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INVESTIGATION OF THE INFLUENCE OF IONIZATION RADIATION ON GLASSY CARBON COATINGS, AFTER LONG STAY IN THE OUTER SPACE ON THE INTERNATIONAL SPACE STATION (ISS)

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Abstract

In this study two types of samples of spectrally pure graphite, compacted and coated with glassy carbon, were analyzed with liquid scintillation spectrometry, scanning electron microscopy (SEM) and X-ray diffractometry (XRD). "Space" sample has been sent in outer space on the surface of ISS for 28 months. "Space" sample is compared with "reference" sample, made of the same material, but stored on Earth for the same period.

Radiation environment data were collected using R3DR2-Lyulin instrument, located in the outer space very close to the samples, in the same module of ISS. The effect of cosmic radiation leads to slight increase of ^{14}C content, detected by liquid scintillation spectrometry.

SEM and thermal test using XRD did not show any noticeable changes in terms of structure and phase composition. This confirms the high degree of reliability of this material under significantly milder operating conditions in Earth orbit.

Key words: glassy carbon, graphitizing carbon, cosmic ray and gamma radiation, ISS

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1. Introduction. Various materials have been used to construct sensors for measuring direct (DC) and alternating (AC) electric fields in space plasma on board of satellites and satellite systems [1,2]. The main requirement for these materials is determined by the need to increase the accuracy of electric field measurements. Accuracy depends on variations in the separation work function for electrons on the working surfaces of the probes, due to space plasma and solar ultraviolet (UV) radiation. The latter affect only the surface layers of materials [3].

With the development of the technique and methods for measuring the magnitude of the work function for electrons on the surfaces of samples with glassy carbon (GC) coatings, or for monolithic glassy carbon, it was found that they show the highest value (about 5.05 eV for monolithic GC), compared to other materials, and provide minimal point-to-point variation across the surface of the probes. Glassy carbon combines properties of glass and ceramic materials with those of graphite. Glassy carbon is a brittle material that has a nearly gas-impermeable outer surface that resembles inorganic glass.

It is distinguished by very good resistance towards high temperature and high pressure. Glassy carbon is also characterized by extreme hardness, low density, low electrical resistance, significant resistance to chemical agents, as well as impermeability to gases and liquids [4–7].

GC materials are generally two main types – Type I and Type II. GC materials of Type I are usually thermally treated at lower temperatures ($\sim 1000\,^{\circ}$C), while GC materials of Type II – at higher temperatures ($> 2000\,^{\circ}$C). Various manufacturers have different maximum heat treatment temperatures. GC materials of Type I are less compressible, more resistant towards oxidation and less permeable to gases, in comparison with GC materials of Type II. GC materials of Type II contain less impurities and higher electro- and thermo-conductivity.

The reason for the difference in the properties between GC of Type I and Type II has not been fully studied till now [7].

The development and construction of spherical electric sensors, with a glassy carbon coating on the working surface, for measuring electric fields in space plasma, has been successfully applied in a series of scientific instruments that have been sent in space and they have worked without failure on eight satellites [8–10], and also on board the International Space Station (ISS). Results from the experiments, connected with assessment of quasi-direct (DC) and alternating (AC) electric fields, proved their high efficiency, in terms of meeting the requirements for accuracy, sensitivity and reliability of measurements, during their long stay in space. The issues of clarifying the radiation resistance of glassy carbon coatings, their ability to perform certain functions and maintain the specified characteristics, and parameters within the limits, established by the technical requirements of the standards over time, as a result of prolonged exposure to the effects of various space factors, continues to be relevant. For this purpose, experimental block DP-PM, which is part of the International Space Project "Obstanovka 1-step", was

