Effective Oxidation Model for Light-Weight Carbon Preform Ablators

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Porous Microstructure Analysis (PuMA) software is used to perform simulations of molecular beam scattering experiments of hyperthermal atomic oxygen striking FiberForm®, a carbon preform material used commonly as a precursor in thermal protection systems (TPS). The purpose of this study is to investigate the reactive interaction of fibrous carbon with atomic oxygen in a complex microstructure, which is the primary source of carbon removal at lower temperatures. The detailed micro-structure of FiberForm® obtained from X-ray micro-tomography is used in the PuMA simulations to capture the complexity of the porous and fibrous characteristic of FiberForm®. A finite-rate surface chemistry model recently constructed from the molecular beam scattering experiments on vitreous carbon is applied to each fiber of the FiberForm® material. This model consists of detailed surface reaction mechanisms such as adsorption, desorption, and several types of Langmuir-Hinshelwood (LH) reactions to characterize the oxygen-carbon interactions at the surface. Comparison between the experimental and PuMA time-of-flight (TOF) distributions of both O and CO show good agreement. It was also found that a significantly higher amount of CO is generated when the beam interacted with FiberForm®, when compared with vitreous carbon. This is postulated to be primarily a result of multiple collisions of oxygen with the fibers, resulting in an higher effective rate of CO production. Multiple collisions with the different fibers, resulting from the porous nature of FiberForm® is also found to thermalize the O atoms, in addition to the adsorption/desorption process. The effect of micro-structure is concluded to be crucial in determining the final composition and energy distributions of the products. Thus, an effective model for the oxygen interaction with FiberForm®, fully accounting for the detailed micro-structure, for use in Computational Fluid Dynamics (CFD) and material response codes, is presented.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>CO{a}</td>
<td>Weakly bound CO adsorbate</td>
</tr>
<tr>
<td>CO{b}</td>
<td>Strongly bound CO adsorbate</td>
</tr>
<tr>
<td>&lt;E_i&gt;</td>
<td>Average incident energy, [J]</td>
</tr>
<tr>
<td>&lt;E_int&gt;</td>
<td>Average internal excitation energy, [J]</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>k_b</td>
<td>Boltzmann constant, [m^2 kg s^-2 K^-1]</td>
</tr>
<tr>
<td>m</td>
<td>O atom mass, [kg]</td>
</tr>
<tr>
<td>m_s</td>
<td>effective surface mass, [kg]</td>
</tr>
<tr>
<td>O^c</td>
<td>catalytic oxygen atom</td>
</tr>
<tr>
<td>(s)</td>
<td>Empty surface site</td>
</tr>
<tr>
<td>T</td>
<td>Temperature, [K]</td>
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</tbody>
</table>

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Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>DSMC</td>
<td>Direct simulation Monte Carlo</td>
</tr>
<tr>
<td>IS</td>
<td>Impulsive Scattering</td>
</tr>
<tr>
<td>LH</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>MB</td>
<td>Maxwell-Boltzmann distribution</td>
</tr>
<tr>
<td>TD</td>
<td>Thermal Desorption</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-flight</td>
</tr>
<tr>
<td>TPS</td>
<td>Thermal protection system</td>
</tr>
</tbody>
</table>

Greek

\( \alpha \) Variance

\( \Phi \) Surface site density of carbon, [atoms/m²]

I. Introduction

Thermal protection systems (TPS) of space vehicles are exposed to extreme environments during hypersonic (re-)entry. Extreme heat loads as well as reactive interactions of the materials with the partially dissociated atmospheric gases of \( \text{N}_2 \), \( \text{O}_2 \), \( \text{NO} \), \( \text{N} \), and \( \text{O} \) lead to the alteration of the surface and the boundary layer flow surrounding the vehicle. Accurate modeling of ablation processes and prediction of the heat loads and recession of the TPS materials are critical to the space vehicle heat shield design.

