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CONTACT ANGLE AND AFM ANALYSIS OF GLASSY CARBON COATINGS AFTER AN EXTENDED STAY ON THE INTERNATIONAL SPACE STATION (ISS)

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Abstract

The proposed work presents the results for contact angle and atomic force microscopy (AFM), which are applied to characterize the surface of two types of samples, "reference" sample and "space" sample, both made of the same material – graphite covered with glassy carbon coating, but stored for 28 months in different environments (conditions). One "space" sample was mounted outside the International Space Station, and the other "reference" sample was stored on Earth.

The technique applied to measure the contact angle of wetting of the surface of the samples (hydrophilicity-hydrophobicity) is using water droplets. Values of the energy surface area of the sample surfaces were determined by measuring the contact angle with the substances formamide and diiodomethane. Atomic force microscopy (AFM) was applied to characterize the glass surface morphology of carbon coatings.

Key words: glassy carbon, graphitizing carbon, cosmic ray and gamma radiation, Contact angle and Atomic Force Microscopy (AFM)

Introduction. Glassy carbon, also called glass-like carbon or vitreous carbon, is a non-graphitizing carbon that combines glassy and ceramic properties

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with those of graphite. Glassy carbon is a brittle material which has an almost gas impermeable outer surface that resembles inorganic glass. The main advantages of glassy carbon are its isotropic physical properties, high hardness and thermal stability. Other important properties are its high temperature resistance, low density, low electrical resistance, low thermal resistance, exceptional resistance to chemical agents, and impermeability to gases and liquids [1, 2]. Glassy carbon is easy to process and can be produced in a variety of shapes, sizes and cross-sections. Therefore, it is also used in the production of different types of sensors for measuring parameters of space plasma on board satellites [3–8]. All these valuable qualities are the basis of the choice of glassy carbon for covering graphite samples intended to participate in measuring instruments that have been in open space for a long time [9–11].

The surface wettability of glassy carbon coatings is an important property depending on both the chemical composition and the geometric microstructure of a contact surface, which can play a key role in the application of this material in industry [12].

It is important to establish, at a macroscopic level, the surface wetting angle ratio for glassy carbon coatings deposited on graphite for two types of samples "reference" and "space" stored for 28 months under different conditions. In particular, the change of wetting properties due to the influence of cosmic ionizing radiation of various origins, energy characteristics, and temperature changes varying in a wide temperature range from $-120\,^{\circ}$C to $+150\,^{\circ}$C for the "space" samples was studied. For this purpose, theoretical calculations were also carried out to evaluate the change in the surface tension values of the investigated glassy carbon coatings, when measuring the contact angle.

Materials and methods. ***Materials.*** Two types of graphite samples with glassy carbon coatings were analyzed. 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", and the other of the same material was stored on Earth for the same period, "reference".

The "space" samples were subjected to cosmic ionizing radiation, differing in origin, energy characteristics, composition and location of the station. Temperature changes vary over a wide operating temperature range from $-120\,^{\circ}$C to $+150\,^{\circ}$C in 2 h depending on the material's illumination from the Sun.

Characterization methods. Measurements of the contact angle of small water drops (volume ≈ 3 µL) were made using an automatic goniometer/tensiometer, model 290, Ramè-Hart Ltd with DROP images Advanced v. software 2.4 (Succasunna, NJ, USA) at room temperature. The contact angles of ten consecutive drops of 3 µL positioned at random locations of the samples were measured. A mean angle and a mean error were taken from them. To determine the values of the surface tension *sigma/w*, as well as the values *sigma/ab* of the surface tension of "reference" and "space" samples, the determination and measurement of

drops with the substances formamide and diiodomethane were carried out. The contact angles of five drops of 2–5 μL were measured for both formamide and diiodomethane substances, positioned in the centre and at the periphery of the samples, which are formed and deposited by the Ramé-Hart automatic dosing system.

AFM imaging was performed on the NanoScope V system (Bruker Ltd, Germany) operating in tapping mode in air at room temperature. Silicon cantilevers (Tap 300Al-G, Budget Sensors, Innovative solutions Ltd, Bulgaria) with 30 nm thick aluminum reflex coatings were used. According to the producer's datasheet the cantilever force constant and the resonance frequency are in the range 40 N/m and 300 kHz, respectively. The tip radius was less than 10 nm. The scan rate was set at 1 Hz and the images were captured in height mode with 512×512 pixels in JEPG format. Subsequently, all images were flattened by using NanoScope software. The same software was also used for section and roughness analysis.

