IR and Py-GC/MS investigation of composite PTFE/PEO coatings on aluminum

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HIGHLIGHTS

- The electrolyte with PTFE particles and siloxane-acrylate emulsion is used.
- The outer layer of the coating has a polymeric nature.
- Polymer-like layer contains the products of destruction of PTFE and emulsion.

GRAPHICAL ABSTRACT
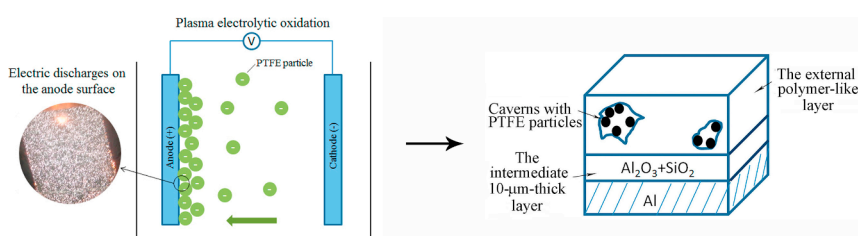
ABSTRACT

The data on the composition of polytetrafluoroethylene (PTFE) + Al$_2$O$_3$ coatings obtained on an aluminum alloy by the single-stage method of plasma electrolytic oxidation (PEO) are presented. The coatings are formed in an alkaline silicate electrolyte with introduction of dispersed PTFE particles stabilized with siloxane-acrylate emulsion. The comparative study of the surface of initial oxide and PTFE/Al$_2$O$_3$ coatings, dispersed PTFE powder, and dry emulsion residue has been performed by the method of IR spectroscopy. The method of pyrolytic chromatography – mass spectrometry was used to obtain the data on the composition of the emulsion dry residue, dispersed PTFE powder, and PTFE/Al$_2$O$_3$-coatings. The surface and the main bulk of compact polymer-like PTFE/Al$_2$O$_3$ coatings do not contain aluminum and silicon oxides. They consist of the products of destruction of emulsion and PTFE formed under effect of electric discharges during PEO and contain PTFE particles in pores and caverns.

1. Introduction

A rather substantial attention of researchers is focused on fabrication and study of hybrid coatings, i.e., those containing, aside from the oxide component, compounds of the nature similar to that of organics, such as graphite, graphenes, polymers, and carbon nanotubes and nanofibers [1–6]. Introduction of the above fillers can impart coatings with new properties. In particular, introduction of polytetrafluoroethylene ([-C$_2$F$_4$-]$_n$, PTFE) results in the decrease of the friction coefficient and the increase of anticorrosion and hydrophobic parameters of the final composites [6–13].

Plasma electrolytic oxidation (PEO) consists in formation of oxide layers on metals and alloys under electric spark and microarc discharges [14]. The method does not require special surface pre-treatment before oxidation; it allows one to form the oxide layers with high adhesion to the metal on the samples with complex geometry and to fabricate protective coatings on various details [14–17]. The PEO application is studied in view of formation of inorganic layers of various

chemical compositions on metals, which are characterized by specific physical–chemical properties, such as: biocompatible [18], biocide [19], hydrophilic [20], hydrophobic [21], heat-scattering [22], and with certain magnetic [23] or catalytic characteristics [24]. The introduction of polymers into such coatings can significantly improve their protective properties. Therefore, the development of methods for modifying PEO coatings with polymers, including PTFE, obtaining data on the composition, structure, and properties of PTFE/PEO coatings is of scientific and practical interest.

It was suggested to form PTFE/PEO-coating composites within as single stage [5,11–13] as several stages [7–9]. In the latter case, a PTFE-layer composed of dispersed PTFE particles is formed by the methods of impregnation [7], electrophoretic deposition [9], or mechanical rubbing [8] on the preliminarily obtained PEO coating. To attain homogeneity of the deposited layer, it undergoes compact annealing at 200–300 °C.

During the single-stage formation, dispersed PTFE particles are additionally introduced into the aqueous electrolyte, in which the PEO-coating is formed [5,10–13]. To stabilize dispersed hydrophobic PTFE particles in the aqueous solution bulk, it was suggested to use surfactants [10] or acrylic [11], siloxane–acrylic [12], or styrene–acrylic emulsions [13]. Through enveloping the PTFE particles and producing a negative charge on them, surfactants and the above polymers improve the stability of an aqueous suspension electrolyte over time and promote mobility of PTFE particles to the anode-polarized metal to be treated during PEO. In this case, the processes of PEO-coatings formation and dispersed PTFE particles electrophoretic deposition into the growing coating occur simultaneously.

The difference in two approaches (single stage or several stages) also consists in the fact that at fabrication by the methods of rubbing, impregnation, and electrodeposition with subsequent annealing at 200–300 °C the layer deposited on the PEO-coating must be more similar in composition to the initial PTFE powder than that obtained within a single stage. During PEO, temperatures from hundreds to several thousand degrees and substantial pressure gradients are realized in the pulse mode inside local sites of the impact of spark and microarc discharges [14-17], which could result in destruction of PTFE molecules in these sites. At the same time, hydrophobic coatings characterized with low friction coefficient and significantly increasing the resistance to mechanical wear, as compared to unmodified coatings, are formed in both cases [5,7–13].

To predict possible fields of application, it is of importance to determine the composition, structure, and properties of PTFE/PEO-coating composites formed through more technologically sound single-stage PEO-method, in particular, in suspension–emulsion electrolytes (latexes). The use of suspensions-emulsion electrolytes with PTFE particles for the formation of PTFE/PEO-coatings on the surface of valve metals has been initiated relatively recently. The number of publications on the subject is small [11–13,25–28]. In work [11], PTFE/PEO-coating composites on an aluminum alloy in the $Na_2SiO_3 + NaOH$ electrolyte with addition of 60 vol % of PTFE-containing acrylate emulsion (55 wt %) were formed using a bipolar pulse current source. According to the XPS data, CF_2-groups are present in the coatings, which indicates to embedding of PTFE particles into them. Upon PTFE embedding, the number of large pores on the surface decreases, the corrosion resistance increases, and the friction coefficient decreases several-fold.

Authors [13] formed PTFE/PEO-coating composites on the aluminum alloy in the $Na_2HPO_4 + KOH$ electrolyte with introduction of 5 wt % of PTFE-dispersed styrene–acrylate emulsion. PTFE/PEO-coatings composites are hydrophobic, and the limiting wetting angle is equal to 137°. The authors concluded that the coatings contained mostly PTFE, styrene–acrylate emulsion, γ-Al_2O_3, and traces of α-Al_2O_3. PTFE particles are distributed in the styrene–acrylate emulsion matrix, thus forming a composite coating. Introduction of PTFE decreases the friction coefficient and increases the coating anticorrosion and

tribological resistance.

