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X-Ray Microanalysis of Polyvinyltrimethylsilane Surface after Impact of Accelerated Oxygen Plasma Flow

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Abstract—The elemental composition and surface structure of polyvinyltrimethylsilane exposed in oxygen plasma flow accelerated to an energy of 20–30 eV are studied by scanning electron microscopy and X-ray microanalysis. A microrelief is developed on the surface of the material reflecting its fibrillar supramolecular structure: the oxygen concentration increases, but the carbon concentration decreases. The surface is contaminated with Cu and F atoms as a result of their emission to the plasma due to the wear of the accelerator components.

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INTRODUCTION

The study of the effect of the oxygen plasma on polymers is of interest in order to estimate the applicability of materials on the external surfaces of spacecrafts. During flights in the ionosphere, the greatest damaging effect on polymers is produced by the approaching flow of atomic oxygen. The energy of the oxygen atoms in the approaching flow at a spacecraft velocity of 7–10 km/s is 4–8 eV. Due to its high chemical activity and the additional energy obtained, atomic oxygen has a considerable damaging effect on the polymeric materials of the external surface.

Study and selection of materials stable to atomic oxygen are carried out both in natural conditions onboard spacecrafts in special flight experiments and in laboratory facilities simulating flight conditions [1].

Natural and simulative studies have shown that organosilicon materials demonstrate low erosion and mass losses under the effect of atomic oxygen. This is explained by the manifestation of the conversion of the silicon-containing groups of the polymeric chain to the silicon oxide at their oxidation, forming a protective layer inert to atomic oxygen.

It is of interest both to determine the mass losses and to follow the changes of the structure and composition of the surface layer of such polymers at the imitating impact in the oxygen plasma flow, as well as to determine the contamination degree of the surface by the emission products from the walls of the experimental setup.

EXPERIMENTAL METHODS

In the experiment, the morphology and elemental structure of the surface of initial and exposed in oxygen plasma flow samples of the material were determined by scanning electron microscopy (SEM) and X-ray microanalysis (XRMA). This also allowed us to study the influence of the experimental conditions on the effects under investigation from the point of view of the condensation of contaminations of the sample emitted by the plasma source and walls of the experimental setup. The surface of the sample played the role of a impurity deposition.

Organosilicon polymer, polyvinyltrimethylsilane (PVTMS) $(C_5H_{12}Si)_n$ [2], was chosen for the analysis. PVTMS samples in the form of plates with dimensions of 20×20 mm and about 1 mm thick were used in the studies.

The samples were subjected to oxygen plasma flow formed by a plasma accelerator on an simulative setup of the Skobeltsyn Institute of Nuclear Physics (Moscow State University) [3].

The accelerated oxygen plasma flow consisted of atomic and molecular ions, fast atoms and molecules of oxygen with an energy of up to 40 eV (less than 10%), and plasma electrons with an energy of several electronvolts.

During irradiation by the accelerated oxygen plasma flow, the specific mass losses of samples outside of the chamber before and after the irradiation were measured on an HR-202i analytical balance with a scale factor of 0.01 mg.

The degree of polymer destruction was quantitatively estimated from the erosion coefficient value calculated by the ratio of the specific mass losses of the material to the so-called effective fluence (EF) of atomic oxygen, which was in turn determined from the specific mass losses of the witness sample made of the