Continuum modeling approaches are not always valid at all regions of the flow-fields surrounding a hypersonic flight as a result of the high altitude and high speed nature of the flow.\(^1,2\) A molecular description of the gas is required for the accurate modeling of the highly rarefied regions in the shock, near the surface, etc. Hence, it is essential that the surface chemistry models contain details required for such a molecular description of the gas-surface interaction. Although there exists a vast literature on the modeling of surface chemical reactions using the continuum approach, relatively few studies have examined it using kinetic mesoscale methods such as direct simulation Monte Carlo (DSMC).\(^3,4,5\)

In this study we focus on the carbon preform of Phenolic Impregnated Carbon Ablator (PICA) known as FiberForm\(^\text{®}\) a rigid preform made of rayon-derived carbon fibers. Although several finite-rate reaction models exist for the air-carbon system,\(^6,7,8\) recent studies performed by Candler et al.,\(^9,10\) showed considerable difference between the different models. Furthermore, the study stated that careful validation against experimental measurements are required to improve the accuracy of the models. In addition, all of these models only contain macroscopic information while the kinetic solvers require additional information regarding the microscopic interactions. In order to obtain high-fidelity solutions in the rarefied regions near the surface, additional information regarding the microscopic interactions like the sticking coefficients, energy barriers, angular scattering distributions, etc., is essential.

Although numerous experiments focused on the interaction of a carbon surface with the partially dissociated air environment have been conducted over the past several years,\(^11,12,13,14,15,16,8\) the development of a generally applicable gas-surface interaction model has proven to be challenging. This is mainly due to the difficulty in identifying and isolating the various complex and coupled interactions of the multi-scale, multi-physics processes. The macroscopic information obtained from these experiments can be a result of numerous highly coupled microscopic phenomena. Furthermore, these macroscopic quantities (product fluxes, mass loss, etc.) were also found to be extremely sensitive to the freestream conditions.\(^17,18,19,20\)

Recently, however, molecular beam experiments using a hyperthermal beam performed by Minton and co-workers\(^21\) have provided an excellent way to isolate the surface mechanisms from the gas-phase kinetics and study the detailed reaction pathways of different surface processes. The use of a molecular beam and near-vacuum conditions ensures that the reaction products are a result of only the gas-surface interactions. With the detailed time-of-flight (TOF) and angular distribution information obtained from these experiments, it is possible to isolate different reaction mechanisms occurring at diverse time scales forming the same gas-phase product. This helps to capture the relative rates of the different processes and provide insight into the fundamental microscopic interactions on the surface. Poovathinugal et al.,\(^22,23\) first employed such molecular beam experimental data to construct a finite rate model, which was further developed by Swaminathan-Gopalan et al.\(^24,25\) This work continues such modeling efforts of molecular experiments and focuses on the simulation and analysis of the scattering from FiberForm\(^\text{®}\) to develop and improve the surface chemistry models for the air-fibrous carbon system.

The current work is part of a larger effort to develop a kinetic meso-scale simulation tool for carbon preform ablators. Owing to the complicated fibrous micro-structure of carbon preform, it is very difficult to isolate the effect of geometry from the surface reactions in the final observed experimental data of the scattered products. Hence, a study was first carried out to establish a gas-surface interaction model based on the analysis of beam scattering experiments on vitreous carbon.\(^24\) Vitreous carbon is non-porous and relatively flat (compared to carbon preform) and thus can be used to study the pure reactive and inelastic scattering interactions on the surface. Vitreous carbon was chosen as the
template for developing the surface reaction model, owing to their similarity in chemical structure and sp² bonding of carbon. The main aim of the current study is to investigate the validity of applying the vitreous carbon surface chemistry model (herein referred as the VC model) to carbon preform. Thus, simulations of the molecular beam scattering experiments are carried out with a detailed FiberForm® micro-structure, where the gas-surface interaction on fibers was based on the surface chemistry model developed for the vitreous carbon in our previous work. These results are then compared with the FiberForm® experimental data.