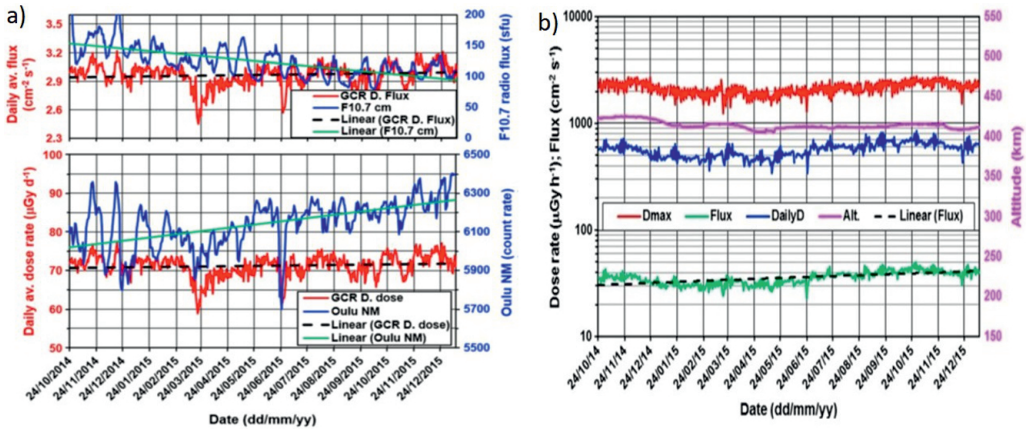


Fig. 1. a) Variations in the averaged GCR daily dose rates and flux; b) Variations of the IRB daily-averaged dose rates and flux and in the period from 24 October 2014 to 11 January 2016 [11]

planned and carried out. The experiment was conducted on the Russian module of the International Space Station (ISS) in the period 2013–2015, with a record of the radiation conditions during its implementation. The Radiation Risk Dosimeter Radiometer (R3D)-R2 solid-state detector performed radiation measurements of: (i) galactic cosmic ray particles and their secondary products; (ii) protons in the South Atlantic Anomaly region of the inner radiation belt (IRB); (iii) relativistic electrons and/or bremsstrahlung in the outer radiation belt (ORB); and (iv) solar energetic particle (SEP) events [11].

A previous study [11] performed simultaneous radiation observations for four primary radiation sources, along with secondary protons, neutrons, and heavier than H+ ions (secondary particles), generated in the R3DR2 detector or nearby. Preliminary information about the observed cosmic radiation time profile during the EXPOSE-R2 mission was published by Dachev et al. [11].

Average daily dose of 925.6 μGy/d1 reported in [11] is applied and the accumulated dose in samples is evaluated (309 mGy) using spectrally pure graphite compacted and coated with glassy carbon for the period 1.11.2014–30.09.2015. In order to assess the dose accumulated during the period 1.06.2013–31.10.2014, the same daily dose rates for the contribution of the charged particles from the inner and outer radiation belts, 567 μGy/d and 278 μGy/d, respectively, are used. During this period the solar activity was a bit lower than during 1.11.2014–30.09.2015, and the galactic cosmic rays (GCR) flux a bit higher [12], so 72 μGy/d for the contribution of GCR is used instead of the value 71.6 μGy/d used in the referenced paper [12]. During the discussed period there were several solar energetic particles (SEP) events, one of them – on 06.01.2014 lasting 7 days [13] with registered by GOES 15 satellite energetic protons with energies > 100 MeV. Daily dose rate of 9.1 μGy/d is used for the contribution of the SEP and secondary particles. In summary it gives average daily dose rate 926.1 μGy/d. For the period of 518 days

from 1.11.2014 to 30.09.2015 a dose of 480 mGy is measured. Thus for the whole period 1.06.2013–30.09.2015 the accumulated dose is evaluated to be $\sim$ 789 mGy.

The main aim of the paper is to investigate the effect of radiation and other effects on glassy carbon (type I) coatings in electric field measuring equipment on International Space Station. These investigations will involve determination of ^{14}C in the samples in space, whereas ^{14}C is formed as a result from the effect of space radiation. Influence of the temperature will be also assessed by using XRD before and after heating the samples.

^{14}C is a radioactive isotope of carbon and its presence in organic materials is the basis of the radiocarbon dating method. ^{12}C and ^{13}C are both stable, while ^{14}C is unstable and it has a half-life of 5700 years [14].

^{14}C is converted to into ^{14}N through beta decay. One gram of carbon containing one atom of ^{14}C per 1012 atoms emits 0.2 beta particles per second. The primary natural source of ^{14}C on Earth is cosmic ray action on nitrogen in the atmosphere, and it is therefore a cosmogenic nuclide. However, open-air nuclear testing between 1955 and 1980 increased ^{14}C content.

Small amounts of ^{14}C are not easily detected by typical Geiger–Müller detectors; because this method has problems to measure radioactive contamination of less than about 100 000 disintegrations per minute (0.05 µCi). Mass spectrometry and liquid scintillation counting can be used in this case.

