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Physico-chemical behavior, thermo-optical and mechanical properties of glassy carbon up to 2100 K under low energy proton and VUV irradiations

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Abstract

In the frame of mission for the Sun approach, to understand the effects of the heating of the solar corona and the acceleration of the solar winds, research was carried out to study the behavior of glassy carbon that can be used for the heat shield. The physico-chemical behavior of glassy carbon from 1600 K up to 2100 K with or without protons bombardment and VUV irradiation was studied together with the measurement of the thermal optical properties, the ratio of the solar absorptivity to the total hemispherical emissivity conditioning the thermal equilibrium of the heat shield. Experimental results obtained on massive glassy carbon samples are presented through mass spectrometry, mass loss rate and microstructural characterization (XRD, SEM...), mechanical and thermo-optical properties. Finally, the synergistic effect of high temperature, protons and VUV radiation has a low impact on this material.

Keywords: glassy carbon; proton irradiation; high temperature; VUV radiation; emissivity; mechanical properties.

1. Introduction

Such as Parker Solar Probe (PSP), a new mission for a closest Sun approach is under study (Ref 1). In the case of PSP, the probe will plunge directly into the Sun atmosphere into a region that no other spacecraft has ever entered in order to understand the heating of the solar corona and the acceleration of the solar winds (Ref 2, 3). At the closest approach, the probe will be exposed to huge solar flux that can reach temperatures around 2000 K according to the thermal optical properties of the material selected and also to the design and shape of the heat shield and of the trajectory. Thus a well-designed thermal protection system (TPS) must protect the instrumentation and communication devices of the probe to secure the mission

and minimize the risk. In this way, the physico-chemical behavior of materials designed for the heat shield must be studied in the extreme conditions close to the ones it will encounter (high temperature, ions bombardment, VUV radiation). Then, glassy carbon was one of the different carbon-based materials we have studied to be part of the heat shield of solar probes.

A lot of papers about the modification of glassy carbon using laser (Ref 4) or submitted to energetic ion bombardment with quite high Z ions (Ref 5-9) can be found but scarce are the ones about the interaction with protons or hydrogen atoms (Ref 10-14) and these studies are mainly carried out at low temperature.

Güttler et al. have shown that the etching of H atoms with glassy carbon leads mostly to the formation of C₂ hydrocarbons with a maximum yield at 600 K (Ref 11). Working at lower temperature (470 K), Terranova et al. have observed the formation of tree-like structures on the glassy carbon submitted to hydrogen atoms due firstly to the heterogeneous H-induced erosion of carbon followed by the condensation in nanoscale aggregates, this leading to porous mesoscopic structures (Ref 12).

Jovanovic et al. (Ref 13) have irradiated glassy carbons at room temperature with high energetic protons (15 keV) with fluences between 10¹⁶ and 10¹⁸ ions cm⁻² and have observed significant changes for a critical fluence of 2-5 x 10¹⁷ ions cm⁻² and they have converged to the same conclusions made by Terranova et al. (Ref 12). They have observed by AFM the formation of nanometer scale protusions due to the previous formation of dangling bonds that are nucleation centers for the deposition of carbon. The erosion of the glassy carbon surface leads to an increase of the roughness. Meanwhile they have observed, making thermal desorption experiments up to 1200 K, that the implanted protons are unstable in the material and evolve to the formation of atomic and molecular hydrogen and also to water (Ref 14).

Nevertheless, even if glassy carbons surfaces are bombarded with high Z ions such as Sr at fluence of 2 x 10¹⁶ ions cm⁻² at room temperature (Ref 6), annealing at high temperatures, 900 K during 1 h and up to 2300 K during 5 h, resulted in the respective partial and total recovery of the glassy carbon structure except a lower intensity of the D peak.

2. Conditions encountered by the heat shield

In the way to set the experimental parameters as close as the environmental conditions during the PSP mission, these data have to be determined precisely. Thus, the temperature, the energy and flux of protons and the VUV photon flux have been calculated taking into account

the spacecraft trajectory at 9.5 Rs perihelion and are detailed in (Ref 15-18). They are heavily drawn from the design of the NASA STDT studies of 2005 (Ref 2) and 2008 (Ref 3).

The TPS should either have a low mass, or shall be operating at temperatures as low as possible in order to meet the outgassing aspects. This fact shall be considered due to the risk of contaminating the scientific sensors, photovoltaic cells and other critical components. This means that the selection of inappropriate TPS materials or inadequate temperature predictions may put the entire mission at risk. The design of the heat shield is also dependent of the distance to the Sun surface. At 9.5 Rs, a flat heat shield could be used. This shape gives a maximum allowed temperature of 1600 K for a α/ϵ ratio of the solar absorptivity α to the total hemispherical emissivity ϵ equal to 1. The energy and the flux of ions (mainly protons) that will simulate the solar winds are respectively equal to 2 and 4 keV and to 5×10^{15} and 10^{15} ions $\text{m}^{-2} \text{s}^{-1}$. In the simulation test, the energy of the ions was fixed at 2 and 4 keV representative during the trajectory of the slow (majority) and fast solar winds and the ion flux was fixed at a higher level to keep safety margins of around 10^{17} ions $\text{m}^{-2} \text{s}^{-1}$.

