SYNERGISTIC EFFECTS OF HIGH TEMPERATURE AND VUV RADIATION ON CARBON/CARBON COMPOSITES FOR SOLAR PROBES

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ABSTRACT
The aim of solar probe missions (PHOIBOS, Solar Probe+), approaching as close as 3 solar radii above the sun surface, is to fly into one of the last unexplored regions of the solar system, the sun corona, to understand its existence and the driving of solar and solar-type winds. The Thermal Protection System (TPS) for these probes can be a C/C composite shield (coated or not) to protect the instrumentation and communication devices (Fig. 1). At the closest approach, the shield is exposed to a total solar incident flux of about 21 MW and can reach temperatures of nearly 2100-2400 K according to the chosen material ($\alpha/\varepsilon$ ratio).

Fig. 1: Artist view of Solar Probe+ (Courtesy of NASA)

Synergistic effects of protons coming from the solar winds and vacuum ultraviolet (VUV) photons, particularly with the most intense line, the H-Lyman $\alpha$ at 121.6 nm, have to be studied. Physical sputtering, chemical erosion and radiation-enhanced sublimation of the TPS can be observed during the mission, as also VUV degradation of the materials and the emitted gaseous species.

In this paper we will present the impact of different parameters characteristic of the solar winds, modelled using various simulation codes (TRIM, TRIDYN and GEMINI) and experimental results on the physico-chemical behavior of different C/C composites under coupled aggressions (high temperature + VUV irradiation) using the MEDIASE facility implemented at the 1MW solar furnace. The gaseous species emitted by the treated materials and the mass loss rate of the samples are followed during the experiment and the thermo-radiative properties are also measured to obtain the ratio of the solar absorptivity to total hemispherical emissivity $\alpha/\varepsilon$ that governs the thermal equilibrium of the TPS.

1. CONTEXT
The objective of the solar probes is to understand how the Sun’s corona is heated and how the solar wind is accelerated: two fundamental questions that still outstanding in the field of heliophysics [1, 2]. At closest approach, the TPS constituted of a C/C composite primary shield can reach temperatures up to 2400 K, according to the material thermo-radiative properties. The Sun environment is also dominated by protons with various energies. Radiation effects on the TPS depend on the temperature and the incident ion flux. Thus, physical sputtering, chemical erosion and Radiation Enhanced Sublimation (RES) of the material could be induced. All these phenomena have to be considered in the way to evaluate the physico-chemical behavior of the TPS of solar probes.

2. NUMERICAL STUDY

2.1. Calculation codes
The main goal of this study is to reproduce the interactions between incoming ions of the solar wind and the material of the TPS. A previous work was led by Paulmier [3-5]. The following calculations are more accurate, taking into account both hydrogen and helium ions and the different incidence energies characteristic of the slow and fast solar winds. The various codes used were initially developed to describe plasma surface interactions in fusion devices (TRIM, TRIDYN and PSIC) or thermochemical reactions (GEMINI). TRIM is a Monte Carlo computer program which simulates slowing down and scattering of energetic ions on amorphous target [6]. It was developed for determining ion range and damage distributions as well as angular and energy distribution of backscattered and...
transmitted ions. However, all the simulations realized with TRIM are performed with a static target, which is only valid in the limit of low implantation fluences. In order to simulate the resulting phenomena of fluence-dependent ion implantation and atomic mixing, a dynamic version of the TRIM code, based on the binary collision approximation, has been developed: TRIDYN [7]. Then, parameters such as depth profiles of all the atomic species in the target as function of the incident fluence and composition changes due to implantation and sputtering can be calculated. It should be noted that simulations with these two codes are only valid for systems which are dominated by collisional effects. No thermochemical phenomenon is included in a computer simulation of the present type. PSIC is a set of subroutines based on empirical formulae [8]. This code provides data for plasma-surface interaction processes like physical sputtering of any monoatomic target or chemical erosion and RES of graphite.

