than 30 g/L of the PTFE powder with particles of sizes of $\sim 1 \mu m$ introduced in the form of dispersion to 100 mL of siloxane–acrylate emulsion exhibited a layered structure. A fairly compact and uniform external polymer-like layer, the thickness of which depended on the PTFE-powder concentration in the electrolyte, consisted of products of the PTFE-powder destruction and the emulsion copolymer. Ensembles of the PTFE particles at the state of introduction into the electrolyte were present in pores and cavities of this layer. A transition-oxide layer of a thickness of $\sim 10 \mu m$ providing external-layer adhesion was located between the external polymer-like layer and the substrate metal. These layered coatings exhibited hydrophobic properties, the wetting angle attained a value up to $\sim 105^\circ$, and they were resistant to mechanical wear. The wear resistance was presumably determined by the external polymer-like layer acting as a solid lubricant. At temperatures of $\sim 200^\circ C$, the polymer-like layer transformed into a viscous flow state and filled up the surface pores, which dramatically improved the anticorrosive properties of the coatings. At temperatures of $> 200^\circ C$, there started evaporation of the external polymer-like layer.

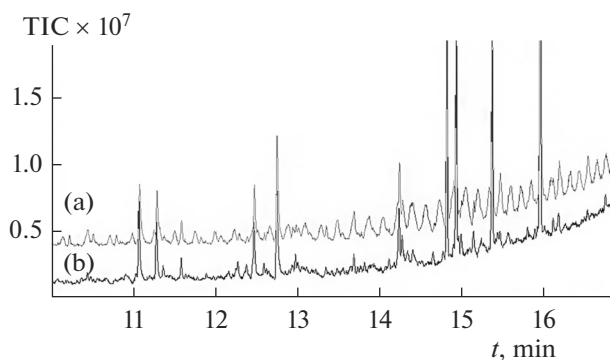


Fig. 4. Chromatograms of the solid residue of the PTFE particles' dispersion in the siloxane–acryl emulsion (a) and the PTFE/PEO coating (b).

In our opinion, the regularities of the formation process, composition and properties of the hybrid PTFE/PEO coating formed within a single stage in suspension-emulsion electrolytes established in this and other [11, 12, 14–17] studies can serve as a basis for further development of methods of formation of coatings with hydrophobic and protective properties on aluminum and titanium. In addition, these regularities can be applied in producing composite layers of varied compositions, for example, those containing products of destruction of required polymers, polymer mixtures, and dispersed hydrophobic particles of various nature. As was shown in [15], the application of suspension-emulsion electrolytes with dispersed graphite particles of a size of $\sim 50 \mu m$ allows fabricating graphite oxide PEO coatings.

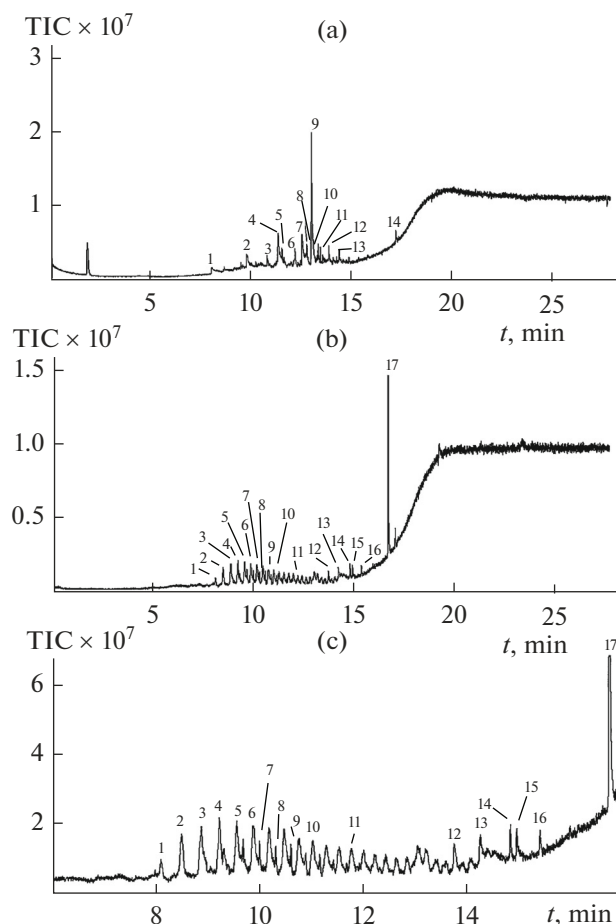


Fig. 5. Chromatograms of the PTFE/PEO coating obtained at a pyrolysis temperature of 100 (a) and 200°C (b) and a fragment of it (c).

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