Although the recently developed VC model accurately captures the carbon oxidation at the mesoscopic scale, it requires the detailed microstructure of the FiberForm®. Thus, it can only be employed directly within the kinetic mesoscale solvers like DSMC and PuMA. In the case of macroscopic solvers like CFD, which does not account for the microstructure of the FiberForm®, direct application of the VC model would result in erroneous predictions. Therefore, carbon oxidation model which includes the effect of both the surface oxidation as well as the inherent microstructure of the FiberForm® is required for use within CFD. These models effectively capture the complete interaction of oxygen within the microstructure (including multiple collisions) within single collision against a flat plate, and thereby termed as effective models.

This paper is organized follows. A brief description of the molecular beam experiments and the corresponding modeling in PuMA is provided in Section II. The VC finite-rate model developed from molecular beam experiments performed on vitreous carbon is outlined in Section III. Section IV describes the micro-tomography procedure used to obtain the FiberForm® samples. The extension of the VC model to FiberForm and comparison with the corresponding FiberForm® experimental results is presented in Section V. The development of the effective surface oxidation model of fibrous carbon is discussed in Section VI. Finally, the conclusions and future work are summarized in Section VII.

II. Molecular Beam Experiments and PuMA Modeling

Molecular beam experiments using a hyperthermal beam source can be used to understand the detailed reaction mechanisms at the surface. Recent molecular beam experiments performed by Minton and co-workers have presented many details regarding the reaction products generated at the FiberForm® surface. A hyperthermal O/O₂ beam composed of roughly 92% O and 8% O₂ (mole ratio), was directed at a FiberForm® sample at incident angle of 45 degrees. The number density distribution as a function of arrival time at the detector, N(t), for the products exiting the surface were collected at various final angles that were in the plane of the beam and the surface normal. These distributions are referred to as time-of-flight (TOF) distributions. Angular flux distributions can be derived by properly integrating the TOF distributions at every final angle. The angular distributions were obtained at two temperatures of 1023 K and 1623 K. The TOF data was collected at fixed final angle of 45 degrees for various temperatures ranging from 1023 K to 1823 K.

The Porous Microstructure Analysis (PuMA) software was used in this study to simulate the beam experiments. PuMA is a suite of tools for the analysis of microstructural data, including material properties and material response simulations. For this study, a custom particle method was implemented and parallelized in the PuMA software to simulate the transport of reactant and product particles, particle-surface collisions, adsorption and surface chemistry of adsorbed particles. Similar to DSMC, each PuMA particle represents a large number of real particles. However, unlike DSMC, PuMA does not model the particle-particle collisions explicitly. It uses random walk statistics (based on Poisson distribution) to perform particle collisions based on the input mean free path. Thus, PuMA framework has a significant speed increase compared to traditional DSMC solvers, though the application is limited to regimes where particle-particle collisions can be ignored (free-molecular regime), or can be modeled based on random walk statistics (e.g. diffusion). The vacuum conditions in the experiments results in negligible particle-particle collisions, thus making PuMA an ideal choice for modeling these experiments. At higher particle densities, particle-particle collisions will become important and DSMC must be used to model the system. This will be carried out as part of the future work.

In PuMA simulations, we set up the domain that mimics the experimental configuration. The frequency of the pulse is 2 Hz and the beam spot diameter is 1.3 mm. Thus, in the PuMA simulations, the particles were released at regular intervals of 0.5 s from a 1.3 mm diameter circular region (source). In the experiments, all the particles within a pulse were released over a very short interval of time, hence the PuMA model assumes the emission of all the particles to occur at the same instant. The velocity distribution of the beam particles was explicitly accounted for by drawing them from a Gaussian distribution fitted to the experimental data obtained from the TOF distribution. The surface reactions in PuMA are modeled using the detailed surface chemistry framework developed by Swaminathan-Gopalan et al. The maximum number of adsorbed O atoms was restricted by the surface site density of carbon which was taken as 3.5 × 10¹⁹ atoms/nm² following the recommendation of Zhulkov and Abe and Alba. This value was derived based on the inter-atomic distances between carbon atoms in a pristine sample assuming a smooth surface.
III. Finite-Rate Model From Beam Experiments on Vitreous Carbon