The VUV radiation emitted by the Sun mainly comes from the upper layers of the chromosphere. Its spectrum includes several typical lines but the most intense is the hydrogen Lyman- α (H Ly- α) line at 121.6 nm. At 1 AU (astronomical unit), this flux is near $5 \times 10^{-3} \text{ W m}^{-2}$. Using the conservation law, the VUV flux being inversely proportional to the square of the distance, the VUV flux received by the heat shield at perihelion for H Ly- α is around 2.5 W m^{-2} for PSP.

3. Numerical simulation of proton bombardment

Computer programs allow modeling various interactions between an incident particle beam and a target. In this work, TRIM (Ref 19) was used to evaluate the physical sputtering. TRIM is a Monte Carlo computer program that simulates slowing down and scattering of energetic ions in amorphous targets. It was developed to determine ion range and damage distributions as well as angular and energy distributions of backscattered and transmitted ions. Roth and al. have summarized the different erosion processes of graphite under proton irradiation in the frame of fusion devices application (Ref 20). Basically, depending on the environmental conditions, one can expect physical sputtering, chemical erosion and radiation enhanced sublimation (RES) (Ref 21).

In the frame of this study, considering the applied experimental parameters (i.e. temperature range, proton fluxes and energies), it can be expected that the main erosion processes will be RES and thermal sublimation for temperatures up to 1800 K and above 2000 K respectively. However, the overall carbon erosion will be a combination of all these processes.

To simulate these phenomena, the target material is mainly described by three different binding energies of its atoms: the displacement energy, the lattice binding energy and the surface binding energy. In the case of carbon, these three binding energies are given by the TRIM code and respectively set by default to 28, 3 and 7.41 eV (SRIM version of 2012). However, all the simulations realized with TRIM are performed with a static target, which is valid only for low implantation fluences. Effectively, ion beam induces changes of the target due both to implantation of the projectiles and to sputtering. The density of the glassy carbon is taken into account at 1.5 g cm^{-3} . To assess the influence of density, simulations were also carried out with that of graphite at 2.25 g cm^{-3} . We then compare the results of the implantation of protons, the sputtering, and finally, the vacancies created within the material due to the proton bombardment for 2 or 4 keV at 0° or at 60° (compared to the normal at the surface) on glassy or vitreous carbon (VC) and 4 keV at 0° or 60° on graphite carbon (GC).

Figure 1 shows the results of the simulations of the implantation of H^+ ions within the material during an ion bombardment of 2 or 4 keV at 0° or at 60° on glassy carbon and of 4 keV at 0° or at 60° on carbon graphite.

Figure 1. Proton implantation rate in the target material as a function of the target depth

Going from a kinetic energy of 2 to 4 keV leads to a greater average implantation distance, this phenomenon is nevertheless reduced when the flux bombards the target with an angle of 30° (60° compared to the normal of the target). Indeed, a low angle of attack during the bombardment induces an accumulation of protons near the surface. Likewise, increasing the density from 1.5 to 2.25 g cm⁻³ results in an accumulation of protons near the surface.

The average implantation distance is directly obtained by TRIM and is given in Table 1. Finally, a decrease in density from 2.25 to 1.5 g cm⁻¹ (ratio 1.5) leads to an increase in the same proportion of the average implantation distance. The sputtering yield can be calculated by dividing the number of atoms ejected by the number of ions sent to the target, and these data for the sputtering yield are also presented in Table 1.

Table 1. Average implantation distance and sputtering yield for the two carbons: vitreous VC and graphite GC with 2 different ions kinetic energies (2 or 4 keV) and angle of incidence (0 or 60 °)

Carbon nature (VC vitreous, GC, graphite), ions energy, angle	Average implantation distance (Å)	Sputtering yield (at./ion)
VC, 2 keV, 0°	492	0.012
VC, 4 keV, 0°	881	0.008
VC, 2 keV, 60°	327	0.017
VC, 4 keV, 60°	529	0.019
GC, 4 keV, 0°	587	0.010
GC, 4 keV, 60°	354	0.027

Thus, the increase in the kinetic energy of the protons leads to a higher number of atoms torn from the target in the case where the flow is directed at 60°. In the event that the flux hits the target perpendicularly, the sputtering goes from 1.2 to 0.8% as the energy of the flux is increased from 2 to 4 keV. In fact, the deeper average path of the ions does not allow the surface atoms to be ejected from the target. When the target is made of a denser material the sputtering is increased.