Theoretical considerations and interpretation of the experimental data. To theoretically determine the surface tension of glassy carbon coatings after measuring the contact angle with the substances formamide and diiodomethane, the Lifshitz–van der Waals (LW) theory was applied to determine surface tension (or surface free energy per unit area) [13,14]. According to this theory, the total surface tension of liquids can be measured by various methods.

According to the Lifshitz–van der Waals theory, once the total surface tension of a liquid (L) is known, the surface tension component σ^{LW} of *two* (*partly*) *polar liquids* can be found by *measuring the contact angle* θ on a completely *apolar surface* (S) using a variant of Young's equation:

$$\sigma_L(1+\cos\theta) = 2\sqrt{\sigma_S^{\mathrm{LW}}\sigma_L^{\mathrm{LW}}}. \tag{1}$$

In many non-metallic condensed materials, liquid or solid, in addition to apolar Lifshitz–van der Waals interactions, polar hydrogen bond-type interactions such as electron-acceptor – electron-donor interactions, or Lewis acid-base (AB) interactions often occur (which include the special case of the interaction of a hydrogen donor and a hydrogen acceptor). These AB interactions are also called polar interactions.

Unlike the apolar Lifshitz–van der Waals interactions, electron-acceptor – electron-donor interactions or polar interactions are essentially asymmetrical. Thus, the electron-acceptor and electron-donor parameters of the polar component (σ_i^{AB}) of the surface tension of compound i are expressed as σ_i^+ and σ_i^-, respectively.

The electron acceptor and electron donor parameters of the polar component (σ_i^{AB}) of the surface tension of compound i are thus expressed as σ_i^+ and σ_i^- , respectively. There is a well-known relation

$$\sigma_i^{\mathrm{AB}} = 2\sqrt{\sigma_i^+\sigma_i^-}. \tag{2}$$

By measuring the contact angle of the liquid on various solids, two of which must be polar, σ_L^{LW}, σ_L^+ and σ_L^- can be determined. It is always necessary to determine (or know) the value of σ_L (see Eq. (2))

$$\sigma_L(1+\cos\theta) = 2\left(\sqrt{\sigma_S^{\mathrm{LW}}\sigma_L^{\mathrm{LW}}} + \sqrt{\sigma_S^+\sigma_L^-} + \sqrt{\sigma_S^-\sigma_L^+}\right). \tag{3}$$

Knowledge of σ_L is also useful in connection with the additivity rule of surface tension components

$$\sigma = \sigma^{\mathrm{LW}} + \sigma^{\mathrm{AB}}. \tag{4}$$

Results and discussion. Water contact angle measurement is a technique used to evaluate the affinity of surfaces to water. The degree of hydrophobicity of glassy carbon coatings depends on the storage conditions of the material. After the measurements, the water affinity of the glassy carbon coatings of the "space" and "reference" samples was evaluated. The surface of the glassy carbon coatings "space" samples S-1 and S-2 (front side) is hydrophobic, with a contact angle of 70°. The contact angles of the same samples (back side) are 73° and 75°. The differences in the hydrophilicity of S-1 – front side and S-1 – back side, as well as between S-2 – front side and S-2 – back side are small and can be assumed to be within the experimental error. In this case, the contact angles for the "reference" sample R-1 and the "reference" sample R-2 are 50° and 65°, respectively. The more hydrophilic contact angle of the "reference" sample compared to the "space" sample is probably associated with the presence of microcracks on the surface.

Figure 1 shows the measured contact angles of ten consecutive water drops, located at random places on the front and back side, on two types of samples "reference" and "space". The mean angle and mean error are shown in Fig. 1.

To determine the surface tension *sigma/w* values as well as the surface tension *sigma/ab* values of the "reference" and "space" samples, drops with the substances