As mentioned previously, the experimental data on vitreous carbon were used to construct a gas-surface interaction (non-reactive and reactive) model. The reactive scattering was studied by modeling the bombardment of the O/O\textsubscript{2} beam on a vitreous carbon surface, which was used to construct a finite-rate surface oxidation model. The detailed TOF information of the scattered products was used to distinguish between the time scales of the various reaction mechanisms. A total of 9 reaction mechanisms was inferred: adsorption, desorption of atomic oxygen, Langmuir-Hinshelwood (LH) type 3 formation and desorption of two types of CO (labeled as CO\{a\} and CO\{b\}), and LH type 1 formation of O, CO and CO\textsubscript{2}. CO\{a\} is weakly bound and exits the surface quickly, while CO\{b\} is strongly bound to the surface and desorbs from the surface much more slowly. The prompt LH type 1 mechanisms include a catalytic adsorbed oxygen atom following theoretical studies.

Once the reaction mechanisms were identified, the flux of the products formed as a result of each of the mechanisms was computed from the TOF and angular distributions. The detailed TOF information was only available at a 45 degree final in-plane angle at most of the temperatures. The angular distributions obtained at 800 K and 1875 K were used to approximate the total flux. The out-of-plane scattering information was not available from the experiments. All the thermal products were treated as uniformly distributed over the out-of-plane angle since the particles fully accommodated to the surface are known to scatter without exhibiting an azimuthal angular dependence. However, the flux of impulsively scattered (IS) O atoms might be expected to vary significantly with the azimuthal angle, hence a cosine power law decay was used to approximate the out-of-plane scattering distribution following Glatzer et al.

Some of the scattered products that desorb slowly from the surface were not initially modulated in the experiments and were characterized as background signal. It was proposed that one type of CO (CO\{b\}) was bound very strongly to the surface and hence responsible for missing atoms in the TOF data. Since the rate of this slow reaction cannot be determined exactly from the experimental data, the value of the steady state surface coverage at each temperature cannot be computed precisely. However, from the experimental data, it was clear that the surface coverage was decreasing with increase in temperature.

The rate constant for desorption of O and LH type 3 desorption of CO\{a\} were obtained directly from fitting of the decay rate of these products in the TOF distribution. The rate constant of CO\{b\} desorption was calculated from the missing flux and the assumed steady state surface coverage values. Next, the rate constants for the prompt LH type 1 reactions and the LH type 3 formation reactions were computed. The determination of the reaction probabilities from the final flux of the products is not straightforward for these reactions owing to the transient nature of the pulsed beam. The local surface conditions are expected to vary widely within the duration of the pulse. Hence, the methodology proposed by Swaminathan-Gopal et al. is employed, which captures the transient nature of the beam to provide accurate surface reaction rate constants. At each temperature, the rate constant values and the instantaneous surface conditions determine the probability of each of the products. Thus, for each temperature, the value of the rate constants must be determined such that final product compositions are similar to those observed in the experiments. A fitting algorithm, known as the particle-swarm algorithm, was used to obtain the rate constant values. Various initial values were prescribed for each of the reaction rate constants within the fitting procedure, and the complete beam simulations were carried out similar to DSMC to obtain the final product composition formed via each reaction mechanism. The difference between the obtained compositions and the experimental values was defined as the error. The fitting procedure then tries to minimize this error by varying the values of the reaction rate constants. This process was then repeated at each temperature to obtain the rate constants for each of the reactions. Finally, the rate constant values at each temperature were fitted to appropriate functional forms shown in Table 1. The complete details of this VC model can be found in Ref. 25.