We have fabricated PTFE/PEO-coating composites on an aluminum alloy and titanium in $Na_2SiO_3 + NaOH$ electrolyte with added siloxane–acrylate emulsion (100 ml/L of electrolyte) and different concentrations of the dispersed PTFE particles of an average diameter of ~ 1 μm [12,25–28]. The thickness h, the limiting wetting angle θ, and the time of mechanical wear-off of the formed coatings increased gradually, starting from the PTFE particles concentration in the electrolyte > 30 g/L. The coatings formed at the PTFE particles concentrations in the electrolyte of 60 g/L had $h \sim 80$ μm and $\theta \sim 110°$. The averaged composition of the coating surface layer on aluminum alloy was as follows (from the X-ray spectrum analysis data, at. %): 58.1 C; 12 O; 29.2 F; and 0.6 Si. From the XPS data, 7.6 F and 58.2 C (at. %) are contained on the surface in the groups' composition: CF_2 ($\sim 9\%$ of total C quantity); CO_2; CO; C–C, C–H ($\sim 65.5\%$); CF. These facts as well as the measured characteristics of the coatings allowed assuming that the coating main bulk is composed of the products of destruction of siloxane–acrylate emulsion and PTFE. During PEO, under spark and microarc, they are transformed into a homogeneous polymer-like substance.

Thus, the coatings with PTFE particles fabricated by the single-stage PEO method in suspension–emulsion electrolytes are promising in practical application. They are hydrophobic, resistant to mechanical wear, and exhibit anticorrosion properties.

When using such coatings, it is important to know their composition, structure, and ways of controlling them. However, as shown above, the literature on the composition and structure of such coatings is inconsistent. In one case, PTFE particles are included into the coating [11]. In another case, this is a composite coating, the PTFE particles are distributed in emulsion matrix [13]. In the third case, it is a composite coating containing in the outer part of the products of destruction of emulsion and PTFE [27,28]. In Ref. [28], pyrolytic chromatography-mass spectrometry method (Py-GC/MS) was used for the first time to study such coatings and it was shown that the chromatograms of the evaporated PTFE powder and the coating material are qualitatively different. This fact was interpreted as yet another proof that the main bulk of coatings is mainly constructed from the destruction products of PTFE particles and emulsions.

In the present work, the Py-GC/MS chromatograms and the IR spectra of the PTFE powder, the solid emulsion residue, the mixture of solid emulsion residue with particles of PTFE and PTFE/PEO coatings are analyzed and compared for the first time in order to determine the composition of the PTFE/PEO coatings formed in suspension-emulsion electrolytes.

2. Materials and methods

2.1. Materials

Composite layers were formed on samples made of an aluminum alloy 5056 of a size of 20 × 20 × 0.5 mm. The choice of the alloy is due to its wide industrial application. The samples pretreatment included their mechanical grinding with subsequent chemical polishing in a mixture of acids H_3PO_4: H_2SO_4: HNO_3 = 4: 2: 1 at 90–100 °C.

To prepare the base electrolyte, distilled water and commercial reagents ($Na_2SiO_3 \cdot 5H_2O$, and NaOH) were used.

The commercial product FORUM® (trademark registered in Russia) was used as the dispersed PTFE powder; the PTFE particles main fraction size was ~ 1 μm, see Fig. 1a.

The commercially available siloxane–acrylate emulsion KE 13–36 (Russia, solid phase content 50%, average micelle size 160 nm, viscous nontransparent liquid of white color, pH 6–7) was used as an emulsifier.

2.2. Electrolyte preparation and PEO-coatings formation

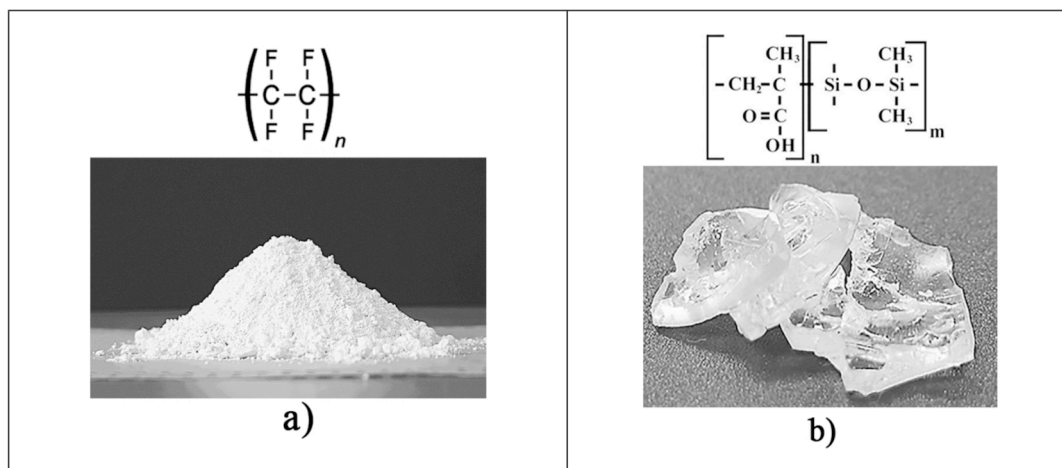The working suspension–emulsion electrolyte was obtained by

Fig. 1. Dispersed PTFE powder of the FORUM® grade (a); siloxane–acrylate emulsion dry residue (b).

mixing the base electrolyte and a dispersion of PTFE particles in the siloxane–acrylate emulsion. The base aqueous electrolyte contained 10.6 g/L $Na_2SiO_3 \cdot 5H_2O$ and 2 g/L NaOH. The dispersion was obtained by mixing 100 mL of emulsion and 50 g of PTFE powder with subsequent intensive stirring using a magnetic stirrer for at least 30 min until producing a homogeneous mass. The produced dispersion was added to the base aqueous electrolyte to obtain total volume of 1 L and the final mixture was intensively stirred. The whole process yielded the working suspension–emulsion electrolyte.

Electrochemical treatment of aluminum samples was carried out in the working electrolyte placed into a vessel made of heat-resistant glass, Fig. 2. A hollow coil made of nickel alloys, through which tap water was fed, served as a counter-electrode. The solution temperature in the treatment process did not exceed 30 °C. A computer-controlled TER–100/460 thyristor device (Russia) operated in the unipolar mode served as a current source. The electrolyte was stirred using a magnetic stirrer. The coatings on anode-polarized samples were formed for 20 min in the galvanostatic mode; the effective current density was 0.05 A/cm^2. The samples with coatings were washed with distilled water

and dried in air.

2.3. Preparation of dry emulsion residues and dispersion of PTFE particles in emulsion

10 mL of emulsion or dispersion was dried in air for 10 h at 80 °C. Fig. 1b shows the general appearance of the dry residue of the siloxane–acrylate emulsion.