4. Material, experimental device and protocol

Glassy carbon was studied as we did for other different carbon materials (Ref 16-18). In this section, are described the material chosen, the experimental device and protocol to study the synergistic effect of high temperature treatment, protons bombardment and VUV radiation on glassy carbon samples.

4.1. Material

The glassy carbon selected is the variety V25 from Mersen. It is a form of pure carbon produced by the thermal decomposition of a three-dimensionally cross-linked polymer, it has been heat-treated after the elaboration process to around 2800 K. It has a high flexural strength and it can be used up to 2800 K in vacuum. The characteristics of this type of graphite known as glassy or vitreous carbon are just like those of glass. Pesin has done an interesting review on the properties of glassy carbon among them the crystalline structure, electric and magnetic properties, and also on its characterization by Raman and Auger spectroscopies (Ref 22).

Table 2 reports its main properties given by the manufacturer. Samples of 40 mm diameter and 2 mm thickness were used.

Table 2. Physical properties of glassy carbon V25 from Mersen

Physical properties	Unit	Value
Density	g cm^{-3}	1.50-1.55
Open porosity	%	0
Impurities	ppm	50 S; 2 B
Flexural strength	MPa	60-80
Compressive strength	MPa	150-200
Young modulus	GPa	22
Vickers micro-hardness (30 g)		150-175
Thermal expansion @1300 K	K^{-1}	3.5×10^{-6}
Thermal conductivity @ 300 K	$\text{W m}^{-1} \text{K}^{-1}$	8
Resistivity	$\text{M}\Omega \text{ cm}$	4500

4.2. Experimental device

The MEDIASE set-up has been developed and instrumented to simulate the Sun environment in collaboration with CNES (Ref 17, 18, 23, 25-27). This reactor is placed at the focus of the 1 MW solar furnace in Odeillo, France. The material can be heated in high vacuum (10^{-4} Pa) up to 2500 K using the solar concentrated radiation that allows reaching high temperatures in a few seconds. A mass spectrometer (MS, Hiden HAL4 EPIC300N quadrupole) placed at around 40 cm from the sample in the normal direction analyzes the gaseous species emitted by the material and a Quartz Crystal Microbalance (QCM, Leybold-Inficon IC/5 Thin Film Deposit Controller) allows to record in situ the mass loss rate of the samples during the experiments. A Fisons EX05 ion gun was used with hydrogen (Alphagaz 2, Air Liquide). It is also located at 40 cm distance from the sample and irradiates it with a 45° angle of incidence. The beam on the target is 15 mm in diameter. The fluence and the size of the beam at the target are determined with a Faraday plate collector which can be placed between the ion gun and the target to adjust the gun parameters. Temperature measurements are carried out by a pyro-reflectometer developed at PROMES-CNRS laboratory (Ref 24) and the radiance measurement for the emissivity evaluation is done using a radiometer and a motorized system to have the

angular dependence of the emissivity (Ref 23, 25).

4.3. Experimental protocol for the physico-chemical behavior

The experimental protocol can be divided into three different steps:

- A first batch of samples is tested only at high temperature. Each sample is successively heated at 1600, 1800 and 2100 K at a heating rate of around 5 K/s. These three levels of temperature correspond nearly to the calculated heat shield temperature at perihelion for the first one, 1600 K, taking a α/ϵ ratio of around 1.2 while the two following temperature levels, 1800 and 2100 K, could be reached in case of an accidental reduction of the perihelion or during an exposition to solar flares or for higher α/ϵ ratio, for example. The duration of each temperature level is around 15 min, allowing making physico-chemical measurements during the stationary regime. For each temperature level, the gaseous species emitted and the mass loss are recorded.
- A second batch of new samples is then tested simultaneously up to 2100 K and under VUV radiation in the same conditions of temperature and duration than the samples of the first batch. The same measurements are also performed.
- A third batch of new samples is then tested simultaneously up to 2100 K with ions bombardment at different energies (different samples) but for a constant flux of 6×10^{16} ions $\text{m}^{-2} \text{s}^{-1}$ (corresponding to a fluence of 7.2×10^{19} ions m^{-2}) and with VUV irradiation. The same measurements are performed.

Preliminary tests were conducted to prove the good reproducibility of the measurements in the experimental conditions of the study. Moreover this reproducibility was also established previously (Ref 16-18).

