Effect of Silicone Coating on Atomic Oxygen Reactivity with Carbon Fiber Preform and Phenolic Impregnated Carbon Ablator

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Abstract

We have conducted a comparative study on how the presence of the anti-dust CV-1144-0 silicone coating from NuSil Technology LLC affects the atomic oxygen oxidation and ablation of heat shields, specifically phenolic-impregnated carbon ablator (PICA) and its carbon fiber preform substrate, FiberForm. Using an atomic oxygen beam-surface scattering apparatus, we measured the scattered products from the surface of the materials at temperatures from 1000 K to 1800 K. Results showed higher nonreactive vs. reactive scattering flux on coated materials compared to their uncoated counterparts up to 1500 K, around which point the silicon-oxide layer decomposed. Upon the breakdown of the oxide layer, the reactivity of the sample reverted to that of its underlying substrate, either that of FiberForm or charred PICA. In addition, a subtle influence of underlying impurities, specifically calcium, was observed in the oxidation of both PICA and FiberForm. PICA appeared to retain the presence of these impurities after ablation at 1800 K, which was attributed to a shielding effect that the phenolic resin matrix provides to the material. The data should be useful for the development of an improved PICA ablation model.

Keywords

FiberForm
silicone
Phenolic impregnated carbon ablator
Molecular beam
Atomic oxygen
Hypersonic

Abbreviations

PICA: phenolic impregnated carbon ablator
TOF: time-of-flight
IS: impulsive (or inelastic) scattering
TD: thermal desorption
TD_{slow}: thermal desorption at a longer lifetime

1. Introduction

Ablative heat shields such as phenolic impregnated carbon ablator (PICA) and its variants PICA-X and PICA-D are used to protect spacecraft from the extreme heat of atmospheric entry.[1, 2] Composed of a carbon fiber preform substrate and a phenolic resin impregnated as the matrix, PICA and its variants are being used in current NASA missions such as Mars Science Laboratory,[1] Mars 2020,[3] the planned Dragonfly Mission,[2] as well as those of private industry such as SpaceX's Dragon capsule.[1] Accurate modeling of what happens to these materials in various atmospheric entry conditions requires a detailed understanding of how the resin decomposes thermally and how the charred material and the carbon fiber preform substrate reacts with boundary-layer species, most importantly atomic oxygen.[4] The thermal decomposition of the resin has been the subject of several studies by our group,[5, 6] and the oxidation of carbon at high temperatures has received increasing attention recently,[7-10] although less is known about the specific oxidation behavior of carbon fiber preform and char. The addition of a silicone anti-dust coating creates yet another variable that must be considered. Thus, we have conducted a study of silicone-coated and uncoated carbon fiber preform and PICA in order to gain a better understanding of how this coating affects the behavior of the underlying material. Knowing how to predict the material response of these heat shields is essential for reducing uncertainty and designing high-performance, light-weight heat shields for future missions.

A number of previous studies have looked at the material response for different types of model systems. These have primarily involved mass-loss measurements of different types of composites, including matrix-inhibited carbon/carbon composites[11-13], chars[14, 15], and C/SiC composites[16-21]. Our group has conducted molecular beam-surface scattering studies to

probe the molecular-level details of the oxidation of vitreous carbon.[22] Vitreous, or glassy, carbon,[23] has an sp^2 -configuration within a disordered carbon morphology that has been used as a model material for oxidation studies of disordered carbon. The molecular beam-surface scattering technique involving the use of a rotatable quadrupole mass spectrometer allowed us to quantify specific products leaving the surface as well as characterize the gas-surface interaction dynamics. Using this technique, Murray et al.[22, 24] was able to characterize vitreous carbon oxidation in significant detail, the data for which led to the development of three different carbon ablation models[25-27] and furthered our understanding of the mechanisms of carbon oxidation. Our group also undertook O-atom beam scattering experiments with the actual carbon fiber preform substrate used in ablative heat shields, and the results showed remarkable similarities with those of vitreous carbon. As described in Poovathingal et al. (2021),[28] much of the behavior, such as the temperature-dependent flux of O and CO, as well as the angular distributions of scattered products, were similar to the dynamics described in Murray et al. (2015),[22] with the primary difference being that O-atom scattering on carbon fiber preform exhibits stronger characteristics of multiple-bounce scattering on the three-dimensional fiber network. Poovathingal et al. investigated the long residence times of O and CO products that were clear in the data on carbon fiber preform and became noticeable in hindsight on the earlier experiments with vitreous carbon; these “slow” products are also important in the data that are presented herein.

In addition to vitreous carbon, studies were conducted on the atomic oxygen oxidation of silicon carbide (SiC),[29] another material of interest for certain heat shields and of relevance to the present study. SiC has received attention mainly for its potential as a coating or a matrix material within a carbon/SiC composite. This study, using a similar molecular beam-surface scattering technique as was used with vitreous carbon,[22, 24] focused on the O-atom interactions

with an SiC wafer that already had an oxide layer on its surface. This study found the oxide layer to be stable up to a certain temperature, the passive-to-active oxidation transition temperature,[30, 31] at which point the decomposition of the oxide layer was rapid and irreversible and produced gaseous Si and SiO. When the incident O-atom flux was lower, a graphitic layer remained on the SiC surface above the passive-to-active transition and was relatively unreactive to O-atom attack. On the other hand, when the O-atom flux was higher, the graphitic layer did not form and the SiC surface was etched by bombarding O-atoms, leading to roughly equal fluxes of volatile SiO and CO products in the process. The formation and removal of a silicon-oxide layer is highly relevant to the present study which examines how a silicone coating affects the oxidation of the underlying material as it is heated under atomic oxygen attack.

