Bulgarian Academy of Sciences. Space Research and Technology Institute.
Aerospace Research in Bulgaria. 35, 2023, Sofia

DOI: https://doi.org/10.3897/arb.v35.e16

SEM AND EDX STUDY OF GLASSY CARBON COATINGS AFTER AN EXTENDE STAY ON THE INTERNATIONAL SPACE STATION (ISS)

Boyko Tsyntsarski[1], Anna Bouzekova-Penkova[2], Urszula Szeluga[3], Georgi Georgiev[1], Petar Tzvetkov[4], Dimitar Teodosiev[2]

[1]Institute of Organic Chemistry with Centre of Phytochemistry – Bulgarian Academy of Sciences
[2]Space Research and Technology Institute – Bulgarian Academy of Sciences
[3]Centre of Polymer and Carbon Materials – Polish Academy of Sciences
[4]Institute of General and Inorganic Chemistry – Bulgarian Academy of Sciences
e-mail: Boyko.Tsyntsarski@orgchm.bas.bg; a_bouzekova@space.bas.bg

Keywords: *Glassy carbon, Cosmic ray and Gamma radiation, Scanning electron microscopy (SEM), X-ray spectroscopy (EDX)*

Abstract

Graphite samples covered with glassy-carbon layers, have stayed for 2 years and 4 months under different conditions - terrestrial conditions and on the International Space Station. The influence of outer space on glassy carbon coatings was studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Raman and infrared spectroscopy. The results show presence of some defects and heteroatoms (traces of O, F, Na, Cl) after staying in space, probably due to radiation and other effects. SEM data provide valuable information about the existence of undamaged glassy carbon layer with thickness of 20 μm. There are no structural changes in the layers of glassy carbon after stay in space. Data show that these materials can be successfully applied for electrical field measurements in ionosphere.

Introduction

Glassy carbon belongs to the family of carbons, which have the ability to form a variety of carbon allotropes (sp, sp2, sp3) [1–4], resulting in complex and versatile microstructure of glassy carbon. Glassy carbon is a black non-transparent material, which have found application as antireflective coatings. Modern physico-chemical methods, like XRD and Raman spectroscopy, help to characterize glassy carbon structures [1–4]. The carbonization of thermosetting resins (poly-aryl acetylene, furfuryl alcohol, phenolic resins) in atmosphere leads to formation of low-ordered, non-graphitizing carbon-based material, denoted ‘glassy carbon’ (GC, known also as vitreous carbon or glass-like carbon). Glassy carbon is a stiff, fragile material, and it exhibits a surface fracture, similar to that presented by the glass (conchoidal fracture), which explains the term “glassy”. Unlike graphite, glassy

carbon is a hard and isotropic material. Besides, glassy carbon low impermeability towards molecules of gases and liquids, excellent chemical and thermal stability, very good thermal and electrical conductivity. Glassy carbon is applied in many fields – electrochemical devices and sensors, energy storage, wastewater decontamination, tools for precision molding, ablative shields. Due to its good biocompatibility, glassy carbon may be also used in medical applications μm heart valves, implants, tissue regeneration [4–7].

In connection with the development of the technique for measuring constant and alternating electric fields in space plasma, various materials are developed and used for the preparation of satellite probes. The increased requirements for these materials are determined mainly by the requirement to increase the accuracy and sensitivity of the measurements. The accuracy of measuring constant and alternating electric fields by the double probe method strongly depends on the variations of photoelectron work function at the surface of each probe in inhomogenous ionosphere-magnitosphere [8–9].

The technology used for the production of spherical probes for measuring electric fields on boards of the satellites IC-Bulgaria 1300, IC-24 Active, IC-25 APEX, INTERBOL-2, the sub-satellites Magion-2, Magion-3, Magion-4, Magion-5 and ISS, for the period from 1981 till now, is invented in Bulgarian Academy of Sciences [8–14], whereas spherical probes with glassy carbon coatings were tested in laboratory conditions, simulating those in outer space (sudden temperature changes, shock and vibration loads, etc.), and then implemented in scientific equipment on the boards of the above mentioned satellites.