2.4. IR spectroscopy

IR spectra of samples in the range 250–4000 cm^{-1} were registered using a Shimadzu FTIR Prestige-21 spectrometer (Japan). To register the IR spectrum of the PTFE powder, it was mixed with a few drops of Vaseline oil, ground in a mortar, and then placed in a KRS-5 dismountable cuvette. The spectra of PTFE/PEO-coating composites and dry emulsion residue were obtained by the method of measurement of reflection spectra using a RAS 8000 accessory.
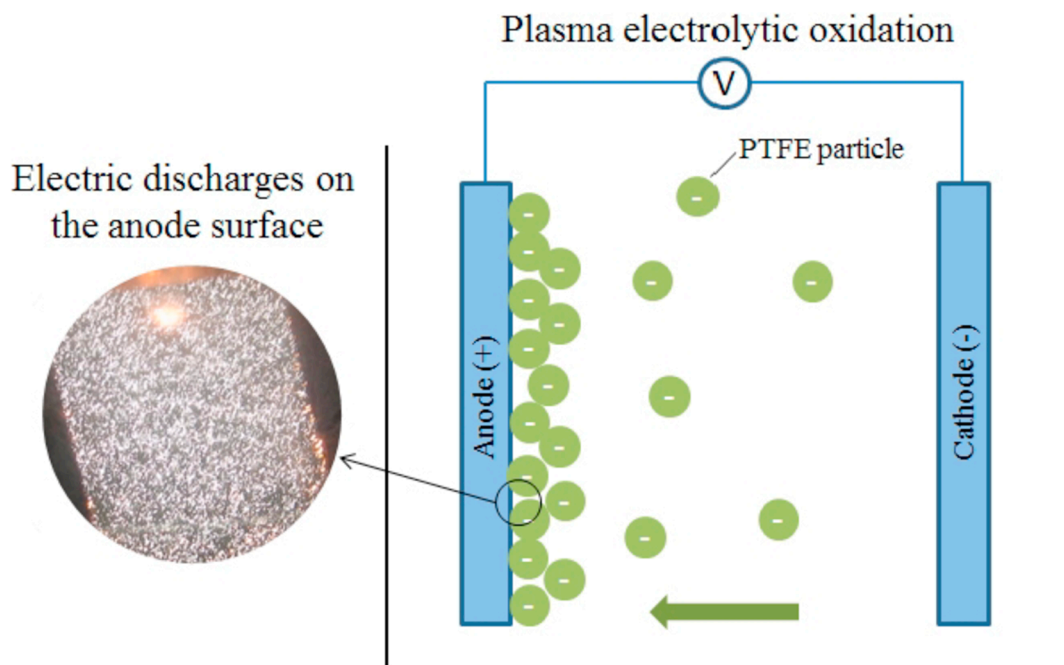

Fig. 2. The scheme of coating formation by PEO technique.

2.5. Pyrolytic chromatography – mass spectrometry

A Double Shot Pyrolyzer PY-2020iD device (Japan) connected to a Shimadzu GCMS QP-2010 chromatograph – mass spectrometer (Japan) was used. The chromatograph and mass spectrometer calibration was performed under standardized conditions recommended in the library for polymer identification F-Search "All-in-One", Ver. 3.10. The pyrolysis temperature selection (500 °C) was determined by previous studies [29,30]; the PY/GC interface temperature was 320 °C. Separation of the pyrolysis products was carried out using an Ultra ALLOY-5 column (length 30 m, internal diameter 0.25 mm, phase film thickness 0.25 μm), carrier gas – helium, 1 mL/min, flow separator 1:50. The column temperature was programmed from 40 °C (held for 3 min), and then the temperature was increased up to 320 °C at a rate of 20 °C/min (held for 8 min). The mass range (m/z) – 29–800, the MSD interface temperature – 280 °C, the ion source temperature – 250 °C, the detector voltage – 1 kV.

The PTFE/PEO-coating was peeled from the aluminum substrate by a scalpel. The samples of coating, emulsion dry residue, or dry residue of the PTFE particle dispersion in the emulsion were placed into a special stainless steel cuvette of the pyrolyzer in solid state. The sample mass was selected in preliminary tests: it was equal to ~1 mg. The stepwise heating from 0 to 400 °C with an increment of 100 °C was carried out without changing the sample, i.e., the same sample underwent heating over the whole temperature range.

3. Results

3.1. IR spectroscopy data

Fig. 3 Shows IR spectra of the used PTFE powder, siloxane–acrylate emulsion dry residue, PEO-coating, and PTFE/PEO composite coating.

The PTFE IR spectrum (Fig. 3a) contains intensive absorption bands characteristic of polymer macromolecules ($-CF_2-$)$_n$: 1215 cm^{-1}; 1155 cm^{-1} – stretching, 640 см$^{-1}$ – radial, and ~511 см$^{-1}$ – pendulum vibrations for CF_2 groups [31]. The intensive lines present in the spectrum (2922, 2852, 1462, and 1377 cm^{-1}) and corresponding to stretching and bending vibrations of CH_2 groups are associated with Vaseline, in which the powder was dispersed during IR spectra registration.

In the IR spectrum of the dry residue of the siloxane–acrylate emulsion (Fig. 3b), the absorption bands at 2960 and 2873 cm^{-1} characterize stretching vibrations, while the band at 1454 cm^{-1} – bending vibrations, of CH_3 groups [32]. The absorption peak at 1741 cm^{-1} corresponds to stretching vibrations of C = O bonds in aliphatic esters [32]. The absorption bands at 1192 cm^{-1} and in the range 850–800 cm^{-1} correspond to vibrations of the $SiOCH_3$ group [33]. The absorption band at 2351 cm^{-1} corresponds to CO_2 [33]. The peak can be associated with CO_2 absorbed from atmosphere by the volume of emulsion or by the surface of its dry residue. In addition, it may be due to the level of CO_2 in the atmosphere has slightly changed between the blank run and the spectrum of the sample. The absorption bands at 1192 cm^{-1} and in the range 850–800 cm^{-1} correspond to vibrations of the $SiOCH_3$ group [33].

In the IR spectrum of the PEO-coating (Fig. 3c), a weak absorption band at 1629 cm^{-1} corresponds to bending vibrations of H_2O [34]. A broad intensive band at 974 cm^{-1} corresponds to aluminum oxide (Al_2O_3) [34]. The band at 779 cm^{-1} corresponds to symmetric stretching vibrations of the Si–O–Si group [33].

The IR spectrum of the composite PTFE/PEO-coating (Fig. 3d) above 1000 cm^{-1} is similar to that of the siloxane–acrylate emulsion dry residue and has the same absorption bands with insignificant shifts: 2964; 2873; 2351; 1749; 1454, and 1192 cm^{-1}. The IR spectrum of the composite coating contains an expressed band at 1274 cm^{-1} that is absent in the spectra of PTFE and emulsion dry residue: it corresponds to the $SiCH_3$ group [33].

To sum up, the IR spectrum of the surface of composite PTFE/PEO coating does not contain absorption bands corresponding to the PEO coating formed in the base silicate electrolyte. PTFE particles are absent on the surface, as there are no intensive peaks corresponding to CF_2 groups. According to the obtained data, the IR reflection spectrum of the PTFE/PEO coating is similar to that of the siloxane–acrylate copolymer dry residue, albeit with some differences consisting in the presence of a band at 1274 cm^{-1} and the spectrum transformation lower than 1000 cm^{-1}.

3.2. Results of pyrolytic chromatography – mass spectrometry

Fig. 4 shows chromatograms of the used dispersed PTFE powder of the FORUM® grade, the siloxane–acrylate emulsion dry residue, and PTFE/PEO coatings. Chromatograms were obtained during the samples pyrolysis at 500 °C. Earlier, chromatograms of the PTFE powder of the FORUM® grade were thoroughly studied in Refs. [29,30]. According to the authors, the PTFE powder of the FORUM® grade comprises a mixture of perfluorocarbons – PTFE homologs with the number of carbon atoms in the chain from C5 to C70. The mass-spectra of perfluorocarbons contain two series of ions – for saturated and unsaturated components, while the spectra themselves are almost indistinguishable for compounds with different numbers of carbon atoms in the chain (see Fig. 4a). For the saturated components, the most intensive is the ion with m/z (ion mass/charge ratio) of 69 (CF_3^+), whereas in the case of unsaturated fluorocarbons this is the one with m/z 131 ($C_3F_5^+$). The intensive ions for the "alkane" series are those with m/z 69, 119, 169, 219 and so on, while for the "alkene" series – with m/z from 131, 181, 231, 281 and so on. The difference in masses of main ions of two series is 50, which is equal to that of the CF_2 group.