4.4. Thermo-optical measurement

Emissivity measurement performed at PROMES-CNRS laboratory is based on a direct method where the temperature and the total or spectral radiance of the sample are measured (Ref 23, 25, 27). The total or spectral directional emissivity is the ratio of the measured radiance to the part of the blackbody radiance in the same conditions of temperature and wavelength according to the formulas:

$$\epsilon' = \frac{L'_{0.6-2.8}}{L_{0.6-2.8}} \quad \text{and} \quad \epsilon' = \frac{L'_{0.6-40}}{L_{0.6-40}}$$

with ϵ' the directional emissivity, L' the material radiance, L_0 the blackbody radiance and in subscripts the wavelength ranges (0.6-2.8 and 0.6-40) expressed in μm .

The hemispherical emissivity is then calculated by integration of the directional values acquired from normal direction 0° up to 80° . In the case of opaque materials, the emissivity in the 0.6-2.8 μm wavelength range is approximated to the solar absorptivity from 0.4 to 2.7 μm . The resulting value of the α/ϵ ratio (in fact equal to $\epsilon_{0.6-2.8}/\epsilon_{0.6-40}$) governs the thermal equilibrium of the material in extreme solar environment encountered at perihelion during the mission. The radiance measurements are performed using a Heimann KT4 (Germany) bolometer equipped with a Cassegrain optics through a thallium iodobromide (KRS 5) window. The measurements are performed using a specific in situ three-mirrors goniometer developed at PROMES-CNRS laboratory in order to cover the whole angular range from normal incidence to 80° incidence by 10° step plus the two angles of 45° and 75° , without moving nor the radiometer nor the sample. The whole system (radiometer + optical window + three-mirrors goniometer) and the pyroreflectometer are calibrated before and after each measurement series on a blackbody.

5. Experimental results

In this section are presented the experimental results obtained from the single or simultaneous treatments of the samples and the emissivity data obtained on the several samples studied. The material characterization using several techniques is also presented.

5.1. Physico-chemical behavior

The samples after cleaning in acetone and alcohol in an ultrasonic bath and dried are placed in the experimental set-up through the cooled sample-holder. In situ measurements are conducted during the experiments using the mass spectrometer (MS) and the Quartz Crystal Microbalance (QCM) recording the sample mass loss. Before each test, using the MS, a baseline mass spectrum is realized in the way to determine which species are initially present in the reactor. This baseline is then subtracted to the mass spectra recorded during the experiments to observe only the species coming from the sample. Mass spectra are realized each 3 min all along the temperature level duration. Figure 2 reports the mass spectra for the three temperature levels studied with the different treatments (VUV, ions at different energies).

Figure 2. Mass spectra for the three temperature levels studied: 1600, 1800 and 2100 K

All the mass spectra realized during the experiments show the same trend, with the appearance of 4 main different groups, characteristic of various gaseous species emitted by the samples. The first group (1 and 2 amu) represents atomic and molecular hydrogen while the 3 following groups correspond to various hydrocarbons constituted of one (from 12 to 16 amu: C, CH, CH₂, CH₃, CH₄), two (from 24 to 30 amu: C₂, C₂H, C₂H₂, ..., C₂H₆) or three (from 36 to 44 amu: C₃, C₃H, ..., C₃H₈) carbon atoms. However, most of the detected species (CH, C₂H, ...) are not thermodynamically stable and come from the dissociation of stable species (CH₄, C₂H₂, ...) in the mass spectrometer detector, considering the electron ionization energy of 70 eV. Other typical species coming from the residual atmosphere in the chamber, such as H₂O, N₂ or O₂ could also be detected during the baseline spectrum acquisition at respectively 18, 28 or 32 amu. For the case at 2100 K, some more species are present with amu from 48 to 54 but in very low amount.

Regarding the gaseous species emitted by the carbon materials during the tests, different behaviors have been noticed. The gaseous species emitted by the V25 samples at 1600 K and 1800 K are nearly the same and it can be noticed that the lowest outgassing concerns the treatment with VUV and protons at 2 (blue) and 4 (orange) keV for which mainly CH₄ and C₂H₂ are slightly reduced (Fig. 2). Increasing the temperature up to 2100 K leads to more species emitted with higher amu (52 to 54 for C₄H₄ to C₄H₆, 80 for C₆H₈ and 98 for C₇H₁₄), and the lowest outgassing is also for the samples being submitted to VUV and proton irradiation simultaneously.

During these measurements, the QCM was set on but little deposit was measured on the quartz indicating that not many condensable species were emitted from the different samples (Tables 3 and 4).