To verify and confirm the results of earth laboratory tests, and also to study the effects of the influence of outer space on the physico-chemical and structural properties of glass-carbon coatings, the technological experiment DP-PM was planned and conducted within the international project "Obstanovka 1-stage", aboard the Russian module of the ISS. For this purpose, graphite samples (30×15×8 mm) were prepared, covered with glassy carbon, and placed in the DP-PM block, which is a container made of aluminum alloy with total dimensions of 185×70×10 mm.

This work is dealing with glassy carbon preparation and its physico-chemical properties, before and after stay in space. The research presented is a continuation of our previous investigations on the same topic [15]. New samples are studied, whereas the analysis and the interpretation of the obtained results are expanded. The aim is to improve the knowledge on the resistance of glassy carbon coatings, deposited on graphite samples, which have stayed in outer space for a long time. The changes in the integrity and structure of the glassy carbon coating are further investigated. The obtained results allow to assess its applicability for the purpose of studying phenomena in the conditions of outer space.

Experimental

Materials

The investigations were performed with two graphite samples covered with glassy carbon. The first sample is called “reference” sample, and it stayed on the earth, and the second sample, called “space” sample, was located on the outer surface of International Space Station (ISS) in the open space. The “space” sample is subjected to radiation (cosmic radiation), which could vary in nature and quantity, according to ISS orbit, ISS coordinates, geophysical and heliophysical conditions. The sample was subjected to temperature changes in wide temperature interval, from down to –120 ^{0} C up to +150 ^{0} C, every 2 h, for a period of 2 years and 4 months.

Methods of characterization

In the present work, an assessment of the changes in “space” samples (cut to investigate the inner morphology), as a result of the cosmic conditions, and comparison with the “reference” samples have been made, by using different methods.

The morphological study was performed using scanning electronic microscope FEI Quanta 250 FEG, with high vacuum and beam deceleration, using an accelerating voltage of 10.0–15.0 kV. FEI Quanta 250 FEG is a large stage environmental SEM with BF/DF STEM detector (Fig. 1).

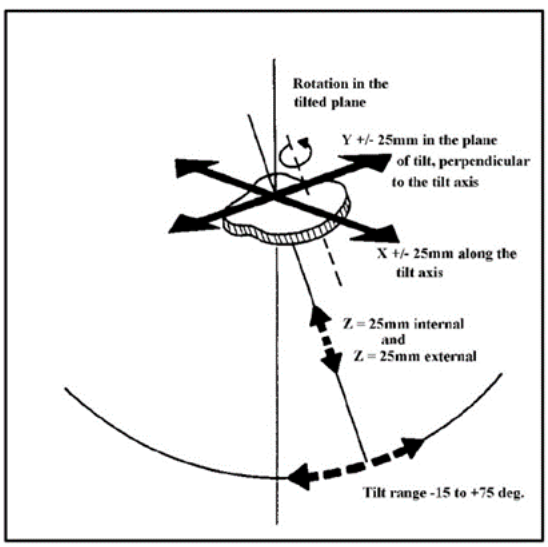

Fig. 1. Scheme of SEM experiment

The equipment has low and extended vacuum mode up to 1000 Pa (ESEM), temperature control range –25^0 to +55^0, and EDX chemical analysis

including elemental and phase mapping. It is possible to perform X-ray mapping of low-Z elements at low voltages. X-Ray Microanalysis (EDX or EDX or sometimes referred to also as EDS analysis) is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. It works as an integrated feature of a scanning electron microscope (SEM) and cannot operate on its own without the latter. Raman experiments (4000–400 cm^{-1}) are performed using Bruker Senterra II Raman Apparatus, with 1 cm-1 spectral resolution, and 514.5 nm laser.