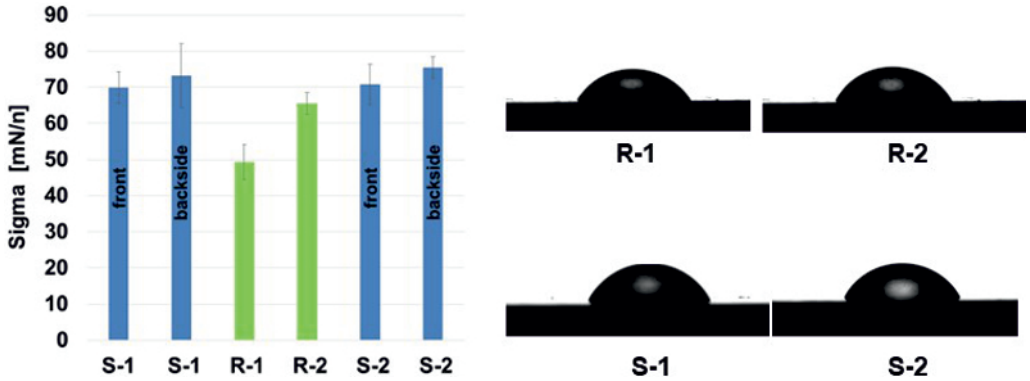


Fig. 1. Average contact angle obtained from water droplets for "space" sample and "reference" sample (the water drop images)

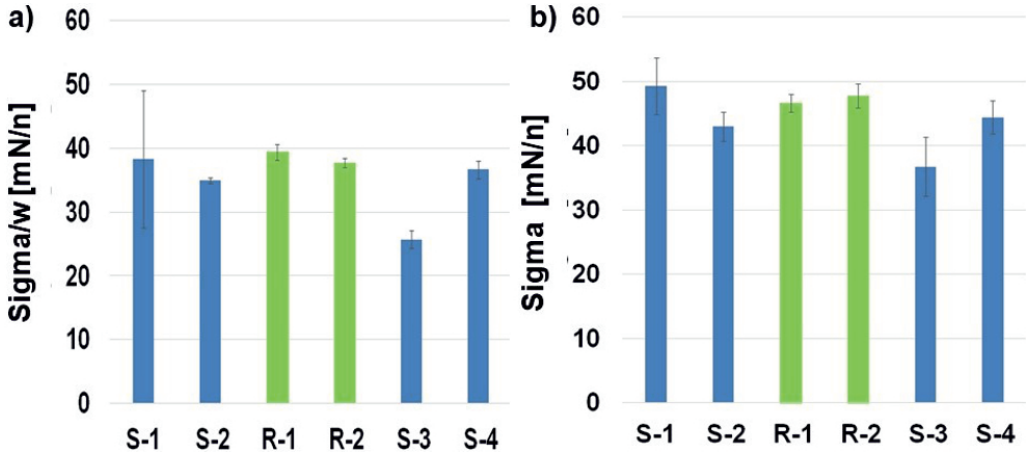


Fig. 2. Comparison of *sigma/w* (a) and *sigma* (b) values for "reference" and "space" samples

formamide and diiodomethane are determined and measured. The contact angles of five drops of 2–5 µL for both substances located in the centre and in the periphery of the samples were measured, and the surface tensions were calculated. The obtained values for the surface tension *sigma/w* for the "reference" samples (R I, R II) as well as the values for the surface tension *sigma/w* for the "space" samples (S-1; S-2; S-3, S-4) are presented in Fig. 2. These data are compared and illustrated in Fig. 2a and b.

From the experimental measurements and theoretical calculations, it was found that the values of the surface tension *sigma/w* for the two "reference" samples are 39.44 mN/n for R-1 and 37.7 mN/n for R-2, respectively. These values are close to the *sigma/w* values for the two "space" samples, which are 38.29 mN/n for S-1 and 36.67 mN/n for S-4. For "space" samples S-2 and S-3, lower values of *sigma/w* are 34.9 mN/n and 25.66 mN/n, respectively (Fig. 2a).

Similarly, for the *sigma* surface tension values only, the "reference" sample R-1 has a close value of 47.78 mN/n in relation to the "space" sample S-1 49.26 mN/n, as well as the "reference" sample R-2 has a close value of 46.58 mN/n in relation to the "space" sample S-4 44.39 mN/n. In the "space" samples S-3 and S-2, lower values of the *sigma* surface tension were determined, 36.7 mN/n and 42.98 mN/n, respectively (Fig. 2b). The "reference" and "space" samples have a high ability for Van der Waals interaction with other surfaces, as the "space" sample S-3 has a relatively high dispersion in this respect, i.e. places with weak and places with high ability for dispersion interaction. This is probably due to the presence of impurities on the surface.