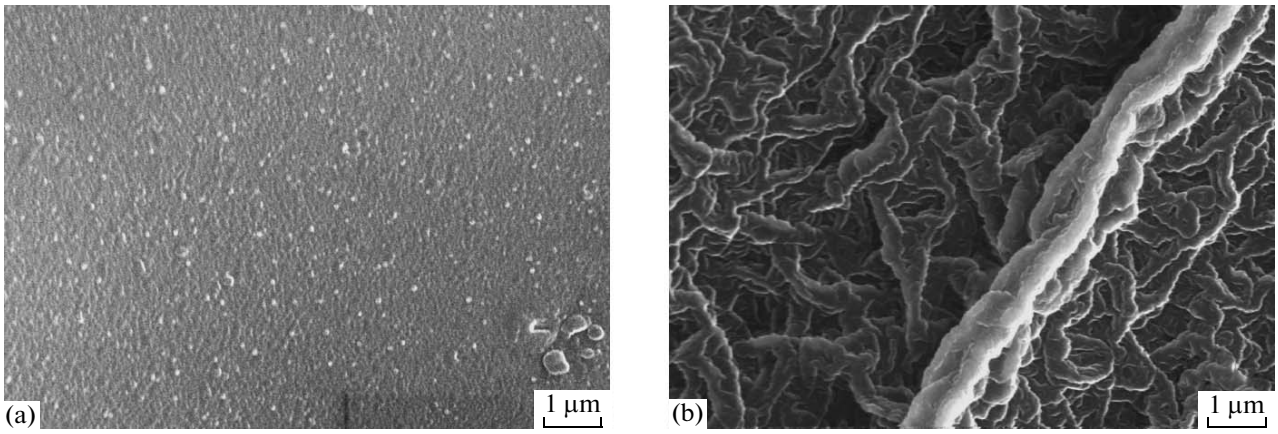

Fig. 1. SEM images of the PVTMS surface before and after irradiation in the oxygen plasma flow. The dimension of the label, 1 μm. Equivalent fluence of atomic oxygen, 4×10^{21} cm^{-2}. (a) Before irradiation; (b) after irradiation.

reference material, polyimide (capton), with a known erosion coefficient. This is a standard method of determining the value of the impact of atomic oxygen in world practice of imitating tests of materials of spacecrafts [4]. According to this method, the real fluence of particles is reduced to some fluence of the oxygen atoms causing equivalent mass losses of the sample at an energy of 5 eV.

After the plasma impact, the surface relief was recorded on an EVO 40 scanning electron microscope (Zeiss) with a limiting resolution of 4 nm in the mode with the energy of the probing beam of 25–30 keV at a current of 15–30 pA. The X-ray microanalysis of the surface was performed with the same beam. The surface of samples before measurement was metallized by sputtering an Al layer 20 nm thick.

RESULTS AND DISCUSSION

The impact of the accelerated oxygen plasma flow on the sample of PVTMS film and the witness sample made of the polyimide film resulted in different erosion degrees. The measured specific mass losses for the first sample were 0.3 mg · cm^{-2}, and those for the second sample were 18 mg cm^{-2}. The equivalent fluence of atomic oxygen of 4×10^{21} cm^{-2} was determined by the mass losses of polyimide. The erosion coefficient of PVTMS was 0.75×10^{-25} g/oxygen atom, which is almost two orders of magnitude less than the erosion coefficient of polyimide.

Figure 1 shows the SEM images of the initial and exposed surface of the samples. Comparison of them shows that the impact of the oxygen plasma results in inhomogeneous etching of the polymer, revealing the features of its structure. These features are obvious during comparison with the morphology of the exposed surface of purely hydrocarbon polymers, for example, polyethylene [5]. The microrelief in this case is formed by the column and cone ledges oriented toward the flow. The height of the ledges exceeds their cross-section dimensions by many times. On the contrary, twisted-strip structures are characteristic for the exposed PVTMS surface, with their dimensions in the irradiation plane exceeding their depth by many times. Such a morphology reflects the fibrillar supramolecular structure of this material.

Figure 2 shows the spectra of the characteristic X-ray radiation that were used to determine the ele-