Attenuated Total Reflection Fourier-Transformed Infrared Spectroscopy (ATR-FTIR) ensures solid (transparent or non-transparent) and liquid samples to be studied directly. ATR-FTIR spectra are collected using infrared spectrophotometer Bruker Tensor 27, at wavenumber 4000–600 cm^{-1}, resolution 0.5 cm^{-1}, with MIRacle-Diamond/ZnSe Crystal Plate ATR accessory - Pike technology.

Results and discussion

SEM and EDX analysis

The structure of glassy carbon was explored using scanning electron microscopy (SEM). Morphology of glassy carbon obtained by SEM is shown in Fig. 2 and Fig. 3. 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.

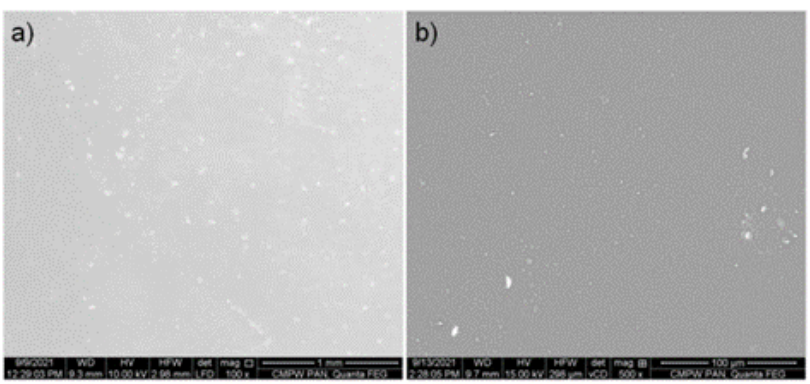

Fig. 2. SEM images of the "reference" sample at different magnification – 1 mm (a) and 100 μm (b)

In Fig. 3a there are shown some traces on glassy carbon surface, which follow the morphology of graphite support. This is an indication of small disturbances 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 noticeable affect the overall coating electrical characteristics of the sample.

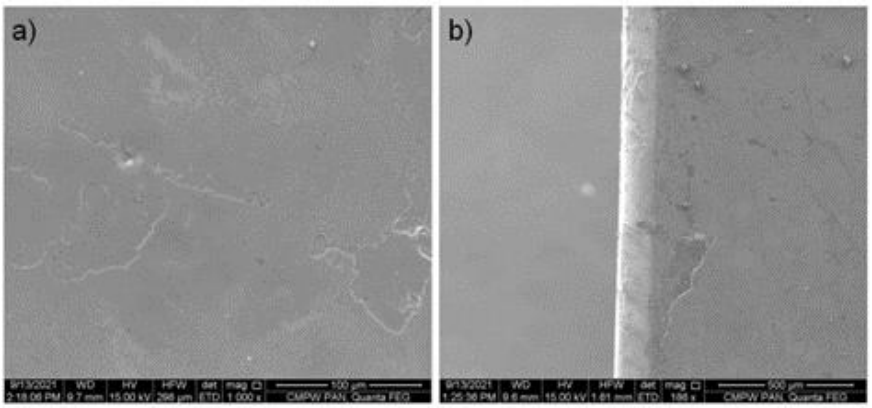

Fig. 3. SEM images of the "space" sample. Image of a) back side and b) lateral side (cut cross-section) under 45^o

To observe the glassy carbon layer and graphite layer, the sample holder is rotated to 45^0 and on the SEM image lateral side (cut cross-section) under 45^0 stage rotation is seen in Fig. 3b. The image in Fig. 3b confirms the presence of glassy carbon (thin light layer) and graphite (right part of the image). The light layer under angle of 45^0 is around 25 μm wide.

SEM data provide valuable information about the existence of undamaged glassy carbon layer with thickness of 20 μm.

EDX study (Fig. 4) shows the elemental analysis on the glassy carbon surface. The main element is carbon (more than 90 wt. %). The results show presence of some defects and heteroatoms (traces of O, F, Na, Cl) after staying in space, probably due to radiation and other effects (space contamination, contact with other devices, transportation, synthesis technology of glassy carbon layers).