<table>
<thead>
<tr>
<th>Type</th>
<th>Mechanisms</th>
<th>Reaction</th>
<th>Rate constant (k)</th>
<th>Units</th>
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<tbody>
<tr>
<td>Adsorption</td>
<td>LH0 O{a} formation</td>
<td>O(ads) → O(ads)</td>
<td>1</td>
<td>m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<td></td>
<td>LH3 CO{a} formation</td>
<td>O(ads) + C(b) + O{ads} → CO(ads) + O{ads}</td>
<td>1.530 \times 10\textsuperscript{-11}</td>
<td>m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<td></td>
<td>LH3 CO{b} formation</td>
<td>O(ads) + C(b) + O{ads} → CO(ads) + O{ads}</td>
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<td>m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<td></td>
<td>LHI O formation</td>
<td>O(ads) → O(TD)(ads) + s</td>
<td>(5.63 \times 10\textsuperscript{3})</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<tr>
<td></td>
<td>LHI CO formation</td>
<td>O(ads) + C(b) + O{ads} → CO(ads) + 2O{s} + 4O{ads}</td>
<td>(5.83 \times 10\textsuperscript{3})</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>LHI CO\textsubscript{2} formation</td>
<td>O(ads) + C(b) + O{ads} → CO(ads) + 2O{s} + 4O{ads}</td>
<td>(5.83 \times 10\textsuperscript{3})</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<td>PS reactions</td>
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<td>O(a)s → O(ads) + (s)</td>
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<td>s\textsuperscript{-1}</td>
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<td>LH3 CO{a} desorption</td>
<td>CO{a} + O{ads} → CO(ads) + (s)</td>
<td>4.855 \times 10\textsuperscript{-11}</td>
<td>s\textsuperscript{-1}</td>
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<td>LH3 CO{b} desorption</td>
<td>CO{b} + O{ads} → CO(ads) + (s)</td>
<td>1.2 \times 10\textsuperscript{-11}</td>
<td>s\textsuperscript{-1}</td>
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</table>
IV. FiberForm® Micro-Structure

FiberForm® is a rigid material with average porosity varying between 85-92%. Its micro-structure is characterized by fibers preferentially aligned at about ±15° with one of the planes (that perpendicular to the direction of compression during manufacturing). The arrangement of the fibers provides the material transverse isotropic properties, with the highest insulation capabilities (lowest thermal conductivity) in the “through-thickness” (TT) direction. The characteristic mean pore diameter of FiberForm® ranges between 50 and 80 µm, and the average fiber diameter is about 10 µm.

The detailed micro-structure of the material was obtained directly from X-ray microtomography (micro-CT) imaging of a sample of the FiberForm® material. Micro-CT volumes were used as computational samples in PuMA. The surface was discretized as triangulated elements, using a threshold-based segmentation. This realistic representation of the FiberForm® micro-structure allows us to account for the actual reactive surface area of the material and also distinguish the effects of surface kinetics and micro-structure geometry.

In order to produce a digital representation of the material’s microstructure for use in DSMC and PuMA, we acquired micro-CT images using the 3D X-ray microscope (Xradia 520 Versa, ZEISS, Pleasanton, CA) of the Stanford Nano Shared Facilities at Stanford University. A 3 mm cylindrical sample of FiberForm® was extracted by cutting a material billet along the principal manufacturing direction. The sample was placed onto the tomography setup and aligned with the axis of rotation of the stage. Radiographs were collected with a setting of the X-ray source at a voltage of 50 kV and a current of 80 µA. A 4× magnification lens was used, and the positions of detector and X-ray source were adjusted to achieve a pixel size of 1.651 µm. This ensured that the sample fit entirely into the field of view. In addition, the selected pixel size was found to provide a suitable resolution of the FiberForm® microstructure during previous investigations. The tomography reconstruction was performed using the instrument reconstruction software. It should be noted that the sample used for imaging is not the same as the one used in the molecular beam experiments. However, the material used in the experiments and that imaged with micro-tomography are contemporary versions of FiberForm® which have comparable porosity and similar micro-structural features.