The surface transformation of silicone by atomic oxygen has been investigated in previous studies with respect to its relevance to materials degradation in low-Earth orbit,[32-34] and a companion study was conducted, involving the specific silicones used for ablative heat shields that are relevant to the present study, CV-1144-0, a spray-on, anti-dust coating, and RTV-560, a binding agent.[35] We exposed these materials to extended atomic-oxygen bombardment at room temperature and 300 °C and examined the exposed surface by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). We discovered that O-atom bombardment of both silicones transformed much of the surface layer to SiO₂, leaving behind far less of the original silicone chemical environment. SEM analysis also revealed cracks and fissures that were apparently formed during O-atom bombardment, with bigger cracks observed with more prevalence after the higher temperature bombardment. Nevertheless, using a room-temperature quartz crystal microbalance, we still observed that high-fluence exposure of the CV-1144-0 to O

atoms resulted in negligible mass loss, especially compared to Pyralin, a Kapton-like PMDA-ODA polyimide.[36, 37]

In an effort to understand how a silicone coating might affect the performance of a carbon-phenolic heat shield in an oxidizing atmosphere, we have conducted a comparative study of the atomic oxygen beam-surface scattering dynamics on relevant model samples: pristine carbon fiber preform (also known as FiberForm), FiberForm with a coating of CV-1144-0, pristine PICA, and PICA with a coating of CV-1144-0. Coated PICA is most comparable to the actual heat shield material used on spacecraft designed for atmospheric entry.[4] Based on our previous studies, we expected that the addition of a silicone coating to FiberForm would both depress reactive product formation as well as dramatically increase O-atom scattering from the surface. We further expected that the inevitable decomposition of the oxide coating that was formed would return the temperature-dependent reactivity of the coated FiberForm back to that of uncoated FiberForm. We also aimed to examine the thermal decomposition products from the materials as the sample was pyrolyzed. Our earlier studies of PICA pyrolysis were available to help in the interpretation of new data on silicone-coated PICA. On the other hand, no prior molecular-beam studies have been conducted on any form of carbon-phenolic ablator, so the new experiments undertaken for the present study did not have a clear benchmark. Therefore, we found it helpful to compare the O-atom scattering dynamics on silicone-coated PICA with those on pristine PICA and silicone-coated FiberForm. One additional factor we wanted to study was whether our previous study on FiberForm was reflective of the way in which this material is actually used. In our prior study,[28] FiberForm was first annealed at ~ 1800 K before data collection began, typically at lower temperatures. FiberForm is known to contain impurities such as calcium,[38, 39] which results in different reactivity with atomic oxygen before and after annealing. In addition, it is known that the

presence of metal catalysts can promote the dissociation of O₂ into atomic oxygen, and thus assist in the net reactivity of O₂ with adjacent carbon.[40] Furthermore, it is possible that pristine FiberForm is not completely pyrolyzed to carbon and a residual organic component might be removed upon annealing, also altering the reactivity of the fibers. Our study aims to shed light on all of these factors that might lead to uncertainties in relating the experimental results to material response in actual ablation environments.

2. Materials and Methods

2.1. Molecular Beam-Surface Scattering Apparatus

This study was conducted using a similar molecular beam-surface scattering technique as those involving the oxidation of vitreous carbon[22] and FiberForm.[28] The apparatus was a crossed molecular beams apparatus reconfigured for beam-surface scattering, consisting of a main chamber where the beam-surface scattering was conducted along with a differentially pumped chamber that functioned as the source for the molecular beam. A pulsed molecular beam composed of hyperthermal O and O₂ was directed at the samples at an incident angle of $\theta_i = 45^\circ$ as measured from the normal of the macroscopic surface plane (hereafter referred to as the “surface”). The main chamber vacuum was maintained near $\sim 5 \times 10^{-7}$ Torr with a large cryogenic pump and a large turbomolecular pump while the beam was running, while that of the source chamber varied between ~ 1 and 7×10^{-4} Torr while the pulsed beam was operating. Detection of scattered products was accomplished with a mass spectrometer detector, which rotated in the plane defined by the incident molecular beam axis and the surface normal. The mass spectrometer consisted of an electron impact ionizer[41] with an electron energy of 160 eV, a quadrupole mass filter, and a Daly-type ion counter.[42] The entire detector was triply differentially pumped with three ion

pumps. The electron-impact ionizer was in the lowest-pressure region, which had an additional turbomolecular pump to assist the ion pump in further reduction of residual gases in the ionization region. The Daly detector's pulses, correlated with ion impacts, were recorded by a multichannel scaler that yielded a signal proportional to the scattered product number density as a function of flight time, t , from the surface to the ionizer, a distance of 34.4 cm. These $N(t)$, or time-of-flight (TOF), distributions were used to derive translational energy distributions, $P(E_T)$, of the scattered products with a density-to-flux conversion that assumed a monoenergetic incident beam.[43, 44] Average energies of the scattered products were determined from the translational energy distributions, which were then integrated to obtain the total relative flux of the scattered products at a particular final, or scattering, angle, θ_f . Flux angular distributions were thus obtained by plotting the flux of the scattered products as a function of θ_f .

A 2 Hz laser detonation source, described in a previous study,[45] was used to produce the molecular beam of hyperthermal $O(^3P)$ [46] and $O_2(^3\Sigma_g^-)$. [47] The beam was characterized by directing it into the detector and collecting TOF distributions and using these to derive translational energy distributions and O/O₂ relative fluxes. A velocity-selecting a chopper wheel, with three equally spaced 1.6 mm-thick slots, rotated at a frequency of 300 Hz and was synchronized to the laser detonation pulse. During analysis of the data, the contribution of dissociative ionization of O₂ (to form $O^+ + O$) was subtracted from the TOF distributions collected at a mass-to-charge ratio of 16 (O^+). The mean translational energies of the O and O₂ components of the beam were 487 and 948 kJ mol⁻¹, respectively, and the average mole fractions of O and O₂ were 91.2% and 8.8%, respectively. These conditions remained quite stable throughout the experiments. Plots detailing the specific translational energy distributions and mole fractions are shown in **Figure S1** in the supplementary information.

2.2. Samples and Surface Analysis

Samples of both pristine and coated carbon fiber preform, sourced from Fiber Materials Inc. and branded as FiberForm, were obtained from NASA Ames. Pristine FiberForm was received in a large block, while coated FiberForm was received in 30 x 30 x 5 mm slabs. The coated samples had one box-coat of the anti-dust silicone CV-1144-0 on one side. Box coating is the process by which the coating is sprayed onto the sample. One box-coat typically represents an approximate coating thickness of 100-200 microns. The thickness presumably decreases deeper into the bulk of the fiber network, but it is unknown how deep the silicone penetration was. The silicone, from NuSil Technologies LLC, was composed of 95.2% polydimethylsiloxane chains and 4.8% polydiphenylsiloxane chains.[48] The coating was applied at NASA Ames and allowed to set at room temperature for seven days. To use these samples in our apparatus, we further cut the FiberForm into small units of 7 x 25 x 2 mm, preserving the silicone-coated sides on the FiberForm. In addition, samples of PICA were prepared using a silicone-coated PICA block obtained from NASA Ames. The PICA block was coated on one side with 1.5 box-coats of CV-1144-0. From this block, we cut 7 x 25 x 2 mm slabs from the coated side, as well as slabs opposite from the coated side to serve as samples of uncoated PICA. An initial oxide was prepared on the coated slabs by exposing the coated surfaces to a fluence of $\sim 2.3 \times 10^{20}$ O-atoms cm⁻² using our atomic oxygen molecular beam source chamber with a technique described previously.[49] Before starting the experiments, SEM and XPS analyses were conducted on these samples, with XPS results shown in **Table 1**. In preparation for the experiments, the samples were mounted in our high-temperature sample mount in the source chamber and heated resistively with an external power supply.[6, 22] Temperature was manually measured using a pyrometer with a disappearing carbon filament.[28, 50]