Table 3. Label of the different samples and associated treatments

Sample name	Treatment: T (K) and hold time (min)
S20	reference
S21	HT: 1600 K (15 min) + 1800 K (21 min) + 2100 K (15 min)
S22	HT + VUV: 1600 K (15 min) + 1800 K (15 min) + 2100 K (15 min)
S23	HT + protons 2 keV: 1600 K (18 min) + 1800 K (21 min) + 2100 K (15 min)
S24	HT + VUV + protons 2 keV: 1600 K (15 min) + 1800 K (15 min) + 2100 K (17 min)
S25	HT + VUV + protons 4 keV: 1600 K (15 min) + 1800 K (15 min) + 2100 K (15 min)

Table 4. Total mass loss rate for each sample at each temperature level

Sample	T level (K)	Δm (mg/m ² s)
S21	1600 / 1800 / 2100	0 / 0 / 0
S22	1600 / 1800 / 2100	0 / 0 / 0
S23	1600 / 1800 / 2100	0.20 / 0.05 / 0
S24	1600 / 1800 / 2100	0.05 / 0 / 0
S25	1600 / 1800 / 2100	0 / 0 / 0.12

5.2. Thermal optical properties

The measurement of the thermo-optical properties was performed on all the samples after the highest temperature treatment at 2100 K with or without ions and VUV irradiations.

Measurements were carried out also at lower temperature and Figure 3 reports the evolution of the emissivity versus temperature. Nevertheless, the most important values are the ones measured at 2100 K corresponding to the highest temperature level during the preceding treatment. For the samples, S21 to S24, the mean solar absorptivity and the mean total hemispherical emissivity are respectively equal to 0.63 and 0.59 leading to a ratio α/ε equal to 1.07, higher values were obtained for the S25 sample with $\alpha = 0.69$ and $\varepsilon = 0.64$ leading to nearly the same value of the ratio. Then it can be concluded that whatever the treatment at 2100 K carried out on the several samples, the thermo-optical properties are not very sensitive.

Figure 3. Evolution of the solar absorptivity (α) and of the total hemispherical emissivity (ε) for the two V25 materials treated in different conditions (S21 and S25)

5.3. Ex situ characterization

Several characterization techniques have been used to investigate the evolution of the microstructure and morphology of the glassy carbon samples, before and after the different treatments at high temperature. The microstructure is analyzed using X-ray diffraction (XRD), with a depth of analysis around 10 μm that gives information on the bulk microstructure. The modifications of the surface morphology are followed using SEM and profilometry. Nanoindentation was also performed to see if there is a modification of the mechanical properties.

5.3.1 SEM and XRD

SEM imaging is performed using the Hitachi S-4500 microscope SEM-FEG field type field effect. For XRD, the PANalytical X'PERT Pro diffractometer is used with incident copper radiation ($\lambda_{\text{Cu}} = 0.154 \text{ nm}$) at 40 kV and 20 mA. The angular analysis range varies from 10 ° to 75 ° with an acquisition time of 10 s/step. X-ray diffractograms were recorded and studied using PANalytical software (Data collector and HighScorePlus).

Figure 4 reports the images obtained by SEM of the surface of the different samples and Figure 5 the XDR patterns of the same materials.

Figure 4. SEM pictures of the glassy carbon V25 samples at reference state (S20) and after the highest temperature exposure (2100 K) without or with VUV radiation and adding proton bombardment. The scale bar is 4 μm.

The surface of the sample treated only at high temperature (S21) seems cleaner than the one of the reference and appears a little bit smoother. For the samples with VUV added (S22), some pores are visible together with a slight peeling of some parts and this phenomenon is increased when adding protons bombardment at 2 keV (S23). In that case, the surface is a little bit more eroded due probably to the formation of hydrocarbons species. Adding the VUV seems to cure the surface compared to the one of S23, and it could be comparable to the one of the reference S20 or the S21. Increasing the proton energy from 2 to 4 keV leads to more important damage of the surface. Later, profilometry measurement will complete these observations.

Figure 5 reports the XRD patterns at around $2\Theta = 25^\circ$ for the different samples and it is clear that the crystallinity is little sensitive to the several treatments.

Figure 5. XRD patterns of the V25 reference and tested samples with different surface treatments

5.3.2 Profilometry

The surface texture of the glassy carbon subjected to the various treatments is systematically characterized using a profilometer equipped with a diamond stylus of 2 μm radius of curvature (Model DEKTAK XT, Bruker). In order to have a visual representation of the surface texture of each sample, a 3D map was produced with a scan length of 1 mm, a scan resolution of 0.16 μm per point and a number of thousand scan lines spaced of 1 μm .

The acquisition duration of an image by profilometry being very long, for each sample the amplitude parameters R_a and R_{ku} were systematically extracted from a series of six 2D surface profiles. Each profile is evaluated over a length of 10 mm with a resolution of 0.55 μm per point and made in the center of the sample. In order to obtain a faithful representation of the surface roughness, the position of the profiles draws the "spokes of a wheel" circumscribed in a circle of 10 mm in diameter and separated from each other at an angle of 30°. In order to quantify the roughness independently of the waviness of the surface, each primary profile collected via the trace of the stylus on the surface of the sample is filtered through a Gaussian Regression Filter adjusted with the wavelength cut-off of 0.8 μm (an example of a 2D profile is shown in Fig. 6). Thus, the parameters R_a and R_{ku} , corresponding respectively to the arithmetic mean of the absolute values of the profile heights and to the flattening factor of the amplitude distribution curve (kurtosis), are extracted according to the ISO 4287 standard.