The values for the surface tension *sigma/ab* for "reference" and "space" samples are presented in Fig. 3. The value of the *sigma/ab* surface tension for two "reference" samples was found to be 7.14 mN/n for R-1 and 10.08 mN/n for R-2, respectively. The value of the *sigma/ab* surface tension of the "space" sample

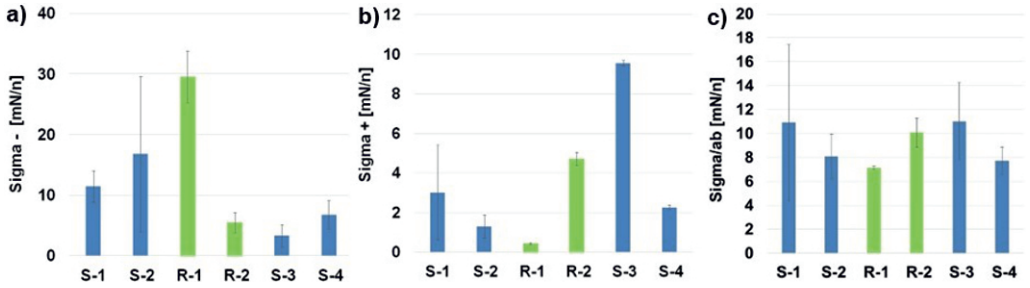


Fig. 3. Comparison of (a) *sigma*, (b) *sigma+* and (c) *sigma/ab* values for "reference" and "space" samples

S-4 is 7.72 mN/n, and that of the "space" sample S-2 is 8.08 mN/n, which are close to the value of 7.14 mN/n for the "reference" sample R-1. The value of the *sigma/ab* surface tension of the "space" sample S-3 is 11.04 mN/n and the value of the "space" sample S-1 is 10.92 mN/n, which are close to the value of 10.08 mN/n for "reference" sample R-2 (Fig. 3c).

"Reference" sample R-1 has a high tendency to be a Lewis basis, i.e. to donate electrons. The highest surface of energy has "space" sample S-3, and the lowest has "space" sample S-4.

The surface topography of the glassy carbon coatings was studied by means of Atomic force microscopy. The AFM images of both types of "reference" and "space" samples were compared and presented in Fig. 4. The morphology of the "reference" sample with a scanning area of 5×5 µm^2 (Fig. 4a) is smooth with presence of small "grain-like" structures in comparison with the morphology of the "space" sample (Fig. 4b). From the cross-section and surface roughness determined for both the "reference" and "space" samples, it was found that the "space" samples have a smoother surface.

Conclusions. The following dependencies have been established from the experimental measurements of contact angles on the glassy carbon surface for "reference" and "space" samples, as well as from the theoretical calculations made:

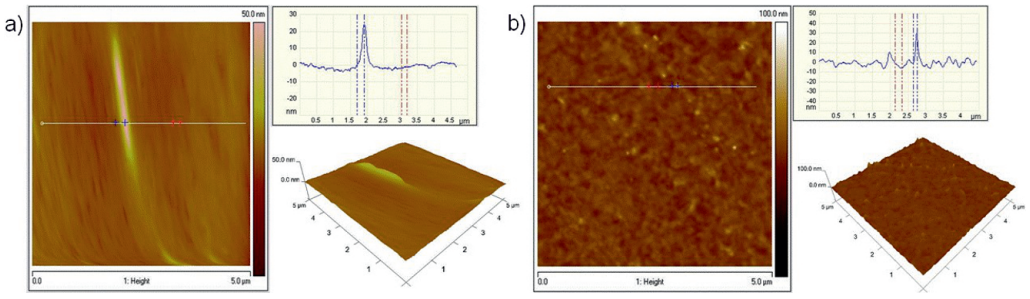


Fig. 4. 2D and 3D topography with cross section of (a) "reference" and (b) "space" samples

1. The main conclusion about the condition of the surface of the tested samples is the high levels of the values of the dispersion component for both the "reference" and the "space" samples. These values are between 40 and 50 mN/m and refer to the weak Van der Waals interactions due to impurities on the glassy carbon surface, which attract the asymmetric molecule of diiodomethane stronger than water.

2. The value of the *sigma/w* surface tension for the "reference" sample R-1 is similar to that for the "space" sample S-1, as well as the "reference" sample R-2 has the surface tension *sigma/w* with a value close to the "space" sample S-4, respectively. Lower *sigma/w* values were observed for the other two "space" samples, 25.7 mN/n for S-3 and 34.9 mN/n for S-2. The reference to the calculated values of the sigma surface tension for the "reference" samples R-1 and R-2, which have close values – 47.8 mN/n and 46.6 mN/n, is similar. The sigma surface tension values for the "space" samples S-1 and S-4 are 49.3 mN/n and 44.4 mN/n. Lower sigma values were also observed for the other two "space" samples, 36.7 mN/n for S-3 and 42.9 mN/n for S-2.