Table 1. Chemical compositions of the macroscopic surfaces of the listed sample materials before and after annealing at 1800 K. “In-beam” refers to the sample surface location where the beam impinged. “Out-of-beam” refers to a position away from beam spot. For all other annealed samples, XPS data were collected at the beam impingement spot.

	Material	C	O	Si	Ca	F
(a)	Pristine FiberForm	96.3	3.4		0.8	
(b)	Annealed FiberForm: In-beam	98.8	1.2			
(c)	Annealed FiberForm: Out-of-beam	100				
(d)	Coated FiberForm	38.4	46.1	15.5		
(e)	Annealed Coated FiberForm	96.9	3.1			
(f)	Uncoated PICA	86.2	13.8			
(g)	Annealed PICA	96	2.6			1.4
(h)	Coated PICA	18.2	58.2	22.8	0.8	
(i)	Annealed Coated PICA	92.8	5.2	1.3	0.7	

2.3. Primary Experimental Procedure

Before conducting detailed experiments, the effect of annealing to 1800 K under high vacuum ($\sim 5 \times 10^{-7}$ Torr) for 30 minutes on samples of uncoated and coated FiberForm was first examined. Afterwards, SEM analysis was conducted on the annealed samples (**Fig. 1**). The primary O-atom beam-surface scattering experiments were conducted on each of the following samples following a specific protocol. First, thermal decomposition products from the FiberForm, PICA, coated FiberForm, and coated PICA samples were monitored with the mass spectrometer as they were heated, in high vacuum, from room temperature at a rate of $0.5 \text{ }^{\circ}\text{C s}^{-1}$, up to a relatively high temperature, typically 1000 K. With coated FiberForm, two experiments were conducted, one in which the initial high temperature was 1000 K and the second in which the initial high temperature was 1600 K. For convenience, the coated FiberForm initially raised to 1000 K will be referred to as coated FiberForm_A, and the coated FiberForm initially raised to 1600 K as coated FiberForm_B. During this initial temperature ramp, the detection (or final) angle was $\theta_f = 5^{\circ}$ from the normal to the macroscopic sample plane facing toward the detector, which will be referred to

as the sample “surface” while recognizing that the three-dimensional fiber network of the sample actually presents many microscopic surfaces, and mass spectra were collected with a scan range of $m/z = 0.1$ to 110 amu and a collection time for each mass spectrum of 11.01 s. A background mass spectrum was collected before the temperature ramp and subtracted from the mass spectra collected during heating. Integrated intensities for each peak were analyzed in OriginPro 2021. After reaching the initial high temperature (1000 K or 1600 K), each sample was held at this temperature for two hours before further experimentation commenced with the hyperthermal O/O₂.

Fig. 1. Pairs of SEM images of eight samples, recorded at two magnifications. (a) Pristine FiberForm that was neither heated nor exposed to the O-atom beam. (b) Uncoated FiberForm that was heated (annealed) to 1800 K in vacuum, in the absence of exposure from the O-atom beam. (c) Coated FiberForm that was neither heated nor exposed to the O-atom beam. (d) Coated FiberForm that was heated to 1800 K in vacuum, in the absence of exposure from the O-atom beam. (e) Pristine uncoated PICA that was neither heated nor exposed to the O-atom beam. (f) Uncoated PICA that was heated to 1800 K in vacuum and simultaneously exposed to the O-atom beam. (g) Coated PICA that was neither heated nor exposed to the O-atom beam. (h) Coated PICA that was heated to 1800 K in vacuum and simultaneously exposed to the O-atom beam.

The sample was then adjusted such that the incident O-atom beam (technically “O/O₂ beam” because of the minor component of O₂) was directed at the sample with an incident angle of $\theta_i = 45^\circ$ with respect to the macroscopic surface normal, and TOF distributions were then collected with various final angles, θ_f , also with respect to the surface normal but on the opposite side of the normal from the angle of the incident beam, θ_i . TOF distributions were collected for $m/z = 16(\text{O}^+)$, $32(\text{O}_2^+)$, $28(\text{CO}^+, \text{Si}^+)$, and $44(\text{CO}_2^+, \text{SiO}^+)$ from $\theta_f = 5^\circ$ to 85° in 5° increments. These TOF distributions were collected by systematically varying the final angle, where θ_f was first increased from 5° to 85° and then decreased from 85° to 5° . This procedure was conducted such that, for each m/z ratio at each θ_f , TOF distributions were collected twice, and these two distributions were added together during analysis of the data. Possible products at $m/z = 17(\text{OH}^+)$ and $60(\text{SiO}_2^+)$ were also investigated, but signals at these m/z ratios were weak or non-existent, so further investigation of these signals was not conducted. From FiberForm, TOF distributions were collected at each θ_f for a total of 17,000 beam pulses at all observed m/z ratios. From coated FiberForm_A, TOF distributions were collected for a total of 17,000 pulses for $m/z = 16$ and 32 and 34,000 pulses for $m/z = 28$ and 44 . From coated FiberForm_B, TOF distributions were collected for a total of 17,000 pulses for $m/z = 16$, 32 , and 28 , and 34,000 pulses for $m/z = 44$. From uncoated PICA, TOF distributions were collected for a total of 17,000 pulses for all m/z ratios. Finally, from coated PICA, TOF distributions were collected for a total of 17,000 pulses for $m/z = 16$ and 32 , and 34,000 for $m/z = 28$.

