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ASSESSMENT OF SOME STRUCTURAL PROPERTIES OF NOVEL GLASSY CARBON COATINGS

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Abstract

The main aim of this work is to investigate the stability at high temperatures, graphitization properties, and possible application of graphite samples coated with a glassy-carbon layer. Two types of samples were stored in two different environments for a period of 2 years and 4 months - one in terrestrial conditions and the other in open space, mounted on the Star module of the International Space Station. The effect of space on the glassy carbon coatings was investigated by Scanning electron microscopy, powder X-ray diffractogram, Raman spectroscopy, and BET experiments.

Introduction

The specific high-technology properties of carbon materials [1–3] and glassy carbon coatings determine their numerous potential use in various fields of science and technology application [4-8] and in the space research for sensors for evaluation of electric fields, by using monolith glassy carbon [9, 10], as well as sensors made of graphite and coated with glassy carbon on their working surfaces have been used in various satellite experiments [11]. Usually, the potential difference between two points in open space is measured using the double probe method of quasi-constant and variable electric fields in space plasma. A major factor affecting the accuracy of electric field measurements is the material for sensor production, which determines the qualities of their working surfaces. Our detailed studies of the qualities of samples of different brands of dense, spectrally pure graphite, differing in both chemical composition and density, as well as their method of production, allowed us to conclude that the optimal material for preparing sensors with glassy carbon coating is the high-density, spectrally pure graphite. The most used sensors are hollow, detachable, thin-walled spheres with a radius of $r\varphi$ = 40 mm and a wall thickness of 2 mm, made of graphite. Their surface is coated with glassy carbon, representing an electrically conductive carbon glass, using our original method [12, 13]. This coating provides minimal variations in the work function for the electron on the surface of the spheres, when irradiated with sunlight, within the range of 0.006 meV, and a very high work function value equal to 4.78 eV [14]. The changes in the electron work function over time, on the surface of each sensor, affect in a complex way the magnitude of the collected current, especially in the case of non-homogeneous plasma, such as ionospheric-magnetospheric plasma. Therefore, it is important to evaluate the properties of the material used in this case, the glassy carbon coating applied to the working surfaces of the sensors, in order to assess the impact of outer space on the material after prolonged operation in extreme conditions. These conditions can cause changes in the characteristics of the coatings and could lead to errors exceeding the magnitude of the measured electrical quantities.

The main aim of this work is to investigate the stability at high temperatures, graphitization properties, and possible application of graphite samples coated with a glassy-carbon layer. Two kinds of samples are produced and studied - some of them stay on Earth, and other samples are sent into the ionosphere plasma, on board the International Space Station (ISS).

Materials and Methods

Sample Types

Specimens made of spectrally pure graphite and coated with glassy carbon were investigated. The coating with glassy carbon is an original Bulgarian technology developed and implemented by a team of scientists from the Bulgarian Academy of Sciences (SRTI-BAS and IMCTX-BAS) and is protected by a copyright certificate [12]. The originality is expressed in the use of certain temperature regimes for compacting and coating refractory materials with glassy carbon. In this way, porous graphite is compacted with glassy carbon, and a layer of the same material is obtained with a thickness of no more than 25 microns. Some of the samples were stored in Earth conditions, conventionally called „reference“ (R), and the other samples were mounted outside the International Space Station for a period of more than two years, „space“ (S) [15].

Methods of study

The morphology of a glassy carbon coating deposited on spectrally pure graphite was investigated using a JEOL 6390 scanning electron microscope with a superconical objective lens, which provides 3 nm resolution at 30 kV, and magnification down to 8x. The equipment gives superior resolution at an analytical working distance of 10 mm.

The texture of glassy carbon coating was studied by low-temperature nitrogen adsorption using Quantachrome Instruments NOVA 1200e apparatus. The specific surface area was determined from Brunauer Emmett Teller (BET) equation, the total pore volume was obtained at a relative pressure of 0.99, and the micropores volume was elucidated by V-t-method.

Raman spectra (4000–400 cm^{-1}) were obtained by Bruker Senterra II Raman Spectrometer with Microscope, with a 1 cm^{-1} spectral resolution, using the green line at 514.53 nm as excitation source. The high-precision motorized stage for samples enables obtaining chemical and morphological information with a minimum step of 50 nm. Raman spectra were collected and processed using Opus software.

A sample of dense graphite substrate with a deposited glassy carbon layer was tested for heat resistance at 600°C for 1 hour under constant argon flow. A heating rate of 5°C/min and high purity argon (99.999%) from Messer were used. The purpose of this research is to simulate the temperature conditions in the ionosphere plasma. The maximal temperature value measured on the surface of the International Space Station is about 150°C, i.e., the experiment is an accelerated test of the thermal stability of the material at higher temperatures.

X-ray diffraction experiments were performed on a Bruker D8 Advance diffractometer equipped with a silicon-strip LynxEye PSD detector and a CuKα X-ray tube operating at 40 kV and 40 mA. Referent data for Graphite was taken from the ICDD PDF-2 (2021) database, PDF # 00-056-0159.