![Figure 1: Triangulated image of a FiberForm® sample obtained from X-ray imaging using microtomography.](image)

The PuMA computational domain was prepared by first down sampling the dataset by a factor of 0.5, resulting in a voxel size of 3.302 µm, then by extracting a 0.5 mm thick slab from the reconstructed dataset. Subsequently, the images were thresholded in correspondence of the local minimum in their bimodal gray-scale histogram. The isosurface was then discretized into a fine set of triangles using a marching cubes algorithm, implemented in PuMA. Fig. 1 shows an example of a FiberForm® micro-tomography and two views of the triangulated surface of the fibers at increasing level of detail. The actual 3 mm diameter puck used for the PuMA simulations is shown in Fig. 2. The surface of the computational domain is discretized with approximately 16 million triangles.

V. Results: Extension of VC model to FiberForm®

For the O scattering from FiberForm®, the reactive and non-reactive scattering parameters obtained from vitreous carbon experiments were used. However, in the case of vitreous carbon, the O atoms do not undergo multiple collisions with the surface. Hence, only the information regarding the interaction of high energy (hyperthermal energy) O with the surface can be obtained from the vitreous carbon experiment. Due to the porous nature of FiberForm®, particles are expected to bounce around and undergo multiple collisions with the surface. Upon repeated interaction with the surface, the particles attain thermal energies. The details of the non-reactive scattering are expected to vary widely when the energy of particles are lower (thermal energies). The interaction of thermal O with the carbon surface was modeled using the Cercignani-Lampis-Lord (CLL) model. The appropriate scattering model (impulsive to
Figure 2: Computational surface used for the simulation. The surface comprises roughly 16 million triangles. The FiberForm® sample has a diameter of 3 mm.

CLL) is selected based on a specified energy threshold of 2 eV for the incident particle energy prior to a surface collision. Particles with energy greater than this threshold value were scattered impulsively, while the particles with lower energies were scattered based on the CLL model. The values for the normal and tangential accommodation coefficients for the CLL model and the energy threshold were modified to obtain the best possible agreement with the experimental data. The reaction probabilities of hyperthermal O atoms were used for the thermal O atoms. This is a reasonable approximation since the products of all the reaction mechanisms are thermal, and are independent of the incident energy. It was also assumed that all species other than O (CO and CO₂) undergo only non-reactive collisions with the surface.

Figure 3: TOF obtained from PuMA simulations (using the VC model) and experiments of (a) O and (b) CO scattering from a FiberForm® surface at incident and final angles of 45° at 1623 K.

Figure 3 shows the experimental and numerical TOF distributions for O and CO, respectively, at 1623 K and a final angle of 45°. It can be seen that a majority of the O and CO scatter from the surface with thermal energies, which is in good agreement with the experimental distributions. When compared with TOF distributions for vitreous carbon experiments at similar temperatures, it can be seen that the fraction of TD atoms in the signal has increased from vitreous carbon to FiberForm®. This is expected since an O atom is likely to experience multiple surface collisions when penetrating the porous FiberForm® material and therefore more likely to become thermally accommodated with the surface. In the case of vitreous carbon, the average number of surface collisions experienced by an O atom is likely to be close to 1 due to its non-porous nature. Fig. 4 shows a histogram plot of the fraction of particles scattered from the surface against the number of surface collisions. The last bin represents the number of particles that underwent 20 or more collisions before being scattered from the surface. This shows that a significant number of particles undergo a large number of collisions, resulting in the thermalization of the particles. Approximately half of the atoms undergo more than one collision with the surface with about 5% being trapped for a relatively long time (undergoing more than 20 collisions). Gas-phase collisions were found to be negligible as a result of the low pressures of the experimental
setup. Accumulation of the particles caused by trapping inside the micro-structure was not observed despite the complex geometry. In the case of CO, both vitreous carbon and FiberForm® show that CO is almost exclusively a TD product at these high surface temperatures.

Figure 4: Histogram showing the fraction of the particles scattered from the surface vs the number of surface collisions. The last bin represents the fraction of particles that underwent 20 or more collisions before exiting the surface.