Because of pyrolysis, the siloxane–acrylate emulsion dry residue decomposes into acrylic acid esters with different fragment lengths (Fig. 4b). The peak 1 corresponds to the methyl ester of acrylic acid, the peak 2 – to its isobutyl ester, and the peak 3 – to its n-butyl ester. Peaks to the left of the peak 1 that are not marked by figures are associated with air, in particular, to carbon dioxide, which perhaps distributed in the siloxane–acrylate dry residue. We have not managed to identify the peaks 4–10 using the available mass-spectra libraries, just like smaller peaks present on the chromatogram.

Fig. 4c shows the chromatogram of the PTFE/PEO coating. The general chromatogram appearance is similar to that of the siloxane–acrylate emulsion dry residue. Peak 1 correspond to carbon dioxide, which must have been contained in coating pores. The peaks correspond to the emulsion decomposition products: 2 – 2-hydroxyacetaldehyde, 3 – butanol, 4 – methyl methacrylate; 5 – isobutyl methacrylate; 6 – butyl methacrylate. We have not managed to identify the peaks 7–15 using the available libraries. There are some peaks of saturated and unsaturated fluorocarbons on the general chromatogram of the PTFE/PEO coating (Fig. 4c). Their small number associated with the fact that the peaks of the siloxane–acrylate emulsion dry residue are superimposed on the most of fluorocarbons peaks, which is clearly seen at analysis of mass-spectra.

On the chromatogram of the PTFE/PEO coating, we have identified the peaks of components associated with the siloxane–acrylate emulsion dry residue and those of fluorocarbons. The main ions on mass-spectra of fluorocarbons are ions with m/z 69, 100, 131, 169, 181, 219, 231, and 269 (Fig. 5). Aside from peaks with typical for fluorocarbons mass-spectra, there were peaks of clear fluorocarbon character, but in their spectra the ions with m/z 113 was predominant. This ion is not present in mass-spectra of the PTFE powder and those of the siloxane–acrylate emulsion dry residue. The intensity of this ion peak (Fig. 5b) indicates to the fact that it is unambiguously present in the PTFE/PEO coating.

The chain fragment with m/z 113 corresponds to the $C_3F_4H^+$ group. The substitution of the fluorine atom by that of hydrogen probably occurs in some unsaturated fluorocarbons at formation of the PEO
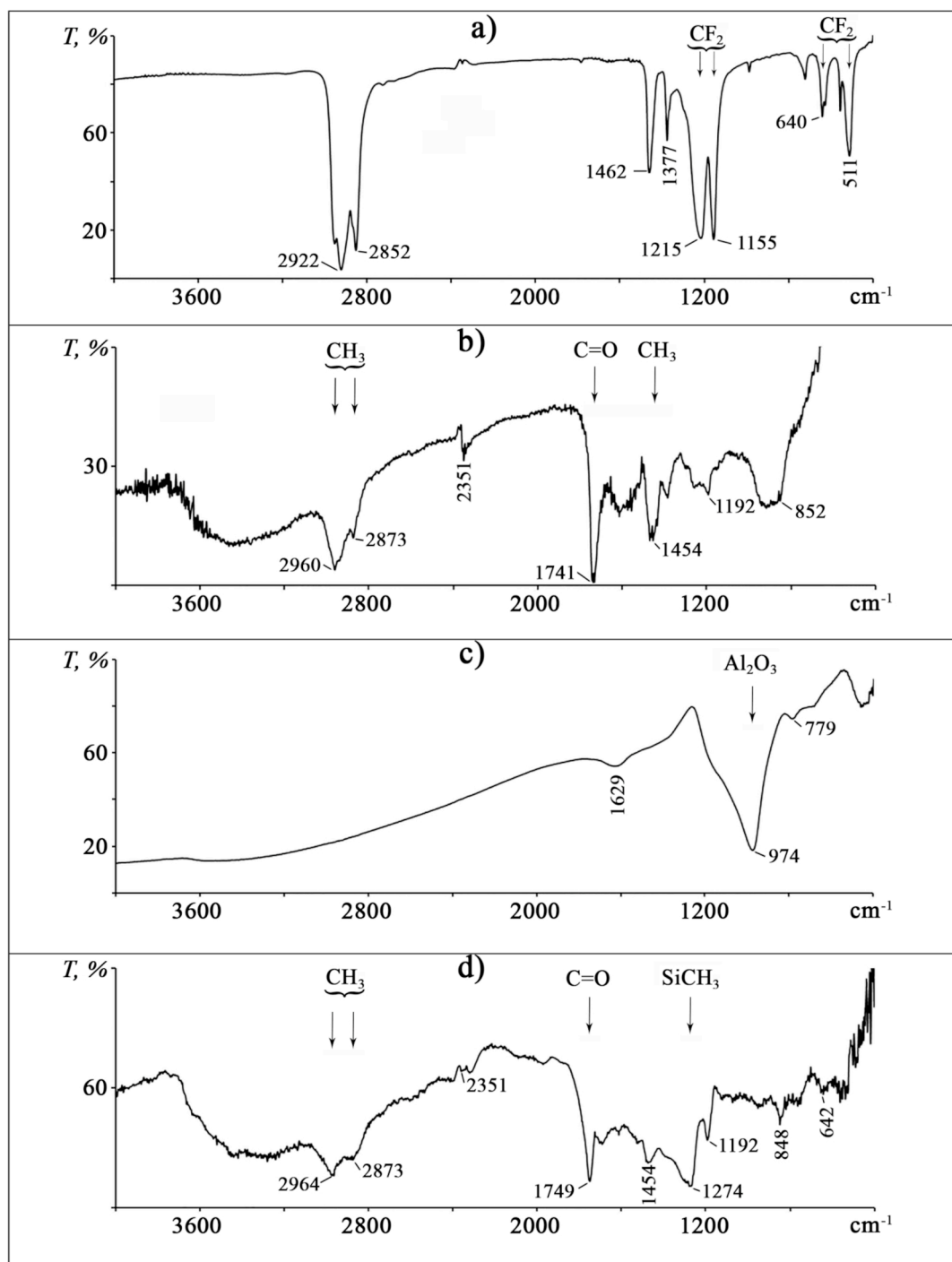
Fig. 3. IR spectra of PTFE (a), siloxane–acrylate emulsion dry residue (b), initial PEO coating (c), composite PTFE/PEO coating (d).

coating. Here, the required energy is provided by realization of spark and microarc discharges in the near-anode area during the PEO process. Besides, hydrogen, including not ionized one, is present in the discharge channels due to electrolysis and water thermolysis. Such a substitution is corroborated by insignificant decrease of the electrolyte acidity upon PEO.