Finally, GEMINI is a software that calculates the thermochemical equilibrium of a system by minimizing its global energy [9]. The minimization method used is based on a global optimisation technique, adapted to the chemical equilibrium. The thermochemical properties always correspond to the substance standard ones and are calculated thanks to the basic data of the elements and compounds.

2.2. Numerical results

Several parameters were taken into account during the numerical study, like the ion implantation and the sputtering yield or the chemical erosion and the RES yields of graphite. The two ions considered were hydrogen and helium, characteristic of the solar wind composition. Ion energies were defined regarding the slow and fast solar winds and the Solar Probe+ trajectory. In this way, the energies for the slow solar wind were respectively set to 2 keV (H\(^+\)) and 8 keV (He\(^{2+}\)), and they reach 4 keV (H\(^+\)) and 13 keV (He\(^{2+}\)) for the fast wind. Moreover, the proportion of these two ions does not change from one wind to another. They are both constituted of approximately 95% hydrogen and 5% helium. The ion angle of incidence is set to 45°, the same as in our experimental set-up in the way to compare the future experimental results to simulation. The ion implantation rate, between 87 and 97 %, is function of the ion mass and incident energy. Thus, the higher the incident energy is (up to 13 keV), the higher the implantation rate (near 97%). Ions coming from the fast solar wind will have a higher implantation rate. Furthermore, at the same ion energy, the model gives that the implantation rate decreases with the increase of the ion mass. Concerning the sputtering yield of carbon, the most influential parameter is the mass of the particle. This tendency is presented on Fig. 2, where is reported the sputtering yield of carbon atoms by hydrogen, helium or both ions coming from slow and fast solar winds. The sputtering yield is the highest with a bombardment of He\(^{2+}\). It can be explained by the fact that a heavier ion could interact and transfer more efficiently its kinetic energy to the atoms of the target. On the other hand, a more elevated incident energy is not synonymous of a higher sputtering yield. One reason seems to be that atoms ejected from their site by the most energetic ions come from the lower layers of material and must cross a larger thickness of material before being ejected leading to a more consequent energy loss. Their energy in this case is not sufficient to allow them to cross the surface potential barrier. Consequently, the slow solar wind, characterized by a higher ion flux and a lower incident ion energy will induce a more important sputtering yield of carbon, in comparison with the fast solar wind.

Regarding the evaluation of the chemical erosion of carbon by hydrogen, an important gap between the slow and fast solar winds at a distance of 10 Rs from temperatures within 1500 and 1700 K is noticed, mainly due to the fact that the ion flux and energy are different in the two cases (2 keV and 4.6x10\(^{15}\) H m\(^{-2}\) s\(^{-1}\) for the slow solar wind, 4 keV and 1.1x10\(^{15}\) H m\(^{-2}\) s\(^{-1}\) for the fast solar wind). Moreover, an evolution with the target temperature is observed: the chemical erosion yield decreases with the rise of temperature. Consequently, the theoretical contribution of this type of erosion is finished over 1800 K for the fast solar wind and subsists up to 2000 K for the slow one.

The last phenomenon to take into account is the RES. The evolution of its yield is calculated for hydrogen or helium, representative of slow or fast solar wind. This process increases exponentially with temperature. The nature of the incident ion plays also an important role regarding the difference between the RES induced by hydrogen and helium on the whole range of temperature.

![Fig. 2: Sputtering yield of carbon by hydrogen or helium ions respectively for energies corresponding to slow and fast solar winds and due to synergetic effect of both ions](image)
Indeed, helium leads to a RES rate five times higher than hydrogen. The calculations with the GEMINI code were realized at atmospheric pressure, arbitrarily with 10 mol of carbon and 1 mol of hydrogen, these initial conditions being without any effect on the result, qualitatively. Impurities consisting of oxygen and nitrogen were added in very low quantity to simulate the residual atmosphere present in our experimental facility. In this way, the products theoretically formed during the reaction between the carbon atoms of the material and hydrogen can be observed. The main products are methane, acetylene and in low proportion C₂H (Fig. 3). Methane is preponderant for temperatures up to 1900 K, while acetylene is mainly produced beyond this point. Concerning secondary products, the most significant (CH₃, C₂H₂ and C₂H₃) are displayed on Fig. 4 and their proportions tend to increase with the temperature.