2. Materials and methods. ***2.1. Materials.*** Two types of samples of spectrally pure graphite compacted and coated with glassy carbon were analyzed [15]. One sample was in outer space, mounted on the Russian module of the International Space Station for a period of 28 months, tentatively called "space". To achieve high reliability in the analysis of the obtained data for the "space" samples, they were compared with a "reference" sample made of the same material, but stored on Earth for the same period [16].

2.2. Methods of characterization. *A) Liquid scintillation spectrometry.* In this study, ^{14}C activity concentration in graphite samples was determined by radiochemical separation and measurement of the prepared sample using low-level Liquid Scintillation Counting (LSC). The radiochemical procedure adopted for ^{14}C determination is described in more detail in [17]. The samples with a mass of 190 to 400 mg, taken by scratching out a powdery sample from the surface of the GC coatings – face and back, were decomposed by digestion using a mixture of acids, H_2SO_4:HNO_3:$HClO_4$ = 4:1:1. The pure carbon fraction was obtained by oxidation of the various chemical forms of carbon in a closed system, and quantitative precipitation of the resulting sodium carbonate with $BaCl_2$ to obtain $Ba^{14}CO_3$. The precipitation was then transferred to a 20 ml LSC vial, 7 ml distilled water and 13 ml of Insta Gel Plus cocktail added and mixed by shaking for LSC.

The measurements were carried out by us using a PACKARD TRI-CARB 2770 TR/SL LSC system. The detector signals were processed in a multi-channel

analyzer (MCA) that separates carbon signals in the sample from those produced by chemiluminescence in two different spectra. The calibration was performed automatically with the use of the unquenched 3H and ^{14}C calibration standards and background standard. In order to determine the counting window, we collected spectra of ^{14}C and background and the window was set to maximize E2/B (Figure-of-Merit). The term Figure of Merit (FOM), expressed as a function of efficiency (E) and background (B), is currently the most widely used parameter to assess counter sensitivity and performance. For our measurements, the energy window for ^{14}C was fixed to 1–100 channels. The detection limit of this method is 0.15 Bq.g^{-1} for ^{14}C, for 60 min, at 95% confidence level.

B) XRD evaluation of the material for high-temperature resistance, graphitization and applicability. The investigations were carried out with a Bruker D8 Advance X-ray powder diffractometer equipped with a LynxEye position-sensitive solid-state detector and an X-ray tube with a copper anode (CuKα = 1.541838 Å) at operating current parameters of 40 kV and 40 mA. The phase composition of the studied samples was determined using the DIFFRAC.EVA v.4 program and a comparative database of reference powder patterns ICDD PDF-2, release 2021. Unit cell parameters and crystallite size were determined using the entire powder pattern profile using Bruker Topas v.4.2 program. The crystallite size was determined by Scherrer's formula from the full-width at half-maximum (FWHM) of the measured peaks

$$D = K\lambda/\beta \cos\theta, \tag{1}$$

where D is the size of the crystallites forming the corresponding reflection, β is FWHM of the corresponding peak, θ is the diffraction angle, K is the constant (0.9), λ is the anode wavelength. To determine the instrumental broadening of the diffraction lines, the method of Fundamental Parameters Approach was used, which mathematically models the contribution of all elements of the optical path of the diffractometer to the profile of the measured powder pattern.

A solid graphite reference specimen, with a layer of glassy carbon deposited on it, was subjected to heat treatment to assess the thermal stability at a temperature of 600 °C, for one hour, in an inert atmosphere of argon. A heating rate of 10 °C/min and Messer high purity argon were used. X-ray diffraction analysis was performed on the sample before and after the heat treatment. The experiment provides information on the thermal stability of the glassy carbon layer in Earth orbit. The maximum temperature reached on the surface of the International Space Station is about 150 °C, i.e. the experiment is an accelerated test of the stability of the material over a longer period of time.

C) SEM investigations. The morphological study was made by scanning electronic microscope FEI Quanta 250 FEG, with high vacuum and beam deceleration, at accelerating voltage of 10.0–15.0 kV.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are suitable methods to analyze the morphology and microstructure of carbon materials [18]. In this study the structure and morphology of glassy carbon was explored using scanning electron microscopy (SEM). SEM pictures of glassy carbon are shown in Fig. 4. Electronic microscope images of the samples, oriented to different directions, are performed. Samples are oriented with the upper side up (electronic beam is running down the sample, which is on the bottom of the chamber), back side up, and lateral side up.