3. In polar interactions, there are significant differences, both between the face and back of the "space" samples and between the latter and the "reference" ones. The larger the angle with the surface of the sample, the lower the adhesion energy, the lower the wettability and the lower the free surface energy. At small contact angles, the surface is hydrophilic with high adhesion energy, good wettability and high free surface energy.

4. The *sigma/ab* surface tension of the "reference" samples R-1 and R-2, has values of 7.14 mN/n and 10.8 mN/n. Higher values of sigma/ab were determined for "space" samples S-1 (11.04 mN/n) and S-3 (10.92 mN/n) compared to the values for the other two "space" samples S-4 (7.72 mN/n) and S-2 (8.08 mN/n).

5. The morphology of the glassy carbon coatings was studied by means of Atomic force microscopy. It has been found that "reference" and "space" samples have smooth surface, such as the roughness of "reference" sample is rougher than that of the "space" sample.

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REFERENCES

[1] Fitzer E., K.-H. Köchling, H. P. Böhm, H. Marsh (1995) Recommended Terminology for the Description of Carbon as a Solid (© 1995 IUPAC), Pure Appl. Chem., **67**(3), 473–506.

[2] Harris P. J. (1999) Carbon Nanotubes and Related Structures, Cambridge, Cambridge University Press, 356.
[3] Maynard N. C., E. A. Bielecki, H. F. Burdick (1981) Instrumentation for vector electric field measurements from DE-B, Space Sci. Instrum., **5**, 523–534.
[4] Stanev G., M. Petrunova, D. Teodosiev, I. Kutiev, K. Serafimov et al. (1982) An instrument for DC electric field and AC electric and magnetic field measurements aboard "Intercosmos-Bulgaria-1300" satellite, Adv. Space Res., **2**(7), 43–47.
[5] Teodosiev D., N. Isaev (2001) Physicochemical properties of probes for measuring electric fields in the Near-Earth plasma, Chem. Phys. Rep., **19**(6), 1165–1175.
[6] Mozer F. S. (1973) Analyses of techniques for measuring DC and AC electric fields in the magnetosphere, Space Sci. Instrum., **14**(2), 272–313.
[7] Teodosiev D. K., I. D. Pechenykov, J. S. Georgiev, P. A. Petrov, R. P. Dobrev et al. (1982) Method for impregnation and coating of porous refractory materials with glass-carbon, Bulgarian Certificate of Authenticity No 31847, MKP C 04 35/84 (in Bulgarian).
[8] Teodosiev D., G. Stanev, G. Galev, S. Neichev, P. Pushchaev (2000) Spherical probes for measurements of electric fields on the INTERBALL-2 satellite in the IESP-2M instrument, Cosmic Res., **38**(6), 574–578.
[9] Neychev S., A. Buzekova, G. Galev, Z. Zhekov, I. Ivanov et al. (2014) Measuring the potential of the body of ISS: Apparatus and first results, Proc. SES 2013, 15–23.
[10] Bouzekova-Penkova A., R. Nedkov, G. Stanev, S. Klimov, V. Grushin et al. (2017) Technological experiment "Environment" on board the International Space Station, J. BAS, **5/2017**, 22–26 (in Bulgarian).
[11] Teodosiev D., A. Bouzekova-Penkova, K. Grigorov, R. Nedkov, G. Stanev et al. (2021) Structural and mechanical properties of glass-carbon coatings after an extended stay on the international space station, C. R. Acad. Bulg. Sci., **74**(2), 197–206., DOI:10.7546/CRABS.2021.02.05.
[12] Vieira, L. De S. (2022) A review on the use of glassy carbon in advanced technological applications, Carbon, **186**, 282–302, https://doi.org/10.1016/j.carbon.2021.10.022.
[13] Good R. J., M. K. Chaudhury (1991) Fundamentals of Adhesion, book (1991) Theory of adhesive forces across interfaces.
[14] Wu W., R. F. Jr. Giese, C. J. Van Oss (1995) Evaluation of the Lifshitz–Van der Waals/Acid-Base Approach to Determine Surface Tension Components, Langmuir, **11**(1), 379–382, https://doi.org/10.1021/la00001a064.

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