3. EXPERIMENTAL STUDY

3.1. The MEDIASE facility

The MEDIASE (Moyen d’Essai et de Diagnostic en Ambiance Spatiale Extrême) test facility has been designed and instrumented to reproduce the solar environment and characterize in-situ materials by analyzing their outgassing and measuring their mass loss and thermo-radiative properties. This set-up is implemented at the focus of the 1 MW solar furnace of the PROMES-CNRS laboratory (Fig. 5).

![Fig. 5: The MEDIASE facility at the focus of the 1 MW solar furnace](image)

The materials can be heated up to 2500 K in few seconds by concentrated solar radiation passing through a hemispherical silica window placed in front of the chamber under high vacuum (10⁻⁶ hPa). On the rear face of the sample, temperature, mass loss and optical measurements can be performed. Several emplacements have been implemented around the chamber to insert the ion and VUV sources and the measuring instruments. The several studied materials were successively heated at 1600, 1800 and 2100 K during 15 min for each level of temperature. They were also irradiated by VUV photons with an Omicron HIS13 source. The operation of the lamp is based on the principle of a cold cathode capillary discharge. The inlet gas used is hydrogen, in the way to obtain the H Lyman α line at 121.6 nm, characteristic of the VUV solar spectra. The photon flux reached is about 1 W m⁻², corresponding to a distance of nearly 15 Rs. The test facility allows to perform several measurements when the sample is heated and irradiated. A Leybold-Inficon IC/5 Quartz Crystal Microbalance (QCM) allows to record the mass loss rate of the samples with an accuracy of 0.2 µg m⁻² and a Hiden HAL4 EPIC300N quadrupole mass spectrometer analyzes the gaseous species emitted by the material during the experiment.

3.2. Experimental results

The experimental study was carried out on polycrystalline graphite and C/C composites to evaluate the impact of different parameters (high temperature, VUV irradiation) on their physico-chemical behavior. The results of this study are presented for three different
materials that underline the interest of using C/C composite. The first material is a polycrystalline graphite (GPoly) from Carbone Lorraine, grade 5890, prepared at 3000 K under pressure of $2.10^5$ hPa containing methane, heavy hydrocarbons, nitrogen and hydrogen. It is therefore purified at the same temperature and pressure. The second (SEPG) and the third (SEPH) material are C/C composites, elaborated by Snecma Propulsion Solide and based on Ex-PAN HR fibres and a 2.5D fibrous preform. The only difference between the two composites is the final thermal treatment of the SEPG after its elaboration.

When the samples are heated for the first time, we can observe an important outgassing due to the sublimation of gaseous species that could be ethanol, acetone (both used to clean the sample), contamination species or polymeric precursors of the elaboration process of the composite.

The gaseous species emitted by the samples SEPH during the tests for two different temperatures are presented in Fig. 6. Four different groups can be observed on the graphs. The first corresponds to hydrogen atom and molecule, while the three others are attributed respectively to $C$, $C_2$ and $C_3$ atoms and their related hydrocarbons. All these species were obtained during the calculations with the GEMINI code. The outgassing of the materials increases with temperature. When VUV radiation is added to high temperature, materials present various behaviors. Thus, at 1800 K, the production of gaseous species is equivalent although it is greatly increased at 2100 K. The outgassing of the tested materials under VUV radiation varies depending on their nature (Fig. 7); it is strongly reduced for GPoly and there is nearly no change for SEPG. The particular behavior of this last material could be due to the final thermal treatment at high temperature it underwent during its elaboration process.