Additionally, Fig. 5 shows the experimental and numerical angular distributions for O and CO, respectively, at 1623 K. When compared with angular distributions for vitreous carbon experiments at similar temperatures, the shapes and relative IS/TD ratio are consistent with the observations from the previous paragraph. However, one important difference between the two materials is that the relative CO to O flux increased in the case of FiberForm®. This difference is also attributed to the multiple collisions experienced by the oxygen atoms within FiberForm®. An O atom has a finite probability of reacting with the surface to form CO, while the nascent CO is assumed to scatter non-reactively. Hence, a greater number of collisions with the surface increases the effective probability of CO formation.

VI. Results: Effective model for FiberForm®

The goal of the effective model introduced in this work is to simultaneously capture the effect of the microstructure in addition to the surface chemistry by defining an effective rate for these processes. The reaction mechanisms and form of the effective model are assumed to be the same as that of the original VC model. This is a valid approximation since the occurrence of multiple collisions within the microstructure does not fundamentally alter the mechanism of the surface reactions. Further, the rate constants for the desorption reactions are retained from the VC model since the desorption process is also unaffected due to the multiple collisions on the FiberForm® surface.

Next, in order to derive the rate constants within the effective model, we employ a similar procedure that was used
to derive the VC model outlined in Swaminathan-Gopalan et al.\textsuperscript{32} Briefly, initial guesses for the different rate constants were assumed, and the surface reactions during the full beam simulations were carried out. The molecular beam is modeled to strike a flat carbon FiberForm\textsuperscript{®} surface without the detailed microstructure similar to the way it is treated within CFD. The product fluxes obtained using these guess values are compared to the FiberForm\textsuperscript{®} experimental data, and the corresponding errors are computed. Based on these errors, the initial guess values are modified in a systematic manner using the particle-swarm algorithm.\textsuperscript{34,33} This procedure is repeated until the error values reach below a specified threshold. The rate constant values thus obtained inherently account for the detailed interaction within the microstructure since they reproduce the multiple collisions within the FiberForm\textsuperscript{®} microstructure by assuming a single collision with a flat plate. The final rate constant values and the mechanisms in the effective model are provide in Table 2. CO\textsubscript{2} was observed only at the lowest temperature in the FiberForm\textsuperscript{®} experiments and this data was not enough to derive a rate constant for CO\textsubscript{2} production reaction mechanism.

Table 2: Reaction rate constants in the current finite rate model.\textsuperscript{25}

<table>
<thead>
<tr>
<th>Type</th>
<th>Mechanisms</th>
<th>Reaction</th>
<th>Rate constant (k)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Adsorption</td>
<td>O(g) + (s) → O(ads)</td>
<td>$k = \frac{1}{s}$</td>
<td>m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<tr>
<td>Adsorption-adsorptionmediated</td>
<td></td>
<td>O(ads) + C(b) + O(ads) → CO(ads) + O(ads)</td>
<td>$k = 837.8 \times 10^{-6}$</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
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<td>GS reactions</td>
<td>LHX O[a] formation</td>
<td>O(ads) → O(ads)</td>
<td>$k = 5.73 \times 10^{-6}$</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>LHX CO[a] formation</td>
<td>O(ads) + C(b) + O(ads) → CO(ads) + O(ads)</td>
<td>$k = 83.5 \times 10^{-6}$</td>
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<tr>
<td></td>
<td>LHX O[b] formation</td>
<td>O(ads) → O(ads)</td>
<td>$k = 5.73 \times 10^{-6}$</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>LHX CO[b] formation</td>
<td>O(ads) + C(b) + O(ads) → CO(ads) + O(ads)</td>
<td>$k = 83.5 \times 10^{-6}$</td>
<td>m\textsuperscript{2} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
</tr>
<tr>
<td>PS reactions</td>
<td>LH3 O[a] desorption</td>
<td>O(ads) → O(ads)</td>
<td>$k = 0.05 \times 10^{-6}$</td>
<td>s\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>LH3 CO[a] desorption</td>
<td>O(ads) → O(ads)</td>
<td>$k = 4.485 \times 10^{-6}$</td>
<td>s\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>LH3 CO[b] desorption</td>
<td>O(ads) → O(ads)</td>
<td>$k = 1.2 \times 10^{-6}$</td>
<td>s\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