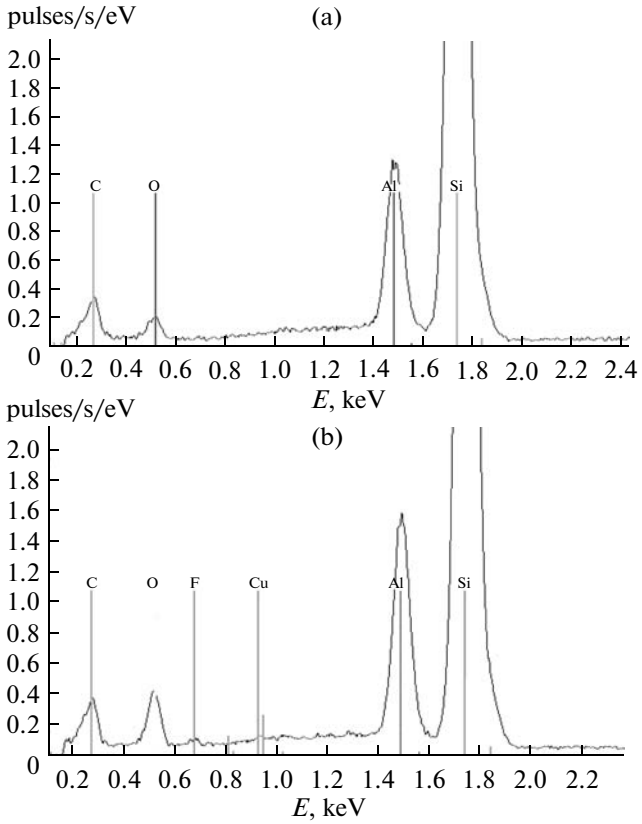

Fig. 2. XRMA spectra of the PVTMS film: initial (a) and exposed in the oxygen plasma flow (b).

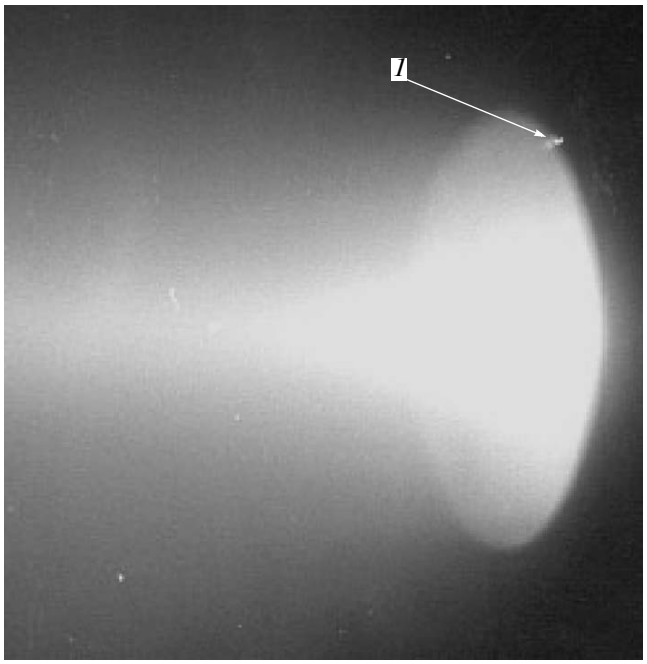

Fig. 3. Jet of the oxygen plasma leaving the anode: (*1*) heated copper oxide particle.

mental structure of the near-surface layer. At an energy of the probing electron beam of 20 KeV, the region of the generation of the main bulk of photons (90%) is in a layer up to 3 μm thick. The depth of the emission of photons is determined as well by their absorption in the surface layer of the material and depends on their energy. For the C line, the emission depth of about 90% of photons was about 0.4 μm, and that for the Si line was 2.8 μm.

The spectrum of the initial surface shows the C, O, Si, and Al lines. After exposition in the oxygen plasma flow, they were joined by the F and Cu lines. Aluminum appeared on the surface during sputtering of the electroconducting layer during the preparation of samples for SEM, and fluorine and copper were condensed on the surface of the sample from the plasma flow.

Data on the analysis of spectra are given in the table. The data in the table are normalized to the sum of the concentration of the elements making the material: C, O and Si for the estimation of their relative changes. Other elements are not in the composition of the material and were not considered at the normalization.

The table shows that the impact of atomic oxygen resulted in reduction of carbon concentration from 48 to 38 at %. This indicates ablation of the organic components of the material due to the formation of volatile carbon oxides. The increase in the oxygen concentration is from 20.5 to 33.5 at %. The silicon concentration changed slightly. The accumulation of oxygen favors the assumption of the formation of the nonvolatile silicon oxide coupling oxygen on the surface and protecting the under-surface material from further erosion. The ratio O/Si hence increases from 0.65 to 1.18. The formed silicon oxide film prevents the contact of the under-surface polymer with oxygen that is manifested in the reduction of the PVTMS specific mass losses (0.3 mg $\cdot$ cm^{-2}) in comparison with polyimide (18 mg $\cdot$ cm^{-2}).