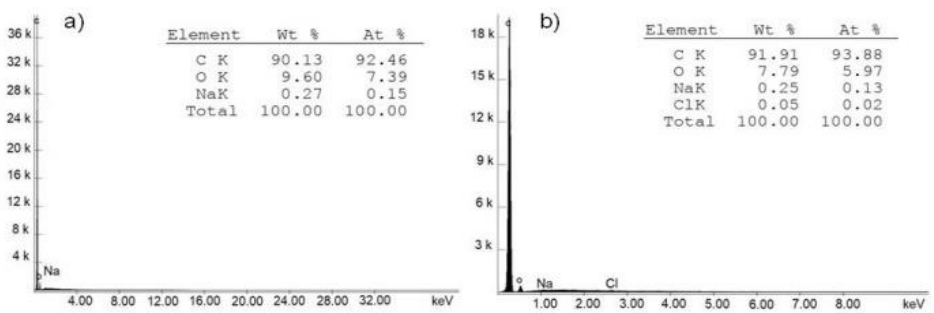

Fig. 4. EDX results for the a) "reference" sample and b) "space" sample

Raman analysis

Raman study was carried out with all the samples (in 2–3 points for every sample), and the Raman spectra are shown in Fig. 5 and Fig. 6.

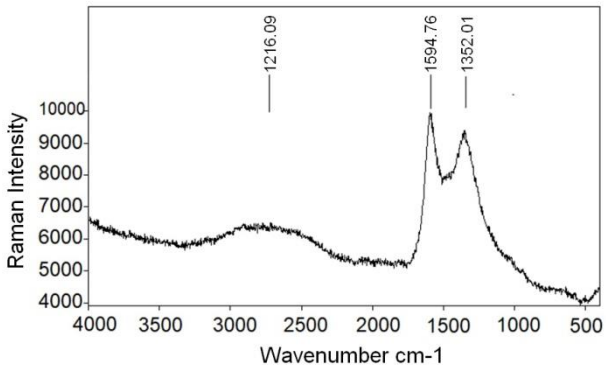

Fig. 5. Raman spectrum of the "reference" sample [15]

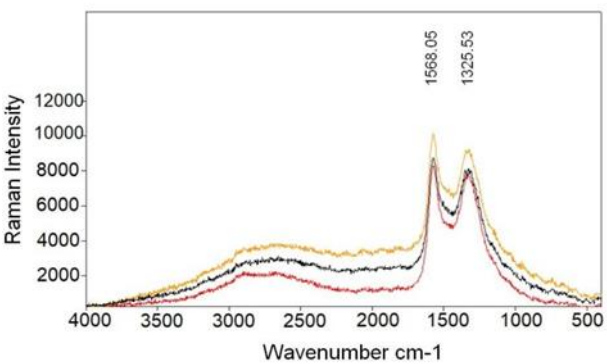

Fig. 6. Raman spectrum of the "space" sample (measured in three different points)

Fig. 5 and Fig. 6 show Raman spectra of "reference" and "space" samples, respectively. Two main Raman bands are detected for both samples – D band (D for defect, representing the disordered structures) around 1350 cm^{-1} and G band located around 1580 cm^{-1}. G-band (G for graphite) arises from the stretching of the C–C bond in graphitic materials and is characteristic for all sp2 carbon systems.

The presence of D- and G- Raman bands with equal intensity are characteristic for existence of glassy carbon layer.

FTIR analysis

Attenuated Total Reflection Fourier-Transformed Infrared Spectroscopy (ATR-FTIR) Spectra of the samples (back) are shown on Fig. 7.

There are almost no surface groups detected on the reference sample.