To corroborate the effect PEO on formation of the compound containing the ion with *m/z* 113 in the PTFE/PEO coating, the dry residue of the dispersion of PTFE particles in siloxane–acrylate emulsion was studied by the method of pyrolytic chromatography – mass spectrometry (50 g of powder in 100 mL of emulsion). The chromatogram of the dispersion dry residue is essentially different from that of the PTFE/

PEO-coating (Fig. 6). The group with *m/z* 113 characterizes only the composite coating. On the other hand, the chromatograms comparison (Fig. 6) shows that the polymer-like layer of the PTFE/PEO-coating evaporated at 500 °C is not a mechanical mixture of the dispersed PTFE coating and the siloxane–acrylate emulsion dry residue.

At pyrolysis of the PTFE/PEO coating (500 °C), the fluorocarbon peaks on the chromatogram are virtually indistinguishable because of a large number of the emulsion components (Fig. 4c). However, during the detailed study of the mass-spectra, one can single out ions characteristic of fluorocarbons. On the other hand, according to [25–28], such coatings contain (from the XRD analysis) up to 29 at. % of fluorine, i.e., rather significant quantities of fluorocarbons. In addition, as was
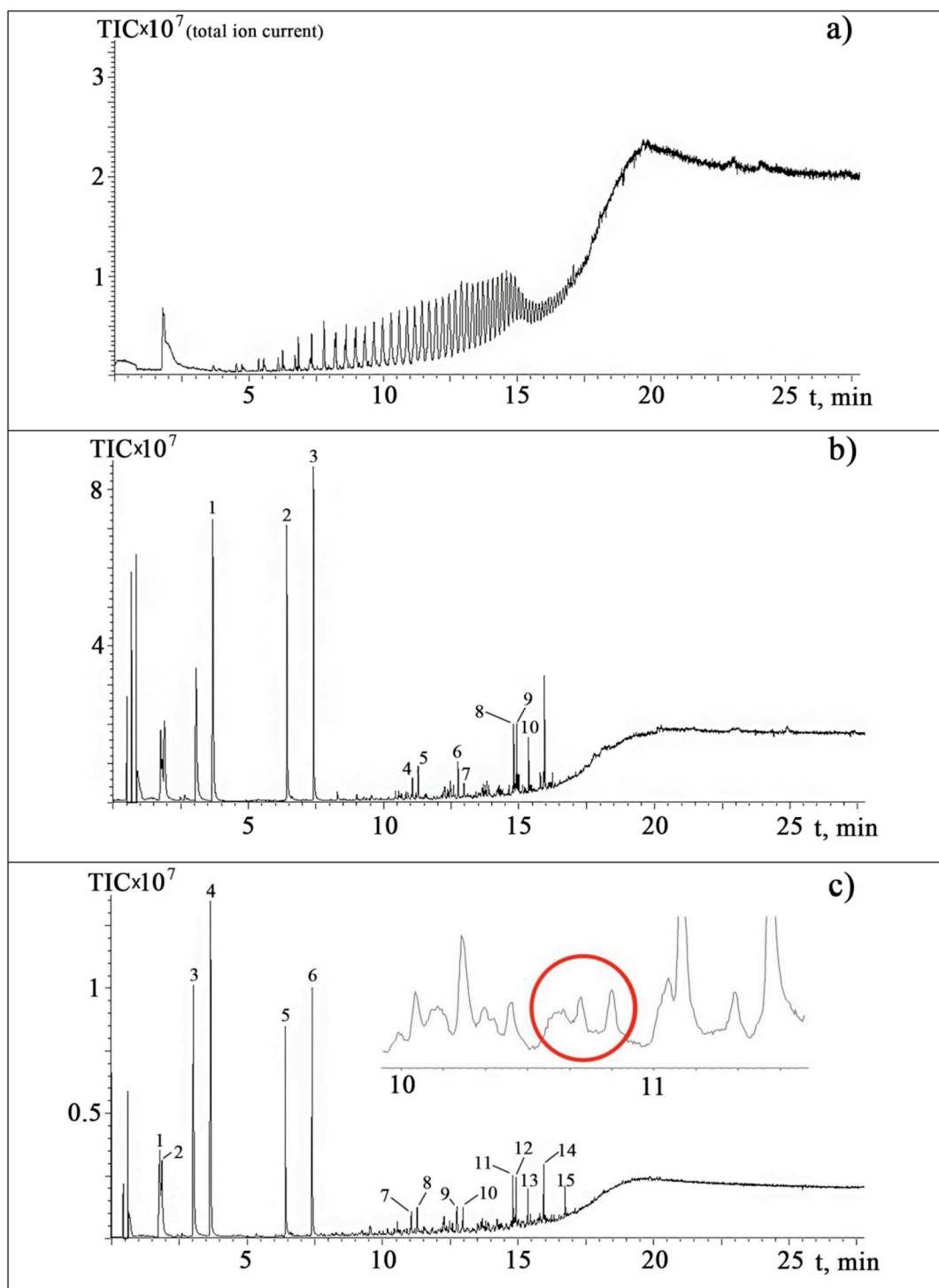
Fig. 4. Chromatograms of the dispersed PTFE powder (a), emulsion dry residue (b), and PTFE/PEO coating (c). There are peaks of fluorocarbons on detailed fragment of the PTFE/PEO coating chromatogram.

shown earlier [27], at temperatures around 200 °C, the polymer-like part of the PTFE/PEO-coating transformed into the viscous-fluid state and filled pores and caverns, whereas at 300–400 °C it sublimates. In other words, at different pyrolysis temperatures, different components can sublimate from the coating. To elucidate this aspect of study, we performed the coating pyrolysis of the same sample with a gradual temperature increase from 0 °C to 400 °C at an increment of 100 °C.

Fig. 7 shows chromatograms of the PTFE/PEO coating obtained at pyrolysis temperatures of 100 and 200 °C. At the pyrolysis temperature of 100 °C, just the products of destruction of the siloxane–acrylate

emulsion dry residue are identified: peaks 1–6, 8, 10, 12–14 – hydrocarbons; peak 7 – diphenyl amine; peak 9–2,6-di-tretbutyl–1,4–benzenediol; and peak 11 – siloxanes. At the pyrolysis temperature of 200 °C, the chromatogram appearance changes dramatically: one can see the spectral structure characteristic of fluorocarbons (compare Figs. 4a and 7bc). In the spectrum, the peaks 1–6, 10, 11 – fluorocarbons, the peaks 7–9 correspond to fluorocarbons with the fluorine atom substitute by that of hydrogen. We have not managed to identify the peaks 12, 13, 16, and 17.