VUV radiation is also of importance as regarding the mass loss rate of the samples, reported on Table 1. Indeed, only submitted to high temperatures, the mass loss rate notably increases with temperature for GPoly from 1600 to 2100 K whereas it is only observed at the last level of temperature for the SEPH composite. On the opposite, for SEPG mass loss is only seen at 1600 K.
Table 1: Mass loss rate (mg m\(^{-2}\) s\(^{-1}\)) of GPoly, SEPG and SEPH under high temperature and under high temperature and VUV radiation

<table>
<thead>
<tr>
<th>T (K)</th>
<th>HT HT+ VUV</th>
<th>HT VUV</th>
<th>HT+ VUV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>1800</td>
<td>0.22</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>2100</td>
<td>0.82</td>
<td>0.03</td>
<td>0.06</td>
</tr>
</tbody>
</table>

When the VUV radiation is added, the mass loss rate tendency changes considerably. For the GPoly sample, the mass loss rate is similar at 1600 K and decreases up to 2100 K. This can be eventually explained by the breaking of the C-C bonds, increasing the volatility of the gaseous species emitted, that no longer condense on the QCM. Low signal on the QCM at 2100 K could also traduce an acceleration of the mass loss kinetics by the VUV radiation: all the species have already outgassed during the previous temperature levels. Concerning the SEPH sample, mass loss rate is significant only at 1600 K, and the value is nearly equal to the GPoly one. The SEPG mass loss is observed at the first heating step. As it has undergone a thermal treatment after its elaboration, this mass loss could be linked to the outgassing of contamination species. Only the mass loss rate of polycrystalline graphite at 2100 K overcomes the mass loss rate requirement established by NASA of 0.44 mg m\(^{-2}\) s\(^{-1}\) for the Solar Probe+ thermal shield.

The morphology of the samples is also studied using SEM (Figs. 8 and 9). We can note that the effect of the high temperatures only is traduced by the material cleaning, revealed by the erosion of the first layers of graphite for the GPoly (Fig. 8, b) and mainly by the elimination of contaminants or polymeric precursors on the surface of the SEPH (Fig. 9, b). When VUV radiation is added, morphological modification is visible. The grain shape of the polycrystalline graphite is sharper and larger porosities appear (Fig. 8, c). Otherwise, the roughness of the C/C composite seems to be slightly increased and traces of contaminants are always present at the surface (Fig. 9, c). Concerning the evolution of the SEPG composite, there is no great modification of the morphology of the material with the addition of VUV radiation. This could be still explained by the final thermal treatment of the material, only difference with the SEPH composite.

Microstructural analysis led by X-ray diffraction was also performed on the different materials (Fig. 10). There is a slight modification of the crystallinity of the GPoly as it was elaborated at 3000 K under pressure of 2.10\(^5\) hPa containing methane, heavy hydrocarbons, nitrogen and hydrogen. On the opposite, C/C composites show important modifications after tests at high temperature only or with added VUV radiation for SEPH. This behavior could be explained by the fact that high temperature increases the crystallinity of the material and it seems that the VUV radiation magnifies this phenomenon for the SEPH composite.
In the way to study more accurately the evolution of the microstructure of the materials, micro Raman spectroscopy was also conducted at 647.1 nm with an argon-krypton laser. Then the defect concentration and the crystallite size were calculated for a mean thickness of the surface layer of 1.5 µm. The defect concentration is obtained thanks to the ratio $I_D/I_G$ and is reported on Table 2 for the different carbon-based materials. The microstructural modification of the polycrystalline graphite is very important, with an increase of the defect concentration about 100%. Concerning the C/C composite, the evolution is not so impressive, even if it is slightly higher for SEPH than for SEPG. For the last one, there is no evolution between the reference and the sample treated at high temperature, due to its higher thermal treatment after elaboration. This result seems in contradiction with the one obtained using XRD, which show microstructural modifications of the material. It could be partly explained by the deep of analysis greatly different with these two techniques: only 1.5 µm for the Raman and few tens of micrometers for the XRD. Thus, it seems that the microstructural modifications of SEPG happen mainly in the bulk.