3. Results and discussion. ***A) Liquid scintillation spectrometry for determination of*** ^{14}***C.*** The activity concentration of ^{14}C in the "reference" sample is lower than the minimum detectable activity (0.15 Bq.g^{-1}). The data obtained for "space" sample ranged from 0.23 to 0.25 Bq.g^{-1} and show that the applied method is characterized by a high reproducibility. The obtained deviations are below 6.0%.

Figure 2 presents β-spectra of ^{14}C in the studied samples.

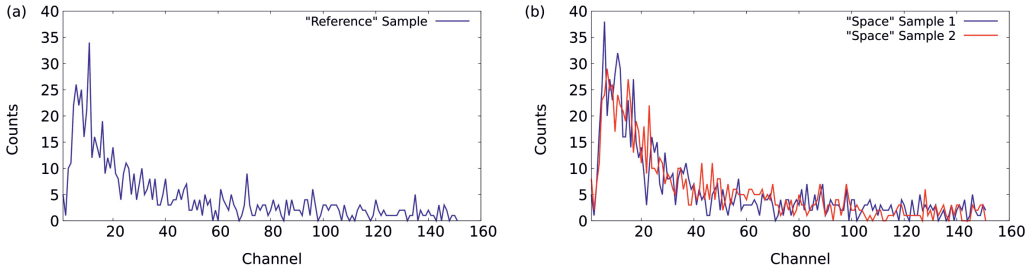


Fig. 2. a) Spectrum of ^{14}C for a "reference" sample; b) Spectra of ^{14}C for a "space" sample

Based on the conducted study of ^{14}C content in "reference" and "space" samples, it can be concluded that the long stay in the Earth's orbit and deposition of solar radiation leads to the formation of ^{14}C with an average specific activity $\sim$ 0.24 Bq.g^{-1}. These results are consistent with those obtained by reflection infrared spectroscopy for the presence of a small amount of carbonyl and carboxyl groups on the surface of "space" samples [19].

B) XRD study of thermal stability of GC. X-ray diffraction studies are sensitive to the state of the substance (crystalline or amorphous) and the phase composition of the sample. By carrying out these studies, it can be determined whether there has been a change in the long-range order of the glassy carbon layer of the "space" and "reference" samples (for example, the appearance of crystal nuclei as a result of a prolonged high-energy impact), as well as additional information about the dense graphite substrate used (polytype and crystallite size).

Figure 3 shows the X-ray powder diffraction patterns of a "reference" sample of glassy carbon layer on graphite before and after thermal treatment. The figure clearly shows the reflections of a well-crystalline substrate of homogeneous

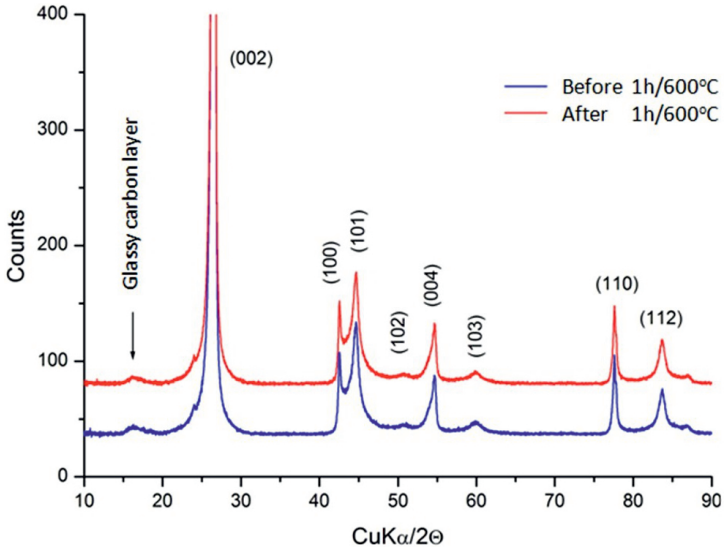


Fig. 3. X-ray powder patterns of a "reference" sample before and after heat treatment 1 h/600 °C in an inert atmosphere of argon

graphite polytype 2H. In the angular range between 15–19° 2θ, a weak glassy carbon amorphous halo is observed, which remains unchanged in position and intensity after thermal treatment.