After TOF distributions were collected for all final angles at the initial high sample temperature, the detection angle was adjusted to $\theta_f = 45^\circ$ (with θ_i remaining at 45°), and a study of the temperature dependence of volatile product evolution was conducted. For all samples, this

temperature-dependent data collection began at 1000 K. Given that the relevant data had already been collected at 1000 K for all samples except coated FiberForm_B, the temperature of these samples was incremented to 1100 K. As for FiberForm_B, the temperature was lowered from 1600 K to 1000 K. The temperature for all samples was raised in 100 K increments to 1800 K and then decreased in 100 K increments back to 1000 K. At each temperature increment, TOF distributions were collected at $m/z = 16, 32, 28,$ and 44 . From the uncoated FiberForm, coated FiberForm_A, and uncoated PICA, individual TOF distributions were collected for 500 beam pulses at each m/z ratio at each temperature. From the coated FiberForm_B, individual TOF distributions were collected for 500 pulses at $m/z = 16, 32,$ and $28,$ and for 1000 pulses for $m/z = 44$. From coated PICA, individual TOF distributions were collected for 500 pulses at $m/z = 16$ and 32 and for 1000 pulses at $m/z = 28$ and 44 .

Finally, after the temperature-dependent data collection had been completed, TOF distributions were again collected at 1000 K over a range of final angles ($\theta_f = 5^\circ$ to 75°), except the final angle was incremented by 10° and data were collected for only one sweep of increasing angles. This second collection of angular distribution data at 1000 K was conducted for both coated FiberForm samples and both PICA samples, while different angular-dependent data were collected with the uncoated FiberForm sample (*vide infra*). From coated FiberForm_A and coated PICA, TOF distributions were accumulated for a total of 4000 pulses for $m/z = 16$ and 32 and 8000 pulses for $m/z = 28$ and 44 , while from coated FiberForm_B, TOF distributions were collected for a total of 4000 pulses for $m/z = 16, 32,$ and $28,$ and 8000 pulses for $m/z = 44$. From uncoated PICA, TOF distributions were accumulated for a total of 8000 pulses for $m/z = 16$ and 4000 pulses for $m/z = 32, 28,$ and 44 . After the temperature-dependent data collection with the uncoated FiberForm sample had been completed and the sample was at a temperature of 1000 K, the temperature was

raised again to 1600 K at which point additional TOF distributions were collected with two groups of increasing and decreasing final angles, over the angular range $\theta_f = 5^\circ$ to 85° , in 5° increments. At this temperature, no signal at $m/z = 44$ was observed, so TOF distributions were only collected at $m/z = 16, 32$, and 28 . For each m/z ratio, TOF distributions were collected for a total of 17,000 pulses. After the completion of all experiments with each sample, the sample temperature was returned to room temperature while in high vacuum, and then the sample was removed to the atmosphere. XPS and SEM analyses were conducted on the exposed faces of each of the five samples. For the purposes of discussion in the present study, angular distribution data collected at the initial high temperature will be labeled with an “up arrow” (e.g., 1000 K $\uparrow$), and angular distribution data collected at the same temperature after the collection of all the temperature-dependent data will be labeled with a “down arrow” (e.g., 1000 K $\downarrow$).

2.4. O₂ Reactivity and Effects of Pre-Heating

To investigate whether pre-heating (i.e., “annealing”) to 1800 K affected the reactivity of the FiberForm, additional experiments were conducted with samples of pristine uncoated FiberForm. Temperature-dependent data were first collected, with $\theta_i = \theta_f = 45^\circ$, as the temperature was raised and lowered from 1000 K to 1800 K in 100 K increments in two groups, while TOF distributions were collected for each temperature at $m/z = 16, 32, 28$, and 44 , collected for 500, 500, 1000, and 500 pulses, respectively, of the hyperthermal O/O₂ beam. Differences in the TOF distributions collected as the temperature increased compared to those as the temperature decreased provided insight into the changes in reactivity of the FiberForm induced by heating to 1800 K. Next, O₂ reactivity on FiberForm was investigated by collecting analogous temperature-dependent data from a pristine FiberForm sample. Instead of using the hyperthermal O/O₂ beam,

the pulsed O₂ beam that exited the source without laser detonation was used instead, in which case the chopper wheel passed a portion of the thermal O₂ beam similar to what it passed with residual thermal O₂ in the beam pulse with laser detonation. The sample temperature was increased in 100 K increments from 1000 K up to 1800 K while TOF distributions were collected for each temperature at $m/z = 16, 32, 28,$ and 44 , with the same collection times used when the laser-detonation source was operating. After a sample temperature of 1800 K was reached, data collection continued as the sample temperature was dropped immediately to 1400 K.

3. Results and Analysis

3.1. Thermal Decomposition of FiberForm, PICA, Coated FiberForm, and Coated PICA

Thermal decomposition products observed while the temperature increased to 1000 K could be observed from all four sample types (**Figs. S2 to S5**). Uncoated FiberForm released few gas-phase products (**Fig. S2**), with products having dominant mass-to-charge ratios appearing at $m/z = 1, 2, 18,$ and 44 being released in significant quantities. Higher-mass products were observed in the vicinity of 400 K, but their signals were very small. The pyrolysis of coated FiberForm_A released many more products, especially above 600 K (**Fig. S3**). The major product released had a dominant mass-to-charge ratio at $m/z = 73$. Smaller peaks were also observed. The settings on the mass spectrometer were optimized for the detection of weak signals from molecular beam scattering, so saturation was observed in the strong signals from pyrolysis gases. Saturation was also observed in the pyrolysis gas signals from both of the PICA samples (**Figs. S4 and S5**). Nevertheless, it was clear that significant decomposition began below 400 K and the release rate of PICA-exclusive pyrolysis products slowed down around 950 K.[5, 6] Despite the saturation in the signals, it could be observed that the primary differences in product release between coated

and uncoated PICA were in the m/z ratios for the silicone decomposition. There was a significant increase in products at $m/z = 73(\text{SiOCH}_2\text{CH}_3^+)$ from the coated PICA, as well as residual products observed above 800 K for $m/z = 15(\text{CH}_3^+)$, $16(\text{CH}_4^+, \text{O}^+)$, $74(\text{SiOCH}_3\text{CH}_3^+)$, and $75(\text{SiOHCH}_3\text{CH}_3^+)$. Considerable release of low-mass products with m/z near 1 was also observed from all five decomposition trials. The mass spectrometer was not optimized to resolve such low-mass products, however, and based on the observed pyrolysis behavior and the similarity to an earlier detailed study of PICA pyrolysis in our laboratory,[5] this peak was assigned to H_2 . Because of the lower quality of the low-mass data with the mass spectrometer settings used, further analysis of the signal in that region was not conducted, although the possible production of H atoms would be interesting to investigate in the future.