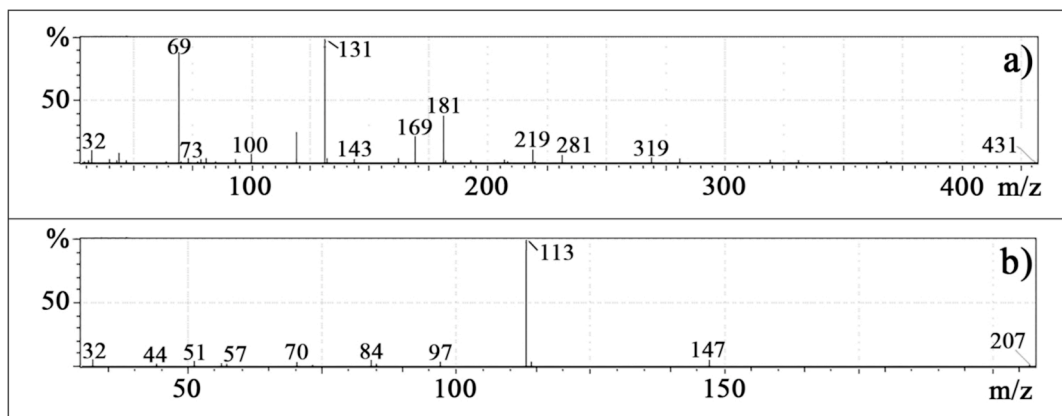The chromatograms obtained at pyrolysis temperatures of 300 and

Fig. 5. Typical mass-spectrum of perfluorocarbon – PTFE homolog (a) and the compound with the $C_3F_4H^+$ ion in the PTFE/PEO coating (b).
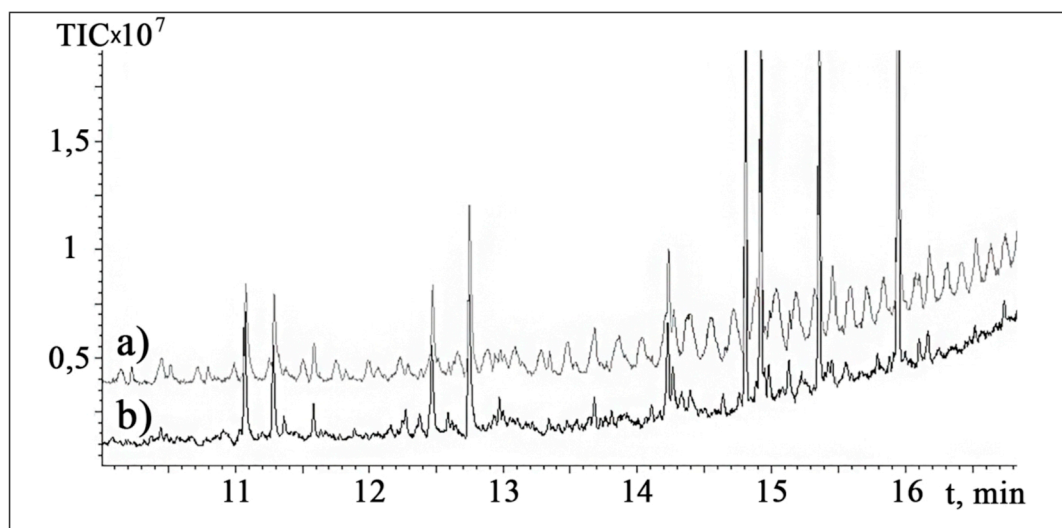

Fig. 6. Comparison of chromatograms: (a) – dry residue of dispersed PTFE particles in siloxane–acrylate emulsion, (b) – PTFE/PEO coating.

400 °C contain numerous peaks corresponding as to various products of destruction of the siloxane–acrylate emulsion as to high-temperature fluorocarbon fractions. Peaks corresponding to pyrolysis products of the siloxane-acrylate emulsion together with fluorocarbon peaks of low-intensity (see the inset in Fig. 4c) prevail on the chromatogram obtained at the temperature of pyrolysis of the entire polymer-like layer at 500°C (Fig. 4c). This indicates a greater amount of destruction products of siloxane-acrylate emulsion in the coating compared with those of PTFE.

4. Discussion

As was shown in the Introduction, to form hybrid PTFE/PEO coatings by a single-stage PEO method, it was suggested to use suspension–emulsion electrolytes with dispersed PTFE particles of sizes from hundreds nm [11,13] to 1 μm [12,25–28] stabilized with acrylate, styrene–acrylate, and siloxane–acrylate emulsions, respectively. In all cases, coatings are hydrophobic with improved mechanical wear resistance.

From the data of [11,13], in the case of PTFE/PEO coatings on aluminum alloys, the surface is more homogeneous and less porous than for the coatings formed in the base alkaline silicate or phosphate electrolyte without addition of PTFE particles and respective emulsion. Here, the coating thickness changes insignificantly. According to results of refs. [25–28], the coatings thickness, wear resistance, and hydrophobic properties depend on the concentration of the PTFE powder

dispersed in 100 mL of siloxane–acrylate emulsion and then added into the alkaline silicate electrolyte. These parameters start to change at the powder content in the electrolyte of > 30 g/L. According to the element distribution along the cross-section (Fig. 8a and b) the regularities of variation with the temperature of the thickness, surface morphology and elemental composition (Fig. 8c, d, e) the coatings have a layered structure. In the temperature range 200–400 °C, the outer polymer-like layer sublimes, and an inner layer containing Al_2O_3 and SiO_2 of thickness ~10 μm remains adjacent to the metal (Fig. 8e). For the coatings under study, at the powder concentration in the electrolyte of 50 g/L, the thickness of PTFE/PEO coatings on aluminum alloys attains ~62 μm. The thickness of the external polymer-like carbon-rich layer is ~52 μm. The surface of such layers is formed within 20 min is heterogeneous and covered by large craters and pores (see Fig. 8c).

As to [11,13], the formed PTFE/PEO coatings are characterized with improved corrosion resistance. As seen from data [27], such coatings satisfactorily protect metal from corrosion damages after their preliminary annealing at 200 °C. Annealing results in transformation of the external polymer-like coating part into the viscous-fluid state and it fills pores and caverns, Fig. 8d.