The absence of lines of copper (0.5 at %) and fluorine (12.6 at %) in the spectrum of the initial surface is seen in Fig. 2 as well.

Analysis of the origin of impurities has shown that copper can be brought onto the irradiated surface by the plasma flow. The contamination of plasma with Cu atoms is possible at its contact with the copper anode of the accelerator. It is known that, during oxidation of copper by atomic oxygen, a Cu_2O layer is formed on its surface with a thickness increasing from 10 to 50 nm during the increase in the fluence of atomic oxygen from 10^{10} to 10^{22} cm^{-2} [1]. The thickness of the oxide film increases according to the linear law up to fluences of the order of 10^{17} cm^{-2} and then according to the logarithmic law, i.e., its increase is slowed. The oxide films formed on the copper surface are characterized by a larger internal stress due to the difference of the lattice parameters of the metal and oxides. The oxide volume exceeds the copper volume that formed it. This results in significant internal stress on the metal–oxide border. At high fluencies of atomic oxygen, this leads to scaling of the oxide and its separation from the surface (peeling). Due to the low heat conductivity, the exfoliated oxide particle is heated in the near-anode plasma to a high temperature, leading to the emission of Cu atoms and contamination of the beam. Figure 3 shows a photo of a jet of the oxygen plasma leaving the anode of the accelerator, showing the possibility of such contamination of the beam. One

Elemental structure of the surface of samples before and after irradiation by accelerated oxygen plasma flow

Element	C	O	F	Cu	Al	Si
At % before irradiation	48	20.5	0	0	3.5	31.5
At % after irradiation	38	33.5	12.6	0.5	4.1	28.5

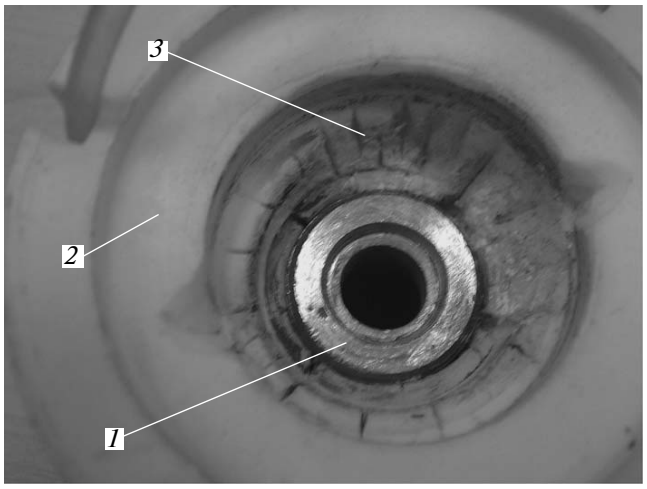

Fig. 4. Traces of the erosion of the fluoroplastic case around the anode of the plasma source: (*1*) anode; (*2*) dielectric fluoroplastic case; (*3*) cracks in the case as a result of the impact of the plasma.

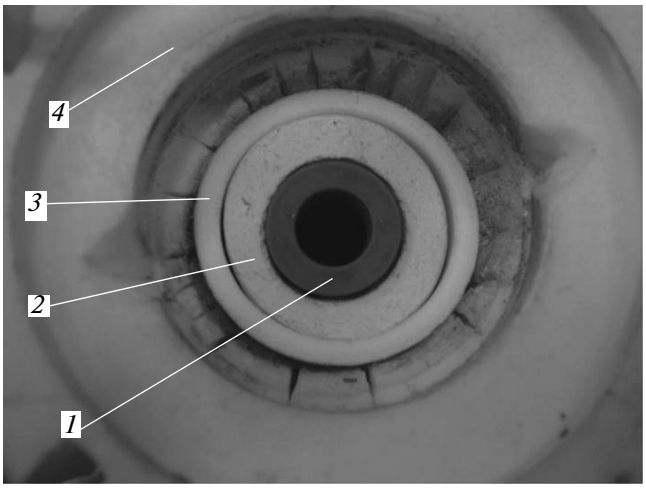

Fig. 5. Anode block of the accelerator after repair. (*1*) ceramic plug in the anode; (*2*) protective ceramic ring; (*3*) centering fluoroplastic ring; and (*4*) dielectric case.

can see an oxide particle heated in the plasma flow on the anode surface, which may be a source of the contamination of the beam.