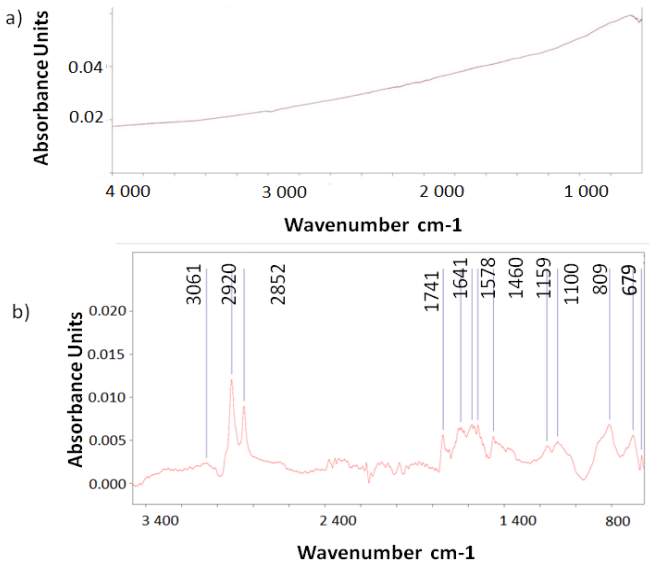

Fig. 7. ATR-FTIR spectra of a) "reference" and b) "space" samples

In the IR spectra of space sample there are bands at 3000–2800 cm^{-1}, associated to aliphatic C-H stretching vibrations at 3000–2800 cm^{-1}, as well as C-H deformation vibrations in the region 1450–1350 cm^{-1}, due to aliphatic structures. The band at 1740 cm^{-1} is assigned to stretching vibrations of C=O. The bands at 1700–1500 cm^{-1} could be due to aromatic ring stretching vibrations or C=C bonds in aromatic structures. The bands detected in the region of 1200–1000 cm^{-1} are assigned to C–O in ethers or ring structures.

Data obtained from IR spectroscopy show, that on the surface of the space sample different surface groups are detected – aliphatic and aromatic C–H groups, carbonyl groups C=O, hydroxyl groups O-H, C=C structures, etc. Most probably formation of surface groups and surface species on the space sample is due to oxidation of the exposed parts of the graphite pad as a result of violations of the glassy carbon coating that occurred during the stay in open space.

Conclusions

Our results show that glassy carbon coatings, due to their hardness and chemical inertness, can stay years in outer space in order to collect accurate data on the plasma parameters. No substantial change was detected in the structure of the glassy carbon layers due to stay is space. The glassy carbon coatings deposited onto graphite substrate can be successfully used for electrical field ionosphere measurements.

The results show presence of some defects and heteroatoms (traces of O, F, Na, Cl) after staying in space, probably due to radiation and other effects.

Acknowledgements: This work is financially supported by the Bulgarian National Science Fund under Project KP-06-H27/2, 08.12.2018.

References

1. Kharissova, O. V., B. I. Kharisov. C. M. Oliva Gonzalez, Carbon–carbon allotropic hybrids and composites: synthesis, properties, and applications, Ind. Eng. Chem. Res., 2019, 58, 3921-3948. https://doi.org/10.1021/acs.iecr.8b05857
2. Uskokovic, V. Disordering the disorder as the route to a higher order: incoherent crystallization of calcium phosphate through amorphous precursors, Cryst. Growth Des, 2019, 19(8), 4340–4357.
3. Inagaki, M., New carbons: control of structure and functions, Elsevier, 2000, 1–13.
4. L. de Souza Vieira. A review on the use of glassy carbon in advanced technological Applications, Carbon, 2022, 186, 282–302. https://doi.org/10.1016/ j.carbon.2021.10.022
5. Field, J., M. Swain. The indentation characterisation of the mechanical properties of various carbon materials: glassy carbon, coke and pyrolyticgraphite, Carbon 1996, 34, 1357–1366. https://doi.org/10.1016/S0008-6223(96)000711.
6. Gaefke, C., E. Botelho, N. Ferreira, M. Rezende. Effect of Furfuryl alcohol addition on the cure of furfuryl alcohol resin used in the glassy carbon manufacture, J. Appl. Polym. Sci. 2007, 106, 2274–2281. https://doi.org/10.1002/app.26938
7. Pesin, L., Review: structure and properties of glass-like carbon, J. Mater. Sci., 2002, 37, 1–28. https://doi.org/10.1023/A:1013100920130.
8. Teodosiev, D., N. Isaev. Physicochemical Properties of Probes for Measuring Electric Fields in the Near-Earth Plasma, Chem. Phys. Reports, 2001, 19(6), 1165 et all. 1175.
9. Teodosiev, D. K., I. D. Pechenykov, J. S. Georgiev, P. A. Petrov, R. P. Dobrev et al, Method for impregnation and coating of porous refractory materials with glass-carbon, Bulgarian Certificate of Authenticity № 31847, МКП С 04 35/84, 1982 (in Bulgarian).
10. Stanev, G., M. Petrunova, D. Teodosiev, I. Kutiev et al. An Instrument for DC Electric Field and AC Electric and Magnetic Field Measurements Aboard "Intercosmos-Bulgaria-1300" Satellite, Adv. Space Res., 1982, **2**(7), 43–47. https://doi.org/10.1016/0273-1177(82)90146-6
11. Teodosiev, D., G. Stanev, G. Galev, S. Neichev, P. Pushchaev. Spherical probes for measurements of electric fields on the INTERBALL-2 satellite in the IESP-2M instrument, Cosmic Research, 2000, 38(6), 574–578. https://doi.org/10.1023/A:1026690701594
12. Triska, P., J. Vojta, A. Czapek, D. Teodosiev, G. Galev, I. Shibaev. Measurements of electromagnetic ULF fields onboard the Magion-4 satellite: The ULF experiment, Aerospace Research in Bulgaria, 2003, 17, 47–53. https://www.researchgate.net/publication/252423766_Measurements_of_electromagnetic_ULF_field_onboard_the_Magion-4_satellite_the_ULF_experiment