According to [11], the coating contains PTFE particles. As to [13], the coating surface layer comprises PTFE particles sealed in the styrene–acrylate emulsion, while the coating bulk contains PTFE, styrene–acrylate emulsion, and aluminum oxides. The results of refs. [27,28] indicate to the layered structure of the formed coatings. It was assumed that high temperatures and pressure gradients realized around
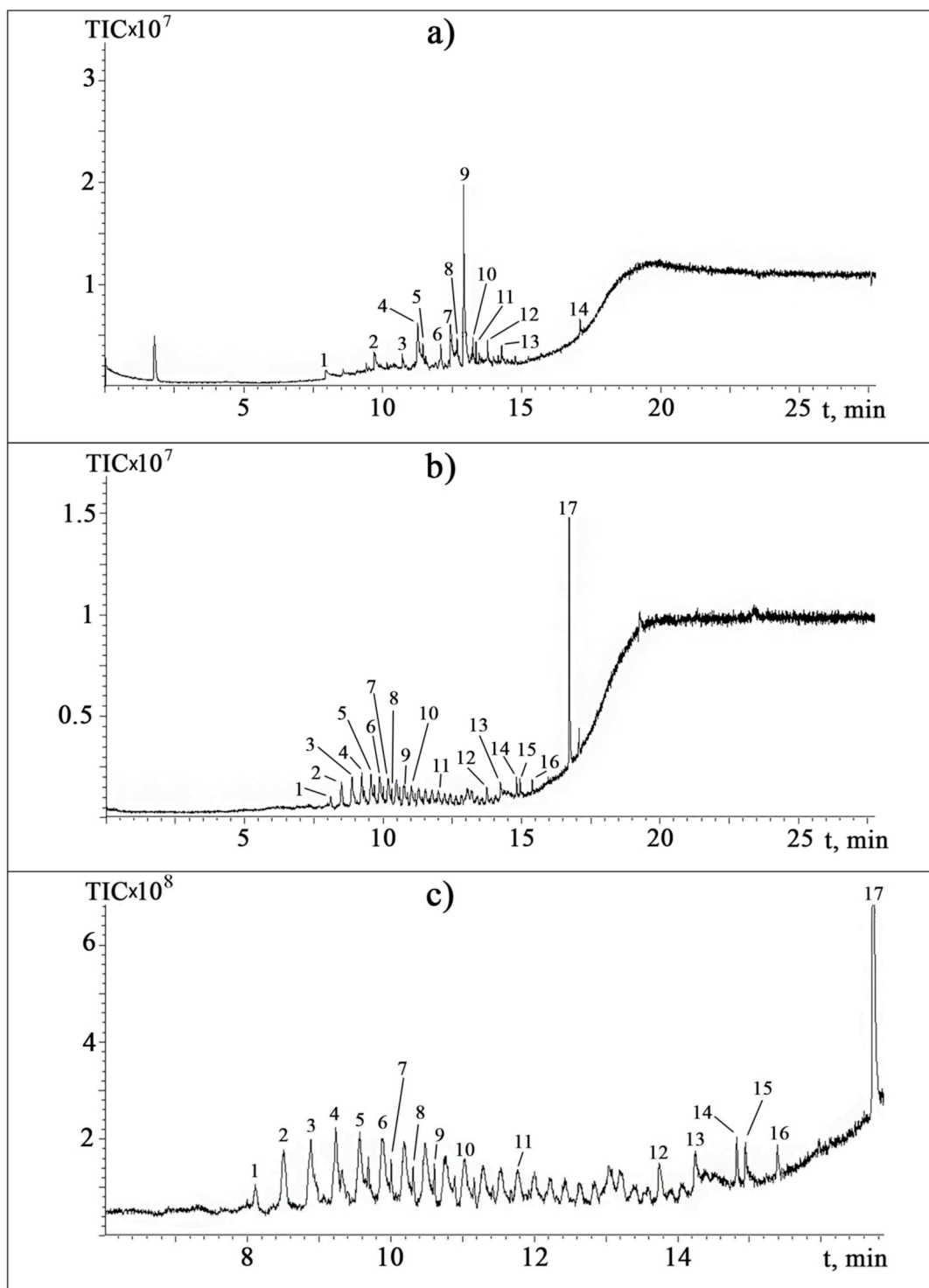
Fig. 7. Chromatograms of the PTFE/PEO-coating obtained at pyrolysis temperatures of 100 (a) and 200 °C – general (b) and fragment (c).

spark and microarc breakdown channels during PEO partially destruct both PTFE and emulsion polymers, and their destruction products form an external compact polymer-like coating layer of homogeneous composition. Agglomerates of PTFE particles in the state of their introduction into the electrolyte are found only in some caverns of the above layer (Fig. 8f and g).

The results obtained in the present work corroborate the assumption made in Refs. [27,28] on the structure of coatings formed on an aluminum alloy in the alkaline silicate with addition of dispersed PTFE particles in siloxane–acrylate emulsion. According to the IR

spectroscopy data, the coating surface does not contain oxides from both treated metal and electrolyte components. PTFE are not attached to the surface. According to the XPS data [26], the coatings surface layer of a thickness of ∼3 nm also contains CF_2 and C–C, C–H groups (with contents of ∼9 and ∼65.5% from total carbon content, respectively). Apparently, it contains fragments of both PTFE and emulsion, i.e., the products of their destruction.

Similarly, the bulk of the external polymer-like layer is not a mechanical mixture of PTFE particles and siloxane–acrylate copolymers. From the data of pyrolytic chromatography – mass spectrometry, it
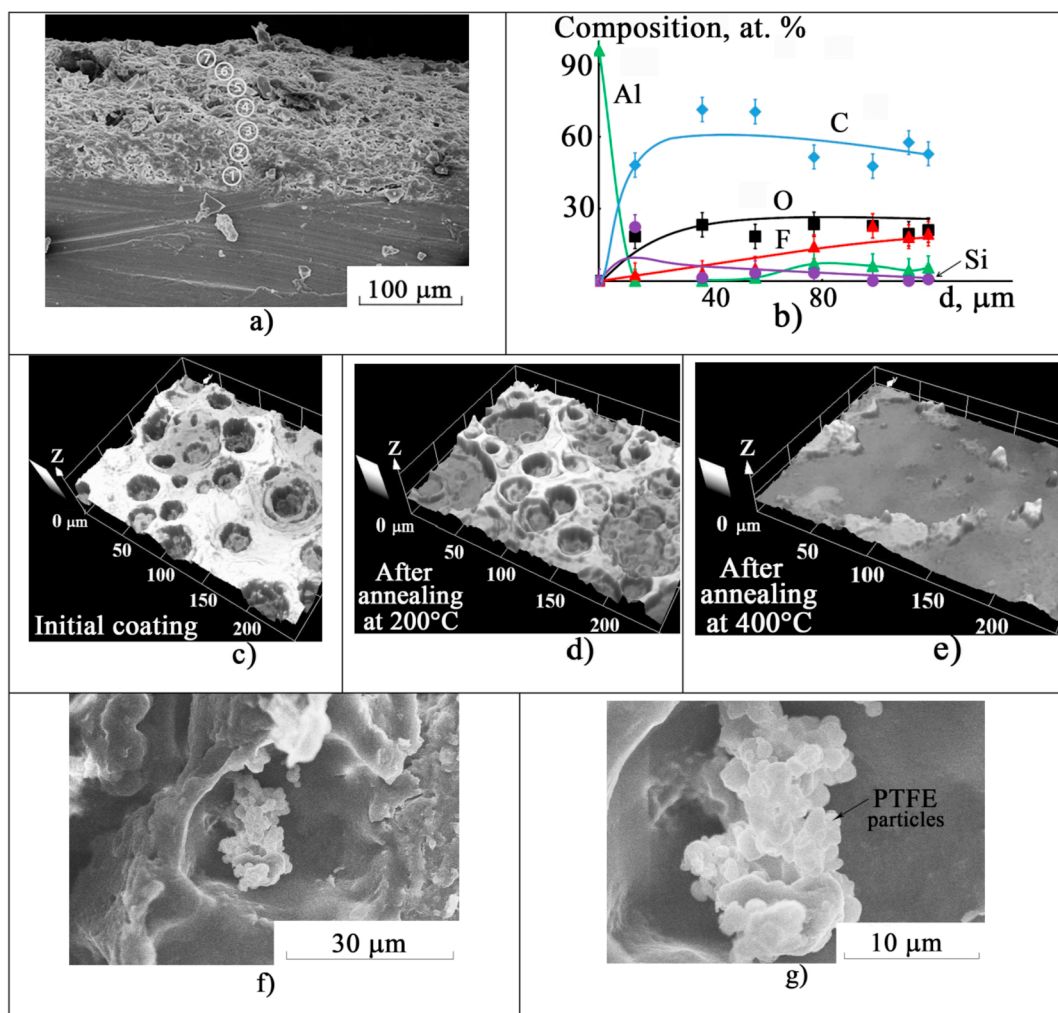
Fig. 8. The coating cross-section (a) and element distribution along the section (b). Surface morphologies of the initial coating (c) and of the coating after annealing at 200 °C (d) and 400 °C (e). Particles of PTFE in the cavern of the inner part of the coating (f, g). Adopted from Ref. [27].

contains fragments of both PTFE and siloxane–acrylate emulsion, whereas a partial substitution of fluorine atoms by those of hydrogen was found for fluorocarbons.