Results and discussion

Figure 1 shows SEM images of a „reference” sample – face (a) and a „reference” sample turned at 45^o (b). Figure 1 (b) shows very clearly how the glassy carbon layer is distinguished, and it follows the morphology of the surface of the graphite substrate. Small scratches are noticeable on the glassy carbon coating, which is probably due to mechanical processing. These scratches are insignificant (< 1 μm) and do not affect the electrical, chemical, and mechanical characteristics of the sample.

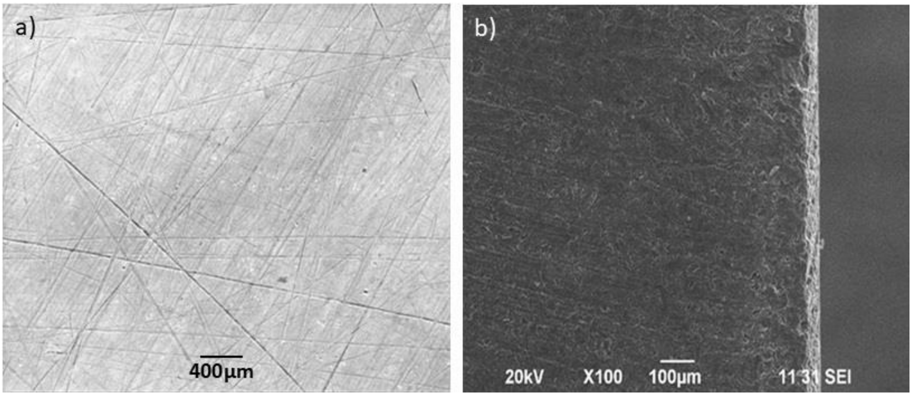

Fig. 1. SEM images of a „reference" sample – face (a) and a „reference" sample turned at 45^o (b)

SEM data provide valuable information about the existence of a well-preserved glassy carbon layer with a thickness of 20 µm, which completely covers the entire sample very well. This ensures the absence of fluctuations in the electrical, chemical, and mechanical characteristics of the sample.

This is confirmed by the adsorption measurements carried out during low-temperature nitrogen adsorption at 77 K. Nitrogen was used because the method is non-destructive. The textural characteristics of a „reference" sample were investigated, with the specific surface area determined by the Brunauer, Emmett, and Teller (BET) method, and it has a very low value of 13 m^2/g. The result obtained is close to the absolute error (10 m^2/g) of the BET method.

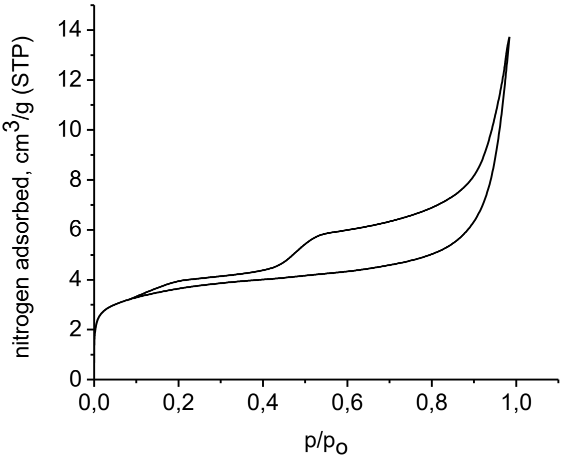

Fig. 2. N_2 adsorption isotherm at 77K of glassy carbon coating

The total pore volume was calculated at a relative pressure $p/p^0 = 0.99$, and it has a very low value. It can be assumed that there are almost no pores on the surface of the glassy carbon coating, or they are in a negligible amount.

Table 1. Textural characteristics of glassy carbon coating

$V_{0.95}$, cm^3/g	0,012
S_{BET}, m^2/g	13
V_{micro}, cm^3/g	0,005
V_{meso}, cm^3/g	0,006

The surface properties of the material were further investigated with Raman spectroscopy, as the „reference" samples are compared to identical samples that had been exposed to outer space, „space" samples.

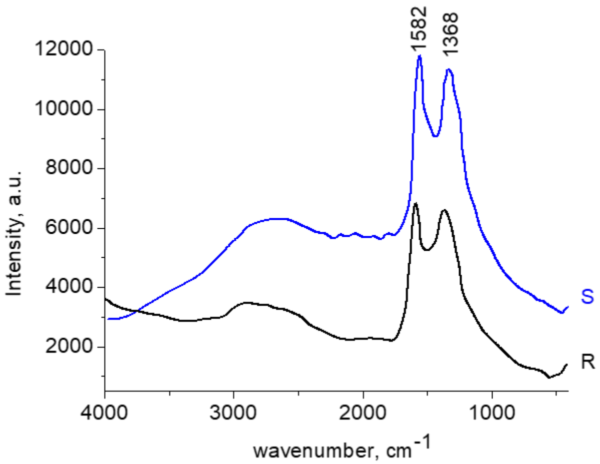

Fig. 3. Raman spectra of a „reference" and „space" sample

Figure 3 shows Raman spectra of a „reference" (R) and a „space" sample (S), respectively. Two main Raman bands are detected in both types of samples – a D band (D from defect, representing disordered structures) around 1350 cm^{-1} and a G (G from graphite) band located around 1580 cm^{-1}. The G band corresponds to C–C stretching vibrations in graphite-like materials and is characteristic of all sp^2 carbon structures.