Figures 6, 7, and 8 compare the TOF, angular distribution and the final product fluxes for both O and CO obtained from the effective model (PuMA simulations) and the experiments. Excellent agreement is observed between the effective model and the experiments. Further, all the features within the TOF and angular distributions are captured by the effective model thus providing validation of the model. This effective model may thus be used as a smooth-wall BC for use in CFD solvers.

![Figure 6: TOF obtained from PuMA simulations (using the effective model in Table 2) and experiments of (a) O and (b) CO scattering from a FiberForm\textsuperscript{®} surface at incident and final angles of 45° at 1623 K.](image)

**VII. Conclusions and Future Work**

PuMA software was used to perform simulations of molecular beam scattering experiments of hyperthermal O striking a FiberForm\textsuperscript{®}, which is a common component of an ablative TPS. X-ray micro-tomography was used to obtain the detailed micro-structure of FiberForm\textsuperscript{®}, which was employed within the PuMA simulations to capture the effect of the complex porous and fibrous geometry. The finite-rate surface chemistry model recently constructed from the molecular beam scattering experiments on vitreous carbon\textsuperscript{21} was applied to each fiber of the FiberForm\textsuperscript{®} material. Comparison between the experimental and PuMA time-of-flight (TOF) distributions of both O and CO at 1623 K.

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showed good agreement. In comparison with the vitreous carbon experiments, the fraction of TD O atoms were significantly higher in the case of FiberForm®. Multiple collisions with the different fibers, resulting from the porous nature of FiberForm® was found to be responsible for the thermalization of the O atoms, while the effect of gas-phase collisions was negligible. In addition, a larger relative CO to O flux is observed for the case of FiberForm® in comparison with vitreous carbon. This was again attributed to the multiple collisions of the O atoms within FiberForm®. The interaction of O atom with the surface can result in the formation of CO with a finite probability, thus increasing the number of surface collisions and resulting in a higher effective CO formation rate.

The details of the micro-structure is crucial in determining the final composition (O/CO) and energy distributions (IS/thermal) of the gas-surface interaction products. The properties of the micro-structure such as porosity and fiber diameter will govern the number of collisions each particle undergoes with the surface before exiting the FiberForm® and thereby the properties of the scattered products. Hence, it is crucial to account for the detailed micro-structure in order to accurately model the gas-surface interactions. However, kinetic-based mesoscale methods, which can capture the microscopic details of FiberForm®, become intractable at the macroscopic scales and cannot be used to describe the flowfield around a spacecraft. Thus, effective surface interaction models which can be employed directly within macroscopic simulation methods like Computational Fluid Dynamics (CFD) and material response codes are necessary.

These effective models must capture the effects of the micro-structure without explicitly modeling them. The effective model reaction mechanisms are assumed to be the same as that of the VC model, as well as the desorption rate constant values. This is a valid approximation since multiple collisions within the microstructure does not fundamentally alter the mechanism of the surface reactions, or the desorption process. Particle-swarm algorithm was used to obtain the rate constants of the gas-surface reactions within the effective model. The effective model thus constructed
provides excellent agreement with the FiberForm® experimental data when modeled with the flat plate. Thus, this effective model can be directly used within the CFD solvers.

This model provides the effective rates at only one single porosity. The properties of the micro-structure varies significantly and non-uniformly as the material ablates. Further, within a single virgin FiberForm® sample there could be considerable variation of the micros-structure properties. Thus, the rate constants within the effective model must also be expressed as a function of the material properties. Future work will involve constructing an effective finite-rate oxidation model for FiberForm® that is a function of the material porosity.

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References