Figure 6. Typical 2D profile with separation of geometric deviations between waviness and surface roughness

In order to clarify the results relative to the loss of species of the material recorded during the various treatments by mass spectrometry and QCM, we converted each 2D primary profile previously obtained into a 3D mapping thanks to the juxtaposition of several identical 2D profiles, an option proposed by Vision64® software which provides access to volume parameters according to the ISO 25178 standard. Thus, we determine the core material volume parameter (V_{mc}) obtained by integrating the cumulative amplitude distribution curve also called the bearing ratio curve or Abbott-Firestone curve. In order to eliminate deep valleys and salient peaks that are not representative of textures, the V_{mc} parameter is calculated with bearing ratio thresholds of 2% and 98% (see the schematic representation in Fig. 7). Then, taking for the glassy carbon a density equal to 1.5 g cm^{-3} , each value of V_{mc} is converted into a mass per unit area expressed in mg m^{-2} . Thus, we determine for each sample, the absolute value of the variation in mass by subtracting the mass of the reference sample (S20). These results will be discussed later.

Figure 7. Surface profile (left) associated with Abbott's curve (right) describes the increase in bearing ratio with increasing depth of the roughness profile. The core material volume corresponding to the hatched part of the profile is calculated with bearing ratio thresholds to 2% and 98%.

The 3D maps obtained by profilometry are shown in Figure 8. A simple visual inspection of the images reveals a change in the surface texture of the treated samples (S21 to S25) compared to the one of the untreated glassy carbon (S20). It is also noticed that the samples subjected to the protons bombardment (S23 to S25) have a fairly similar surface texture, which differs from that, also quite similar, of the treated samples not subjected to the ions bombardment (S21 and S22).

Figure 8. 3D maps of the surface of the studied glassy carbon samples

The amplitude parameters from the 2D roughness profiles are given in Figure 9. The values found partially reflect the visual examination of the 3D maps. Indeed, the treated surfaces have a value of R_a systematically higher than their original value measured around 160 nm (see S20, Fig. 9). There is again a distinction between the treated samples, those subjected to ion bombardment (S23 to S25) and those that are not (S21 and S22), with values of R_a systematically higher for the surfaces subjected to protons and also a value of R_a that increases significantly when going from a bombardment with a kinetic energy of 2 to 4 keV (S23 to S25). These results are in quite good agreement with the SEM images of Figure 4.

The parameter R_a being an arithmetic mean of the heights, it gives no information on the shape of the evaluated profiles. Thus, the R_{ku} amplitude parameter provides additional information on the morphology of textures. A R_{ku} factor > 3 indicates peaks and narrow valleys leading to a narrowing of the amplitude distribution curve, while a $R_{ku} < 3$ indicates less steep peaks and valleys leading to a flattening and widening of the distribution of the heights. The values found for R_{ku} (see Fig. 9) reinforce the visual analysis of the 3D maps, namely the probable existence of two distinct morphologies of surface texture, one linked to HT with a R_{ku} around 3.2 (samples S21 and S22), the other related to the HT associated with H^+

ions with a R_{ku} around 2.4 (samples S23 to S25), the VUV appearing to play a minor role in the changes observed at the resolution scale of the stylus profilometry.

Figure 9. R_{ku} and R_a for the different glassy carbon samples studied

The values of the V_{mc} parameter and the corresponding mass variation are given in Figure 10. The lowest volume is found for the reference glassy carbon, with an average value equal to $0.52 \mu\text{m}^3/\mu\text{m}^2$. The highest volume is found for the S25 sample with an average value equal to $1 \mu\text{m}^3/\mu\text{m}^2$, which corresponds to a mass variation of 730 mg m^{-2} . Obviously, these variations do not correspond to the actual mass loss of the treated samples, nor even to a mass loss evolution, since it is a subtraction of two surface textures recorded at different times. Due in particular to its good mechanical stability (see the nanoindentation section), glassy carbon does not appear to have undergone any structural transformation that could have modified its surface texture. Therefore, this mass variation associated with each treated sample can be considered the minimum amount of material lost per unit area. The comparison of the only mass loss rate recorded by QCM (see Table 4 sample S25), with a loss over the entire duration of treatment equal to 108 mg m^{-2} , and also of the small quantity of species recorded by the mass spectrometer, suggests that mass losses occur primarily in a solid form. Moreover, the

SEM images (Fig. 4) indicate that these losses of solid matter could be due, at least in part, to a degradation process associated with the peeling the surface of the material.