The presence of D- and G-Raman bands of equal intensity is characteristic of the existence of a glassy carbon layer.

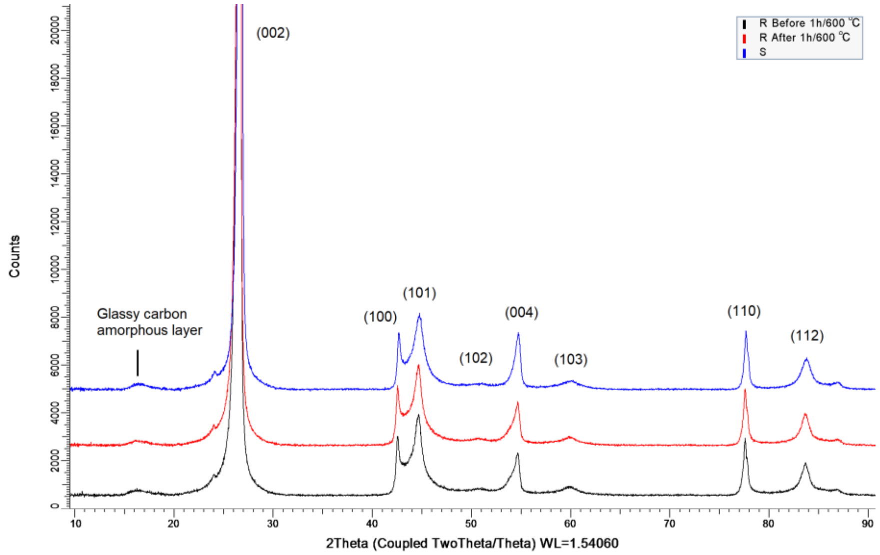

Fig. 4. X-ray patterns of glassy carbon samples before and after heat treatment at 600°C. Indexed Bragg peaks correspond to the graphite substrate.

The X-ray patterns of the investigated glassy carbon samples do not show any changes after the high-temperature treatment at 600°C, compared to the reference one. In Figure 4, clear and intense Bragg reflections of pure graphite are observed, which belong to the substrate. The presence of glassy carbon on the surface can be confirmed by the weak diffuse peak at 26.5° 2Θ. The intensity of this peak remains unchanged before and after heating. This proves that the amorphous layer of glassy carbon is preserved and does not change its thickness as a result of decomposition.

Conclusions

• Using the results from the X-ray diffraction studies conducted with the „space" and „reference" samples, it can be concluded that after a long stay in Earth orbit of the „space" samples, no changes are observed in the structure of the glassy carbon coating. The presence of high-energy radiation and temperature fluctuations does not promote the appearance of new phases as a result of the decrystallization of amorphous carbon. The substrate material used is a well-crystalline, homogeneous pure graphite polytype 2H. The most significant aspect of graphite used is the increased value of the c-parameter of the unit cell, compared to the reference sample.

• The thermal test performed at high temperature in an inert argon environment with the „reference" sample with a glassy carbon coating 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.

• From the scanning electron microscopy study, it can be concluded that the stay in near-Earth orbit of the characterized samples does not have a destructive effect on the glassy carbon coating. No significant differences are observed between the „space“ and „reference“ samples. There is a small scratch on the surface in one of the samples, which is probably due to an accident during transport, although the possibility of contact with a micrometeorite should not be completely excluded.

• The method used to obtain the glassy carbon coating provides a dense, continuous layer that remains stable even in the conditions of open space. The observed fine scratches formed during polishing of the samples affect only the most superficial layer and do not disrupt the coating in depth. Also, the observed closed porosity built up of pores with a wide diameter distribution does not disrupt the hermeticity of the layer and the surface smoothness required for the specific application.

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ОЦЕНКА НА НЯКОИ СТРУКТУРНИ СВОЙСТВА НА НОВИ ПОКРИТИЯ ОТ СТЪКЛОВЪГЛЕРОД

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Резюме

Основната цел на тази работа е да се изследват стабилността при високи температури, свойствата на графитизация и възможното приложение на графитни проби, покрити със стъкловъглероден слой. Два вида проби са съхранявани в две различни среди за период от 2 години и 4 месеца – едната в земни условия, а другата в открития Космос, монтирани на модула Звезда на Международната космическа станция. Ефектът на пространството върху стъкловъглеродните покрития беше изследван чрез сканираща електронна микроскопия, прахова рентгенова дифрактограма, Раман спектроскопия и BET експерименти.