Table 2: Ratio $I_D/I_G$ representative of the defect concentration of the materials

<table>
<thead>
<tr>
<th></th>
<th>GPoly</th>
<th>SEPG</th>
<th>SEPH</th>
</tr>
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<tbody>
<tr>
<td>Ref.</td>
<td>1.55</td>
<td>1.42</td>
<td>1.93</td>
</tr>
<tr>
<td>2100 K</td>
<td>1.76</td>
<td>1.41</td>
<td>2.37</td>
</tr>
<tr>
<td>2100K + VUV</td>
<td>3.34</td>
<td>1.20</td>
<td>2.05</td>
</tr>
</tbody>
</table>

The evolution of the crystallite size of the materials can be seen on Table 3 and is also of interest, as it traduces the crystallinility of the material. Here again, the GPoly undergoes the greater modification. The high temperature only and the high temperature with addition of VUV radiation seem to increase its crystallinity. Regarding the C/C composite materials, there is only a little evolution in the crystallite size for SEPG under high temperature and VUV radiation. Otherwise, whatever the treatment, the modification of the crystallite size is slight.

Table 3: Crystallite size of the materials in nm

<table>
<thead>
<tr>
<th></th>
<th>GPoly</th>
<th>SEPG</th>
<th>SEPH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>27</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>2100 K</td>
<td>24</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>2100K + VUV</td>
<td>13</td>
<td>35</td>
<td>21</td>
</tr>
</tbody>
</table>

The last step of this study concerns the determination of the thermo-radiative properties of the carbon-based materials. Measuring the ratio of the solar absorptivity $\alpha$ (0.6-2.8 µm) to the total emissivity $\varepsilon$ (0.6-40 µm) is a key factor to predict their behavior, as it governs the thermal equilibrium of the TPS. The lower is this ratio, the lower is the temperature reached by the heat shield. In this way, the $\alpha/\varepsilon$ ratio at normal incidence has been determined and plotted in Fig. 11 for each material. The error bar is only mentioned for the GPoly under high temperature but it is the same for all the samples.

Fig. 11: $\alpha/\varepsilon$ ratio for GPoly, SEPG and SEPH versus temperature
The evolution of the \( \alpha/\varepsilon \) ratio clearly depends on the material. The polycrystalline graphite is the material with the lower \( \alpha/\varepsilon \) ratio, increasing a little with the addition of VUV radiation. Otherwise, there is almost no variation of this ratio for the SEPG composite whereas the SEPH exhibits more important differences, particularly at 2100 K, going from 1.20 to about 1.35 and leading to an increase of temperature of near 80 K at four solar radii. Moreover, when the carbon-based materials are submitted to high temperature and VUV radiation, there is systematically an inflexion of this ratio at 1800 K. Further tests have to be realized to understand this phenomenon.

4. CONCLUSIONS

Through this study we try to describe the physico-chemical behavior of carbon-based thermal protection system that can be used on solar probes. As regarding the numerical study, the physical sputtering yield of carbon by solar winds is very low, less than 2 %. However, the implantation rate of the ions is very high, more than 85 %, and the implantation depth is around 100 nm for hydrogen and 150 nm for helium. This could have a great influence on the material properties and its chemical erosion. Indeed, the higher the hydrogen implantation rate, the higher the reaction probability with carbon atoms is. Experimentally, we have seen that VUV radiation has an important influence on the behavior of carbon-based materials. No data can be found in the literature to confirm these experimental observations. C/C composite, particularly when it undergoes a final thermal treatment, seems to be more suitable than polycrystalline graphite, as regarding the different results obtained during this study. Some phenomena could be quite well explained, like microstructural or morphological behavior, but others, such as outgassing or mass loss rates need further analysis to be clearly understood. In the future, more tests have to be performed, and combined effects of high temperature, VUV radiation and ion bombardment have to be investigated experimentally.

5. REFERENCES