Figure 10. Core material volume parameter (Vmc) and corresponding mass variation ($|\Delta M|_{/S20}$) for each treated glassy carbon sample according to their treatment. The mass variation is defined in relation to the Vmc value found for the untreated sample (S20).

5.3.3 Nanoindentation

The influence of the different treatments applied to the glassy carbon on its mechanical properties was also studied. The mechanical properties were investigated by Berkovich nanoindentation with a normal applied load of 400 mN (NanoIndenter II, Nano Instruments Inc.). Glassy carbon contains a proportion of closed micro-porosities linked together by very small strongly disoriented graphitic areas. This architecture explains its low density (around 1.5) as well as its low fracture toughness (around $0.6 \text{ MPa}\cdot\text{m}^{1/2}$) (Ref 28). Another characteristic is its great capacity to recover deformations, which is why it is called super-elastic material (Ref 29). Although for a certain number of them, the deformations produced in nanoindentation appear to be totally reversible, their recovery is not entirely characteristic of an elastic material (Ref 30). Indeed, we note for all the samples analyzed in this study that the unloading is hysteretic (Fig. 11), with the consequence of an absence of permanent depression on the indented surfaces (see AFM image, Fig. 12). However, the shape of the loading curve is not the reverse of that of the unloading, and irreversible indentation work can be estimated from the

area between the two curves. This energy loss seems to correspond to friction, but the mere friction between the indenter and the sample is not a sufficient explanation. Field and Swain attempt to explain this behavior by the possibility of a reversible deformation mechanism, activated by the hydrostatic compressive indentation stress, involving inter-planar sliding and friction along the basal planes of graphitic nanocrystals (Ref 31). Therefore, the Oliver & Pharr model (Ref 30), commonly used to determine Young's modulus and hardness in nanoindentation, turns out to be inappropriate in our case, since it is based on an estimate of the projected area of the permanent depression (Ref 30). So, some authors choose to extract the Young's modulus by converting the load cycle data obtained with a spherical indenter into a stress-strain diagram (Ref 33, 34).

Figure 11. Typical load-displacement curve obtained on the glassy carbon with a Berkovich indenter

Figure 12. AFM image showing a typical impression of nanoindentation on the glassy carbon surface obtained with an applied load of 400 mN. The surface profile does not indicate any measurable residual depression, only the mark of the edges of the pyramid indenter with a triangular base is visible

Here, we chose to determine the modulus of elasticity of the glassy carbon from the experimental loading data, considering it to be purely elastic data. Indeed, the examination of the fit of the load cycle with the equation proposed by Sneddon for an elastic contact turns out to be excellent in all cases ($R^2 > 0.99$), giving consistent values of modulus of elasticity with that displayed by the manufacturer (22 GPa). Thus, assuming a rigid conical indenter and a purely elastic contact, Sneddon finds that (Ref 35):

$$P = E_{eff} \frac{2 \tan \theta}{\pi} \delta^2 \quad \text{Eq. 1}$$

where δ is the penetration depth and P the corresponding applied load. θ is at the half-angle of a conical punch. By choosing $\theta = 70.3^\circ$, the projected area of the cone becomes equivalent to that of a Berkovich pyramid. Since the diamond indenter is infinitely stiff compared to glassy carbon, the effective modulus of elasticity E_{eff} can be roughly compared to Young's modulus. A typical fit plot is shown in Figure 13(a). To characterize the effects produced by different high temperature irradiations on the resistance to plastic deformation (i.e. hardness) of the glassy carbon, we used an alternative approach to that of Oliver & Pharr consisting in determining the parameter K_m . Thus from the work of Loubet et al (Ref 36), Hainsworth et al. (Ref 37) have shown that the loading curve for a homogeneous material can be well described by a linear relation between the load P and the squared displacement of the indenter δ , i.e.:

$$P = K_m \delta^2 \quad \text{Eq. 2}$$

where K_m is a constant depending on the specimen and the geometry of the indenter. The K_m parameter which corresponds to the slope of the $P - \delta^2$ plot is therefore considered to be a material constant which emphasizes hardness, i.e. it mainly tends to reflect changes in hardness for a wide range of material (Ref 37). This method of analysis is also able to locally detect the presence of an inhomogeneity of mechanical properties. This is the case for example with coated systems where the low load portion of the $P - \delta^2$ plot is expected to be a straight line with a slope determined by the properties of the coating, then gradually with increasing loads, the appearance of a second straight line segment with a slope this time dictated by the properties of the substrate (see example in Fig. 13(b) (Ref 38)).