13. Teodosiev, D., P. Nenovski, P. Hristov, R. Koleva, J. Vojta et al, ULF wave measurements aboard the Magion-4 subsatellite: narrow-band wave events observed in the magnetopause regions, Planetary and Space Science, 2005, 53 (1–3), 317–326. https://www.doi.org/10.1016/j.pss.2004.09.058
14. Bouzekova-Penkova, A., R. Nedkov, G. Stanev, S. Klimov et all. Technological Experiment "Environment" on board the International Space Station, Journal of BAS 5/2017, ISSN 0007-3989, 2017, 22–26 (in Bulgarian).
15. Teodosiev, D., A. Bouzekova-Penkova, K. Grigorov, R. Nedkov, P. Tzvetkov, B. Tsyntsarski, A. Kosateva, S. Klimov et all. Structural and mechanical properties of glass-carbon coatings after an extended stay on the International Space Station (ISS), Comptes Rendus de L'Academie Bulgare des Sciences, 2021, 74(2), 197–206. https://www.doi.org/10.7546/CRABS.2021.02.05

SEM И EDX ИЗСЛЕДВАНЕ НА СТЪКЛОВЪГЛЕРОДНИ ПОКРИТИЯ СЛЕД ПРОДЪЛЖИТЕЛЕН ПРЕСТОЙ НА МЕЖДУНАРОДНАТА КОСМИЧЕСКА СТАНЦИЯ (МКС)

Б. Цинцарски, А. Бузекова-Пенкова, У. Шелуга, Г. Георгиев, П. Цветков, Д. Теодосиев

Резюме

Образци от графит, покрити със стъкловъглеродни слоеве, са престояли 2 години и 4 месеца при различни условия – земни условия и на Международната космическа станция. Влиянието на космическото пространство върху стъкловъглеродните покрития е изследвано чрез сканираща електронна микроскопия (SEM), енергийно дисперсионна рентгенова спектроскопия (EDX), раманова и инфрачервена спектроскопия. Резултатите показват наличие на някои дефекти и хетероатоми (следи от O, F, Na, Cl) след престой в Космоса, вероятно поради радиация и други ефекти. SEM данните предоставят ценна информация за съществуването на ненарушен стъкловъглероден слой с дебелина 20 μm. Няма структурни промени в слоевете стъкловъглерод след престой в Космоса. Данните показват, че тези материали могат успешно да се прилагат за измерване на електрическо поле в йоносферата.