The notions on the structure of hybrid PTFE/PEO coatings fabricated in suspension–emulsion electrolytes with dispersed PTFE particles put forward in Ref. [11] (coatings contain PTFE) [13], (coatings contain PTFE, emulsion copolymers, and aluminum oxides) [25–28], and the present work are, in general, in compliance with each other. The differences in conclusions must be related to peculiarities and versatility of the used methods of study and to differences in sizes and concentrations of PTFE particles, types of used emulsions, compositions of base electrolytes, and electric and time conditions of coatings formation.

Thus, according to the data of [12,25–28] and the present work, PTFE/PEO coatings formed in the electrolyte containing more than 30 g/L of the PTFE powder with the particle size of ∼1 μm introduced to the electrolyte in the form of a dispersion in 100 mL of siloxane–acrylate emulsion have the layered structure, Fig. 9. The external rather compact and homogeneous polymer-like layer, whose thickness depends on the PTFE powder concentration in the electrolyte, consists of the products of destruction of PTFE particles and emulsion copolymer. Caverns of this layer contain assemblies of PTFE particles in the same state as they were introduced into the electrolyte. It is impossible to exclude the presence in the outer coating layer of a certain amount of emulsion in the state of introduction into the electrolyte. An intermediate oxide layer of a thickness of 10 μm is located between the external polymer-like later and the substrate metal, thus ensuring this

external layer adhesion. Such layered coatings are hydrophobic, their limiting wetting angle is ∼100°, and they are resistant to mechanical wear. In the latter case, the external polymer-like layer serves as a solid lubricant. At temperatures of ∼200 °C, the polymer-like layer transforms into the viscous-fluid state and fills surface pores, which dramatically improves the coatings anticorrosion properties. At temperatures > 200 °C, there starts evaporation of the external polymer-like layer.

A two-layer model of the structure of the coatings explains their mechanical, anticorrosion and thermal behavior, which is described in Refs. [25,27]. In the alkaline silicate electrolyte containing 100 ml/L of siloxane-acrylate emulsion, the wear resistance of coatings increases starting from the concentration of PTFE powder (particle diameter ∼1 μm) in the electrolyte > 30 g/L. This is because a continuous polymer-like outer layer begins to form on the primary 10-μm-thick layer of alumina and silica. Such outer layer consists of the products of partial destruction of PTFE particles and emulsion with incorporation of PTFE particles into the coating caverns and serves as a solid lubricant. An increase in the anticorrosive properties at an annealing temperature of ∼200 °C is associated with the transition of an external polymer-like layer into a viscous-flowing state and the filling of pores and caverns on the surface of the coating. With further increase in the annealing temperature, such a layer sublimes, which leads to a sharp decrease in the protective properties of the hybrid coatings, as a result, they correspond to the initially formed oxide layer of a thickness of ∼10 μm.
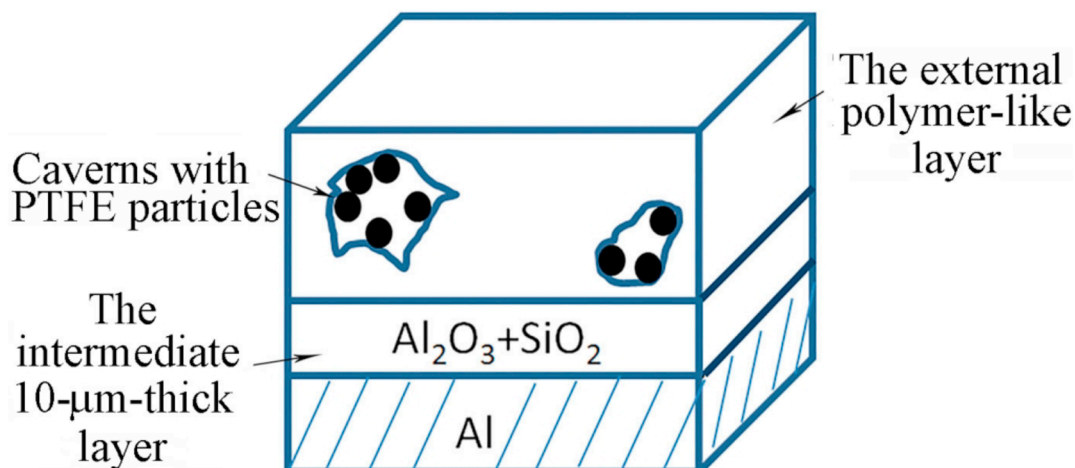
Fig. 9. The schema of the structure of hybrid coating formed in emulsion-suspension electrolyte with PTFE particles.

In our opinion, the established regularities in composition and structure of hybrid PTFE/PEO coatings formed within a single stage in suspension–emulsion electrolytes could form a basis for the development of methods of formation of layered coatings with hydrophobic and protective properties on aluminum and titanium. On the other hand, these regularities can be used in fabrication of composite layers of various compositions, for example, those containing products of destruction of the required polymers and polymer mixtures and dispersed hydrophobic particles of different natures. For example, as was shown in Ref. [26], application of suspension–emulsion electrolytes with dispersed graphite particles of a size of ∼50 μm allowed formation of graphite-oxide PEO coatings.

5. Conclusions

1. According to the IR spectroscopy data, the surface of the PEO coatings formed on aluminum in the aqueous suspension-emulsion electrolyte containing sodium silicate, hydroxide, PTFE dispersed particles, and siloxane-acrylate emulsion does not contain PTFE particles and alumina.
2. According to the pyrolytic chromatography-mass spectrometry data, the volume evaporated during the analysis of the polymer-like coating is not a mechanical mixture of the particles of PTFE and emulsion. It contains the degradation products of both polytetrafluoroethylene particles and the siloxane-acrylate copolymer, with the predominance of the latter.
3. The obtained IR spectra and chromatograms show the presence in the coating composition of groups and fragments of polymers typical only for PTFE/PEO coatings, i.e., formed on the basis of the electrolyte components during the coating growth under electric spark and microarc discharges during PEO.
4. The composition of the products that evaporate during the pyrolysis of the coating material depends on the temperature. When the coating material is pyrolyzed at 100 °C, the degradation products of the siloxane-acrylate copolymer, obviously its low molecular weight fractions, are predominantly evaporated. Pyrolysis at T = 200 °C leads to the predominant formation of degradation products of polytetrafluoroethylene. At T ≥ 300 °C, the destruction products of polytetrafluoroethylene and siloxane-acrylate copolymer are simultaneously formed, with the predominance of the latter.
5. The scope of the data obtained earlier and in this paper allows us to propose a scheme for the structure of the PTFE/PEO coating formed by single-stage PEO technique. It consists of two layers. The outer main layer consists of the products of destruction by electrical discharges of PTFE particles and siloxane-acrylate copolymer, with the predominance of the latter. In its bulk, there are caverns containing

PTFE particles in a state of introduction into the electrolyte. It is not excluded that this part of the coating also contains some amount of siloxane-acrylic copolymer in the state of introduction into the electrolyte. An intermediate layer adjacent to the metal, about 10 μm in thickness, contains aluminum and silicon oxides. The proposed scheme of the structure is in good agreement with the mechanical, anticorrosive properties and thermal behavior of the coatings under study.

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