Thermal decomposition products were also observed from the pyrolysis of coated FiberForm_B (**Fig. S6(a)**) that was raised to 1600 K. Compared to the decomposition of FiberForm_A, there appeared to be a lower intensity of pyrolysis products from FiberForm_B. A closer examination of the mass spectra above 1000 K showed the intensities of products for $m/z = 15, 16, 59, 73, 74$, and 75 continuing to decrease slowly as the temperature climbed to 1600 K (**Fig. 2(a)**). Around 1200 K, the signals of the other species began to increase again, with $m/z = 28$ and 44 peaking above 1400 K before decreasing again (**Fig. 2(b)**). The signal of $m/z = 39$ disappeared around 1400 K while the signal at $m/z = 40$ began to increase around that temperature. In order to identify the signals at $m/z = 28$ and 44 , the intensities of $m/z = 44, 45$, and 46 , as well as $m/z = 28, 29$, and 30 , were measured, and their percent compositions out of the total intensities of each group at each temperature from 1200 to 1600 K were calculated. These percent compositions were then compared to the natural isotopic abundances of silicon (92.2:4.7:3.1 for $m/z = 28:29:30$) to determine how much of the signal at either $m/z = 28$ or 44 consists of Si or SiO.

As **Fig. 2(c)** shows, the curves reflecting their isotopic percentages appeared to converge and level out between 1300 K to 1400 K. Within this level region, the ratios of $m/z = 44:45:46$ on average were 92.6:4.9:2.5, while above 1450 K the curves appeared to diverge, with $m/z = 44$ increasing and both $m/z = 45$ and 46 decreasing. Compared to the natural isotopic abundance of silicon, these values are very similar, suggesting that nearly all the $m/z = 44$ signal within the 1300 to 1400 K region was SiO, while outside that region CO₂ might constitute a larger proportion. As for the signal for $m/z = 28, 29$, and 30 (**Fig. 2(d)**), the curves for each species appeared to be linear, with divergence between $m/z = 28$ and $m/z = 29, 30$ up to 1470 K, at which point $m/z = 29$ and 30 could not be detected anymore. At 1200 K, where the proportions of $m/z = 29$ and 30 are at their highest, the ratios of $m/z = 28:29:30$ are 98.7:0.8:0.4, which suggests that most of the $m/z = 28$ signal was CO rather than silicon. Isotopic percentages were also calculated for $m/z = 73, 74$, and 75 (**Fig. S6(b)**), but these values do not show any discernible pattern.

Fig. 2. Results from mass spectra of products released from coated FiberForm as it was heated from 1200 K to 1600 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Integrated intensities of peaks corresponding to specific m/z ratios, as shown, as a function of sample temperature. **(c)** Intensities of signals detected at $m/z = 44, 45$, and 46 , represented as percentages of the total signal at these three m/z ratios, as a function of sample temperature. **(d)** Intensities of signals detected at $m/z = 28, 29$, and 30 , represented as percentages of the total signal at these three m/z ratios, as a function of sample temperature.

Additional samples of FiberForm and coated FiberForm that were pyrolyzed and annealed up to 1800 K for 30 minutes before being returned to room temperature showed noticeable changes from their pristine counterparts. Images from SEM analysis of the annealed samples are shown in **Fig. 1(b, d)** and **Fig. S7**. The general fiber orientations for both coated and uncoated FiberForm appeared to be random. In the FiberForm oxidation study by Poovathingal et al. (2021),[50] they were able to identify the orientation of the FiberForm pressing plane, but no discernible orientation could be ascertained from SEM images of the samples in this study. At lower resolution, no obvious differences could be discerned between coated and uncoated FiberForm. At a higher

resolution, damage on the individual fibers could be observed, with pits of ~ 100 nm diameter forming on both sample types. Far more extensive damage was observed on the coated FiberForm, with large fractures forming on the individual fibers. Compared to the pristine uncoated FiberForm, the coated samples showed significant surface changes after annealing.

3.2. Gas-Surface Scattering and Analysis

Products could be observed leaving the sample surface at $m/z = 16, 32, 28,$ and 44 , corresponding either to no net reaction in the cases of O and O₂ ($m/z = 16$ and 32), or reaction in the cases of CO and CO₂ ($m/z = 28$ and 44 , respectively). The TOF distributions of scattered products are typically described in terms of two limiting mechanisms: impulsive scattering (IS) and thermal desorption (TD).[22, 24, 51] IS products are the result of scattering trajectories that involve one or a few collisions with the surface and transfer very little energy before the product exits the surface on a time scale too short for equilibrium to be established. In a TOF distribution, IS products appear at short flight times. TD products, in contrast, are the result of significant gas-surface interactions that allow thermal equilibrium to be established before products desorb in thermal equilibrium with a surface. TD products often exit a surface with a Maxwell-Boltzmann (MB) distribution of translational energies given by the surface temperature, although the details of the translational energy distribution depend on the exact nature of the atom- or molecule-surface interaction potential. In addition to the TD mechanism, a second thermal desorption signal was observed in most of the TOF distributions for $m/z = 16, 28,$ and 44 , which was designated as TD_{slow}. An analogous TD_{slow} signal was previously observed in studies on vitreous carbon and FiberForm by Murray et al.[22] and Poovathingal et al.,[28] respectively. This corresponds to the signal at longer flight times in the TOF distribution that suggests a slow reaction or residence time on the surface of tens of microseconds or greater before desorption. The TD component was fit by

assuming that the TD products exited the surface in a MB distribution of translational energies, and for the TD_{slow} component we assumed a convolution of a MB distribution and a 1st-order exponential decay function. The IS component was assumed to be the remaining signal after subtracting the TD + TD_{slow} components from the overall TOF distribution. **Fig. 3** shows representative fits for different TOF distributions. Each component of a TOF distribution may be integrated appropriately to obtain flux, according to the relationship between number density and flux, $I = \sum_j N(t_j)/t_j$, where I is integrated flux, t is flight time, and the distribution of number densities as a function of flight time, $N(t)$, is the TOF distribution. A plot of the flux products at different final angles, θ_f , from the normal (referred to as a “flux angular distribution” or, more simply, “angular distribution”) may thus be derived from TOF distributions collected at different θ_f angles. IS products have no expected angular distribution, but TD products often have angular distributions that may be described by a cosine power distribution, $\cos^x(\theta)$, with x being a real positive value. A flux angular distribution of TD_{slow} products has no expected functional form, and a more rigorous fit for these distributions was not attempted. For the TOF distributions for all species except $m/z = 32$, the IS, TD, and TD_{slow} components could all be fit. For the TOF distributions at $m/z = 32$, only the IS and TD components could be fit. However, the IS signals at $m/z = 28$ and 44 tended to be negligible, so IS was excluded from the flux of the products determined from TOF distributions at these m/z ratios. Background signals for each TOF distribution were also quantified. Before the TOF distribution can be analyzed, the raw signal must be corrected to subtract background and to shift the flight times such that time zero reflects the moment the incident beam pulse strikes the surface, and, for prompt product desorption, the moment when the product leaves the surface. Thus, from a given raw TOF distribution, the