Figure 13. Typical examples: (a) Fit nanoindentation loading data of glassy carbon with Sneddon equation, (b) $P-\delta^2$ plot of a hard coating (ceramic) on a soft substrate (steel), $P-\delta^2$ plot for the glassy carbon samples (c) with a load of 400 mN on S25 and (d) with a load of 2 mN on S25

The values of the effective modulus of elasticity obtained with the Sneddon equation are presented in Figure 14(a). The one of the reference glassy carbon is found at 22.8 ± 0.7 GPa (S20), a value almost identical to that given by the manufacturer (22 GPa). The values obtained for the other samples are comparable to the reference with variabilities included in the measurement uncertainty interval.

Figure 14. Comparison of the effective modulus of elasticity E_{eff} and the constant K_m for the different glassy carbon samples studied

On the other hand, for all the indentation contact scales up to 400 mN, and whatever the sample, there is no change in the slope on the $P-\delta^2$ plots (an example is shown in Fig. 13 (c)). Therefore, at this scale of measurement, proton and VUV radiation do not appear to create a gradient of mechanical properties on the surface of the material. It should also be noted that to probe the effect of proton and VUV radiation at the extreme surface of the samples (around 200 nm in depth), nanoindentation tests were carried out at lower load (a few mN). Unfortunately, they did not make it possible to quantify any mechanical heterogeneity, due to the excessive influence of surface roughness ($R_a > 160$ nm) on the measurements. However, the few exploitable indentation curves again do not seem to show heterogeneities in mechanical strength as shown by the $P-\delta^2$ plot obtained on sample S25 with an applied load of 2 mN (Fig. 14(d)).

The results obtained for the constant K_m are shown in Figure 14(b). As for the modulus of elasticity, the average K_m value of the treated samples (S21 to S25) does not differ significantly from that of the reference sample (S20) measured around 40 GPa.

Thus, nanoindentation measurements have shown that the different treatments applied to the glassy carbon samples do not significantly affect its initial original mechanical properties. From the amplitude parameters R_a and R_{ku} , we also identify two distinct morphologies of degradation of the treated surfaces, one related to high temperature, the other to high temperature combined with H^+ ions, VUV radiation does not appear to have a significant effect on the observed changes. On the other hand, the analysis of the core material volume parameter (V_{mc}) suggests that the mass losses recorded during the treatments are underestimated. As a result, these mass losses would occur largely in a solid form and would be due in part to a peeling of the material surface favored by the subsurface accumulation of H^+ ions. Nevertheless, these material mass losses are to be put into perspective because the visual examination of the treated surfaces shows no visible signs of degradation.

6. Conclusion

The physico-chemical behavior of the V25 glassy carbon from Mersen was studied at high temperature up to 2100 K with or without coupled aggressions such as proton bombardment at 2 and 4 keV and VUV radiation to simulate the Sun approach. Mass spectrometry and mass loss rate measured by Quartz Crystal Microbalance have shown that few species (maximum for hydrocarbons up to C_3 compounds) are emitted after 3 x 15 min treatment and particularly

when adding ion and VUV radiation, and a maximum mass loss rate of 108 mg m^{-2} was obtained for the sample treated at 2100 K with VUV radiation and proton bombardment at 4 keV. Thermo-optical properties have been measured on the samples treated at 2100 K with or without coupled aggressions and it can be concluded that whatever the treatment at 2100 K, the solar absorptivity and the total hemispherical emissivity are quite stable and that their ratio is roughly equal to 1.07. Ex situ characterization was performed to see if some surface modification occurred. SEM images have shown that there is some erosion of the surface of the samples treated at 2100 K with protons at 2 and 4 keV. Some parts of the surfaces present some peeling, the VUV radiation being less significant. On the contrary, XRD patterns have shown no modification of the microstructure of the samples whatever the treatment. Results obtained by 2D and 3D profilometry have confirmed this evolution of the surface with eroded parts on the surface mainly for the sample S25 (2100 K + VUV + ions at 4 keV) presenting the maximum arithmetic roughness R_a of around 360 nm compared to the reference sample S20 with a value of 160 nm. Finally, nanoindentation measurements have shown that the different treatments applied to the glassy carbon samples do not significantly affect the original mechanical properties and a value of the effective modulus of elasticity using the Sneddon equation equal to 22.8 GPa was obtained and it is very close to the Young modulus given by the manufacturer (22 GPa). To conclude, this kind of glassy carbon can be used as a heat shield material for solar missions.

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Credit Author Statement

Marianne Balat-Pichelin: Conceptualization, Methodology, Writing - Original Draft & Review & Editing, Supervision, Funding acquisition. **Julien Eck:** Methodology, Investigation, Validation, Resources, Writing - Original Draft. **Jean-Louis Sans:** Investigation, Methodology, Resources. **Hervé Glénat:** Methodology, Investigation, Formal Analysis, Visualization, Writing - Original Draft.

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