A thermal test performed at high temperature in an inert argon environment on a glassy carbon coated "reference" sample did not show any noticeable changes in terms of structure and phase composition. This confirms the high degree of reliability of this material under significantly milder operating conditions in Earth orbit.

C) SEM investigations. Figure 4 presents upper (a) and bottom surface (b) of the "space" sample. Glassy carbon layers, which follow the morphology of graphite support, are clearly visible on both SEM pictures, represented by light bands on the left side of the SEM pictures. This is an indication of small disturbances (especially with the upper surface of the "space" sample) in the glassy carbon coating, that occurred during the stay of the material in outer space. However, traces are negligible (< 1 μm), and they do not noticeably affect the overall electrical and other characteristics of the sample.

SEM data provide valuable information about the existence of undamaged glassy carbon layer with thickness of 20 μm. This confirms that glassy carbon layer covers the whole sample, which ensures no fluctuations in electrical characteristics.

4. Conclusions.

- The results show that there are no significant changes in structure and phase composition of GC layers. This confirms the high degree of reliability of this material under significantly milder operating conditions in Earth orbit. The

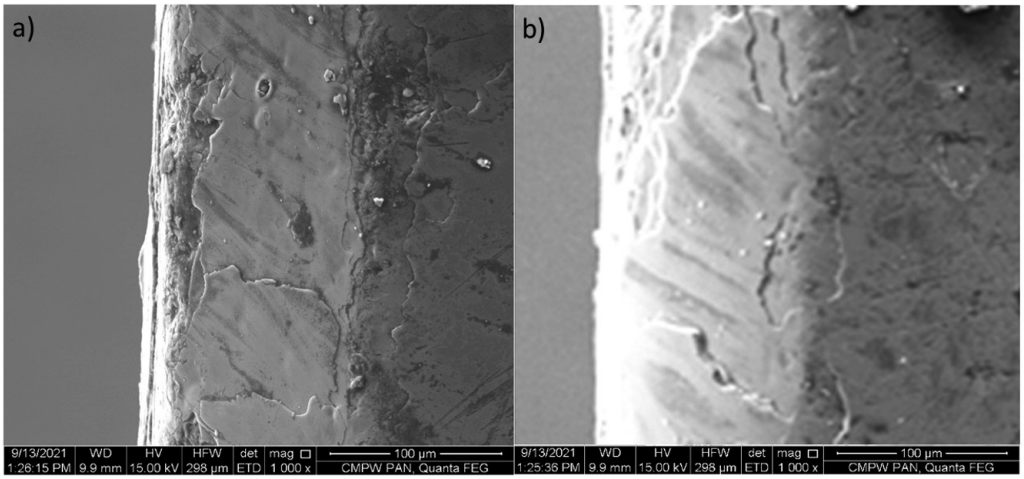


Fig. 4. SEM of "space" sample under 45 °C: a) upper surface, and b) bottom surface

evaluated accumulated radiation dose using R3DR2 is 789 mGy. It was established that this has no effect on GC layers and electrical measurements in the open space.

- The specific activity of ^{14}C was evaluated for two GC coated graphite samples – a "reference" and a "space" sample that had been in outer space for twenty-eight months, on the outside of the International Space Station (ISS). Small differences are observed between the content of the studied cosmogenic radionuclide ^{14}C in "space" and "reference" samples. The "reference" sample was found to have a ^{14}C value below the minimum detectable activity.

- A thermal test performed at high temperature in an inert argon environment on a glassy carbon coated reference sample did not show any noticeable changes in terms of structure and phase composition. This confirms the high degree of reliability of this material under significantly milder operating conditions in Earth orbit.

- SEM data provide valuable information about the existence of undamaged continuous glassy carbon layer with thickness around 20 µm. This confirms that glassy carbon layer covers the whole sample, which ensures no fluctuations in electrical characteristics.

All investigations prove that cosmic rays for 2 years, on circular orbit with diameter around 400 km, at these average radiation levels, the glassy carbon coatings do not change substantially their properties and quality – they remain stable and do not allow fluctuations in measurements of electric fields on board of satellites and satellite systems.

Electrical sensors for measuring electrical fields by double-probe method, which are constructed from glassy carbon coated graphite, can work on geosynchronic orbit for 30 years, without deterioration of the quality of glassy carbon material, regarding the parameters measured.

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