background was quantified by averaging the intensity of the first 300 μs of the distribution before time zero. This measurement thus reflected the steady-state background of a particular species in the region of the electron-impact ionizer (**Fig. 3(d)**).

Fig. 3. Examples of fits of scattering components to TOF distributions. **(a)** O at $\theta_f = 5^\circ$, $T_s = 1600$ K from coated FiberForm_B; **(b)** CO at $\theta_f = 5^\circ$, $T_s = 1600$ K from uncoated FiberForm; **(c)** O at $\theta_f = 5^\circ$, $T_s = 1000$ K from coated FiberForm_A. Yellow symbols in (a), (b), and (c) represent total relative number density with background subtracted. Red lines represent Maxwell-Boltzmann (MB) distributions at the relevant temperature (TD). Green lines represent the convolution of a 1st-order decay with a MB distribution (TD_{slow}). Blue lines represent signal remaining after red and green lines are subtracted from the total signal (IS). No TD_{slow} fit was needed for **(c)**. **(d)** Example of a TOF distribution that has not been corrected for background or the delay from the pulsed valve trigger to the time the O/O₂ pulse struck the surface. The red rectangle indicates the range of flight times used to determine the average background signal. The dashed line shows the time at which the peak of the O/O₂ pulse struck the surface (i.e., “time zero”). The abbreviation, A.U., indicates arbitrary units.

3.3. Temperature-Dependent Flux and Angular Distributions from Uncoated FiberForm

Product TOF distributions and associated fluxes from uncoated FiberForm as a function of temperature are shown in **Fig. 4** for O and CO and in **Fig. S8** for O₂ and CO₂. The total flux for each species, as shown in **Fig. 4(a)**, was corrected for the mass-dependent detection sensitivity of the mass spectrometer. The shapes of the TOF distributions did not exhibit any significant changes

or shifts with temperature. Their background intensities at each temperature are shown in **Fig. S9**. The fluxes for O and CO increased monotonically with temperature from 1100 K, and a clear hysteresis for both species was observed depending on whether the temperature was increasing or decreasing, with O flux being higher at each temperature as temperature decreased, and CO flux being generally higher as temperature increased. The temperature-dependent behavior of the O flux was the result of the substantial TD component (**Fig. 4(b)**), as the IS O-atom flux stayed relatively small and constant throughout the experiment. Although earlier results from our group showed a consistently higher flux of CO for increasing temperatures than decreasing temperatures, this trend was not observed here. In the range of 1300 K to 1400 K, the TD CO flux at increasing temperatures was lower than that when the temperature was decreasing. Given the nearly identical TD_{slow} CO flux (**Fig. 4(c)**) for both increasing and decreasing temperatures, the deviation from earlier observations of hysteresis in the CO product flux must be attributable to the TD CO flux from 1300 to 1500 K. The flux of O₂ was relatively constant with temperature in comparison to the O and CO flux, and this lack of change was reflected as well when considering its IS and TD fluxes individually (**Fig. S8**). CO₂ only had appreciable flux at the lower temperatures investigated, 1000 K and 1100 K, and became negligible above 1100 K. The background signals of all the products did not change substantially with temperature (**Fig. S9**). The background signals of both O and O₂ decreased slightly as temperature increased. The background signal of CO increased at 1200 K as temperature increased, peaking at 1400 K before dropping to its initial, low-temperature, level at 1700 K. On the other hand, as the sample temperature decreased from 1800 K to 1000 K, the CO background intensity remained essentially constant. Finally, the background signal of CO₂ was only elevated at 1000 K as temperature increased and remained relatively constant for the remainder of the experiment. Except for the initial signal at 1000 K, the CO₂ signal almost

certainly reflects residual CO₂ in the detector and was unrelated to the experiment. The presence of some change in the background signals from uncoated FiberForm, most notably that of CO, may be indicative of continued thermal decomposition as the FiberForm temperature increased from 1000 K to 1800 K.

Fig. 4. Fluxes and TOF product distributions from uncoated FiberForm. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. **(a)** Total flux as a function of temperature from $T_s = 1000$ to 1800 K for $m/z = 16, 32, 28$, and 44 products. TOF distributions as a function of temperature, increasing to 1800 K, then decreasing to 1000 K, for **(b)** O and **(d)** CO. Fluxes separated into their IS (O only), TD, and TD_{slow} components shown in **(c)** and **(e)** for O and CO, respectively. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached.

Flux angular distributions collected from uncoated FiberForm at 1000 K and 1600 K are shown in **Fig. 5**. At 1000 K, signal could be detected at $m/z = 16, 32, 28$, and 44 , corresponding to O, O₂, CO, and CO₂, whereas the signal from CO₂ was absent at 1600 K. The O-atom distribution at 1000 K was separated into IS, TD, and TD_{slow} components. Here, the overall IS O flux calculated from the sum of the IS O fluxes from all measured angles was much larger than the overall TD O flux, and its angular distribution had a somewhat lobular shape. The overall TD_{slow} O flux was less than half that of the overall TD O flux. The distribution of O₂ at 1000 K only exhibited IS and TD components. The shape of the IS O₂ angular distribution was roughly equivalent to that of the shape of the TD O₂ angular distribution, with similar overall signals as well. The distributions of both CO and CO₂ at 1000 K were separated into TD and TD_{slow} components. The overall TD_{slow} CO flux was, less than half that of the overall TD CO signal, while the overall TD_{slow} CO₂ flux was less than one fourth that of its overall TD flux. At 1600 K, the O-atom distribution was separated into IS, TD, and TD_{slow} components. The IS O angular distribution was broader than that at 1000 K. In addition, the overall IS O flux at 1600 K was about one fifth that of the overall TD O flux at this temperature. The overall TD_{slow} O flux was very small at 1600 K, being only about one fourth that of the overall IS O-atom flux. The overall IS O₂ flux at 1600 K was slightly smaller than that of the overall TD O₂ flux. The CO distribution at 1600 K was separated into TD and TD_{slow} components. The overall TD_{slow} CO flux was only about one seventh that of the overall TD CO flux.