The origin of the appearance of fluorine was found at dismantling the plasma accelerator. It was found that the source of fluorine atoms was the aligning ring of the dielectric fluoroplastic case in which the anode block of the accelerator is mounted. The ceramic plug separating the plasma column of the discharge from the case was destroyed during the long-term work of the accelerator, and therefore the internal part of the case was subjected to erosion under the impact of the plasma. Traces of the erosion of the fluoroplastic detail are seen in the photo of the anode block of the plasma source given in Fig. 4. To eliminate the erosion of fluoriplastic, the design of the anode block was improved by installing a ceramic plug and aligning ring in the dielectric case as shown in Fig. 5.

Thus, these results indicate the formation of contaminations containing copper and fluorine atoms on the surface of the material due to the impact of the oxygen plasma flow. It is necessary to note that earlier, on the same experimental setup at the initial stage of its work (1990–1995), Rutherford backscattering spectrometry (RBS) with collecting monocrystal silicon probes was used to obtain data that showed the absence of copper and fluorine in the beam and a low content of contamination in the form of Fe atoms of 3.5×10^{-6} Fe/O [6].

Analysis of these results on the contamination of the irradiated surfaces leads to the conclusion that its occurrence results from the long-term work of the accelerator and can be eliminated by improvement of its design and regular preventive maintenance to prevent accumulation of defects in the accelerator components during increase in the fluences of atomic oxygen.

CONCLUSIONS

The erosion of the PVTMS surface at the impact of the oxygen plasma flow with the average energy of particles of 20–30 eV is studied. It is shown that the erosion of this material is almost two orders of magnitude lower than that of polyimide.

SEM studies revealed that a microrelief reflecting its fibrillar supramolecular structure is developed on the surface of the material.

XRMA studies showed that, in these conditions, the structure of the surface layer changed, as is shown in the increase in the oxygen concentration and the reduction of the carbon concentration. The latter indicates ablation of the organic components of the material, and a near doubling of the O/Si ratio alongside low erosion of the material favors the assumption of the formation of the silicon oxide film on its surface protecting the under-surface polymer layer from oxidation and destruction.

Contamination of the surface of the material by copper and fluorine atoms due to erosion of the anode and the insulator of the plasma source that was not observed earlier on the new accelerator was revealed. These data indicate the wear of the accelerator due to its long-term work and the need to improve its design and perform regular preventive maintenance during a increase in the fluences of atomic oxygen.

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REFERENCES

1. *Space Model*, Sci.-Inform. Ed., vol. 2: *Space Impact on Spacecraft Materials and Equipment*, Ed. by M. I. Panasyuk and L. S. Novikov (KDU, Moscow, 2007) [in Russian].
2. S. G. Durgar'yan and V. G. Filimonova, Vysokomol. Soedin. **28**, 329–333 (1986).
3. A. I. Akishin, L. S. Novikov, and V. N. Chernik, "Impact on Spacecraft Materials and Equipment of Vacuum, Ionospheric Plasma Particles, and Solar Ultraviolet Radiation," in *The Novel Science-Rich Technologies Encyclopedia*, vol. 17, Ed. by L. S. Novikov and M. I. Panasyuk (ENTsITEKh, Moscow, 2000), p. 100 [in Russian].
4. ASTM, "Standard Practics for Ground Laboratory Atomic Oxygen Interaction Evaluation of Material for Space Applications," Designation E 2089-00 (2000).
5. V. N. Chernik, A. A. Paskhalov, and A. I. Gaidar, Poverkhnost', No. 3, 49 (2009) [J. Surf. Invest. **3**, 215 (2009)].
6. A. I. Akishin, V. N. Chernik, V. S. Kulikauskas, and V. V. Zatekin, Poverkhnost', No. 1, 89 (1996).