Fig. 5. Flux angular distributions of O, O₂, CO, and CO₂ (1000 K only) products from uncoated FiberForm at $T_s = 1000$ K (left) and $T_s = 1600$ K (right). Red points represent total flux for a particular product. Yellow symbols (O and O₂ only) represent IS flux. Blue symbols represent TD flux. Green symbols (O, CO, and CO₂ only) represent TD_{slow} flux. Dashed lines show cosine power fits for each product's TD distribution. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer.

Images from the SEM analysis of uncoated FiberForm after the experiment with the hyperthermal O/O₂ beam revealed small pits on the individual fibers (**Fig. S10**). This pitting phenomenon was present both in the areas where the FiberForm was exposed and unexposed to the beam. This pitting resembled that of uncoated FiberForm annealed without exposure to the O-atom beam (**Fig. 1(b)**). In addition, XPS analysis of the impact spot (**Table 1(b)**) revealed nearly complete carbon coverage along with a minute fraction of oxygen. XPS analysis of the out-of-beam area revealed only the presence of carbon, with no other elements detected (**Table 1(c)**). Unlike what was observed on pristine uncoated FiberForm (**Table 1(a)**), in both the in-beam and out-of-beam areas of uncoated FiberForm, calcium was not detected.

3.4. O₂ Reactivity on Uncoated FiberForm

Results from the uncoated FiberForm, which was subjected to two cycles of heating with exposure from the hyperthermal O/O₂ beam, with one cycle representative of raising the temperature from 1000 K to 1800 K then back to 1000 K, revealed unusual changes that appeared to be the result of heating the sample initially to 1800 K during the first half cycle. TOF distributions of CO collected at 1300 and 1400 K showed subtle but distinct peaks at a flight times near 3 ms, as shown in **Fig. 6(a)**. This peak disappeared as the sample temperature reached 1500 K and did not appear again for the remainder of the heating cycles. The total flux of CO as a function of temperature also changed after the first heating cycle. For the first heating cycle, the CO flux during the increasing temperature ramp was higher than that during the decreasing temperature ramp at temperatures from 1000 K to 1300 K, whereas for the second heating cycle, the CO flux during the increasing temperature ramp was consistently higher than that during the decreasing temperature ramp, consistent with what was observed in an earlier experiment from our lab. Data collected at the other m/z ratios revealed no significant differences in temperature-

dependent reactivity for the two heating cycles. Examination of the TOF distributions during hyperthermal O/O₂ beam bombardment of the samples of coated FiberForm, uncoated PICA, and coated PICA, also revealed the presence of ~3 ms peaks in their CO TOF distributions (not shown). From coated FiberForm_A, this peak was observed at 1500 K↑ and 1600 K↑. From uncoated PICA, this peak was observed in the CO TOF distributions as temperature increased from 1300 K to 1800 K, and it were still present as temperature was decreased to 1300 K, though it disappeared at 1200 K. From coated PICA, this peak appeared as the temperature increased to 1600 K and did not disappear until the temperature was decreased to 1200 K. In addition, from coated PICA the 3 ms signal was also present in the SiO TOF distributions as the temperature increased to 1700 K, and it did not disappear until the temperature decreased to 1600 K. We hypothesized that a thermal O₂ component in the molecular beam might be giving rise to reactive signals at long flight times; thus, we directed a pulsed thermal beam of pure O₂ at the uncoated FiberForm and investigated the reactive CO signals as a function of sample temperature. The CO TOF distributions collected during bombardment by the thermal O₂ beam are shown in **Fig. 6(c)**. 3 ms peaks were observed on the TOF distributions at 1300 K and 1400 K, and they disappeared as the temperature reached 1500 K. Furthermore, after the sample temperature had been taken to 1800 K, the peak did not reappear when the temperature was reduced to 1400 K (**Fig. S11(c)**). These results with the O₂ beam suggest that the 3 ms peaks observed during the experiments with the hyperthermal O/O₂ beam were caused by reactions of O₂ and not O.

Fig. 6. Results from experiment that investigated O_2 reactivity. **(a)** TOF distributions for CO from uncoated FiberForm bombarded by the hyperthermal O/O_2 beam at 1400 K, with background unsubtracted and flight time plotted to 5,000 μs . Top represents first round of annealing to $T_s = 1800$ K, while bottom represents second round of annealing to the same temperature. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached. **(b)** CO flux during first round of annealing (top) and during the second round of annealing (bottom). Solid symbols correspond to increasing temperature ramp. Open symbols correspond to decreasing temperature ramp. **(c)** TOF distributions for CO as the sample temperature was increased from $T_s = 1000$ to 1800 K and then dropped directly to 1400 K, during bombardment of the sample by a thermal beam of pure O_2 .

3.5. Temperature-Dependent Flux and Angular Distributions from Coated

FiberForm_A

Product TOF distributions for O and CO from coated FiberForm_A as a function of sample temperature are shown in **Fig. 7**; **Fig. S12** shows the analogous distributions for O_2 and products detected at $m/z = 44$. The fluxes, shown in **Fig. 7(a, c, e)**, have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. As seen in Fig. 7(a), the total O-atom flux stayed roughly constant from 1000 to 1300 K and then dropped dramatically between 1300 and 1500 K before increasing as the temperature increased further. The TOF distributions, Fig. 7(b), and corresponding flux distributions separated into various scattering types, Fig. 7(c), provide insight into the nature of the scattering as the temperature was increased and then decreased. As the temperature increased from 1000 to 1400 K, most of the O-atoms exited the sample through the IS channel, with the TD O-atom flux constituting less than half that of the IS O-atom flux. As

the temperature reached 1500 K, the ratio of the IS O-atom signal to that of the TD O-atom signal decreased significantly, and at temperatures above 1600 K, further increases in the O-atom signal came from the TD component. As the temperature decreased from 1800 K, the total O-atom flux also monotonically decreased, with the trend resembling that of the temperature-dependent O-atom flux from uncoated FiberForm. The CO flux also exhibited significant differences when the temperature was increased and then decreased. Very little CO signal was observed until the temperature reached 1500 K, at which point the flux began increasing. This lower-temperature suppression of the CO flux was observed for both its TD and TD_{slow} channels. As the temperature decreased from 1800 K, the total CO flux also monotonically decreased, with the trend resembling that of the temperature-dependent CO flux from uncoated FiberForm. The trends of the individual TD and TD_{slow} CO fluxes as the temperature decreased also resembled those of uncoated FiberForm. The temperature-dependent O₂ flux (**Fig. S12(b)**) remained relatively constant throughout the entire experiment compared to the fluxes of O and CO. There was a slightly more pronounced hysteresis in the TD O₂ flux from coated FiberForm_A (**Fig. S12**) compared to that from uncoated FiberForm (**Fig. S8**). For products from $m/z = 44$, very little flux (likely from CO₂) was observed at 1000 and 1100 K, remaining negligible until higher temperatures were reached. As the temperature increased to 1600 K, a small but significant increase in flux was observed that probably originated from SiO rather than CO₂. As the temperature decreased, the change in the $m/z = 44$ flux resembled the change in CO₂ flux from uncoated FiberForm as it decreased in temperature. The background signals of $m/z = 16$, 28, and 44 (**Fig. S13**) reflected the continuing changes as the temperature increased, representing continued thermal desorption of products such as O-atoms, CO, and SiO and/or CO₂, respectively. These background signals increased at 1200 K, peaked at 1300 K, and then gradually decreased as the temperature reached 1800 K. There was

also a minor increase in the background signal for $m/z = 44$ at 1600 K. The $m/z = 32$ (O_2) background signal remained relatively constant throughout the experiment.

Fig. 7. Fluxes and TOF product distributions from coated FiberForm_A. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. (a) Total flux as a function of temperature from $T_s = 1000$ to 1800 K for $m/z = 16, 32, 28$, and 44 products. TOF distributions as a function of temperature, increasing to 1800 K, then decreasing to 1000 K, for (b) O and (d) CO. Fluxes separated into their IS (O only), TD, and TD_{slow} components shown in (c) and (e) for O and CO, respectively. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached.

Flux angular distributions of products from coated FiberForm_A collected at 1000 K $\uparrow$ are shown in **Fig. 8(left)**. Signal could be detected for O-atoms, O₂, CO, and CO₂. The O-atom distribution was only separated into IS and TD components, as no TD_{slow} component was observed. The overall IS O-atom signal from the sum of the IS O fluxes at all measured angles was much larger than the overall TD O-atom signal, and its angular distribution had a relatively broad shape. The O₂ distribution was separated into IS and TD components, with the overall IS O₂ signal slightly greater than the overall TD O₂ signal, and their angular distributions were roughly equivalent in shape. The CO distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO flux around half that of the overall TD CO flux. Finally, the CO₂ distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO₂ flux being less than half that of the overall TD CO₂ flux. Flux angular distributions collected at 1000 K $\downarrow$ for O, O₂, CO, and CO₂ are shown in **Fig. 8(right)**. The O-atom distribution was separated into IS, TD, and TD_{slow} components, with the overall IS O-atom flux slightly greater than the overall TD O-atom flux, while the overall TD_{slow} O-atom flux was about 1/5 that of the overall TD O-atom flux. The IS O-atom angular distribution had a somewhat lobular shape, similar to the IS O-atom angular distribution from uncoated FiberForm at 1000 K. The O₂ distribution was only separated into IS and TD components, with the overall IS O₂ flux being half that of the overall TD O₂ flux. The IS O₂ angular distribution also had a slightly lobular shape. The CO distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO flux being less than half that of the overall TD CO flux. The CO₂ distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO₂ flux being about 1/6 that of the overall TD CO₂ flux.

Fig. 8. Flux angular distributions of O, O₂, CO, and CO₂ products from coated FiberForm_A at $T_s = 1000\text{ K}\uparrow$ (left) and $1000\text{ K}\downarrow$ (right), with arrows representing whether temperature had been increasing or decreasing before angular distributions were collected. Red symbols represent total flux for a particular product. Yellow symbols (O and O₂ only) represent IS flux. Blue symbols represent TD flux. Green symbols (O, CO, and CO₂ only) represent TD_{slow} flux. Dashed lines show cosine power fits for each product's TD distribution. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer.

3.6. Temperature-Dependent Flux and Angular Distributions from Coated

FiberForm_B

Product TOF distributions from coated FiberForm_B as a function of the temperature are shown in **Fig. 9** for O and CO and in **Fig. S14** for O₂ and products observed at $m/z = 44$. Again, the fluxes have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. The shapes of the TOF distributions of all the species remained consistent as the temperature changed. The O and CO TOF distributions had the same shapes for a given temperature regardless of whether the temperature was increasing or decreasing, and the temperature-dependent fluxes resembled those obtained with uncoated FiberForm. The IS O-atom flux remained essentially constant while the TD O-atom flux increased monotonically (**Fig. 9(c)**). The TD_{slow} O-atom flux also started increasing around 1300 K. Compared to that from uncoated FiberForm, the TD_{slow} O-atom flux from FiberForm_B was higher compared to the IS O-atom flux. Unlike the CO flux from uncoated FiberForm, the CO flux from coated FiberForm_B did not exhibit a decrease as temperature reached 1400 K, with the trend being similar to that of the CO flux from uncoated FiberForm that was pre-heated to 1800 K (**Fig. 6(b)**). The TD and TD_{slow} CO fluxes diverged above 1500 K, with the TD CO flux continuing to increase as the temperature reached 1800 K, while TD_{slow} CO flux decreased within this range. From 1000 to 1500 K, the TD and TD_{slow} CO fluxes were much closer to each other from this material than from uncoated FiberForm. Temperature-dependent hystereses were observed in the O and CO fluxes, with higher O and lower CO flux observed as the temperature decreased. The O₂ flux remained relatively constant throughout the entire experiment, and this was reflected in both its IS and TD components (**Fig. S14**). The behavior of the products observed at $m/z = 44$ was similar to the change in the flux

of $m/z = 44$ products from coated FiberForm_A, with products observed at lower temperatures while the temperature was increasing and decreasing, and products only observed at higher temperatures while the temperature was increasing. The background signals of the four species detected from coated FiberForm_B (**Fig. S15**) were similar to those from uncoated FiberForm, with O and O₂ background signals decreasing as the temperature increased. Small increases in $m/z = 28$ and 44 background signals at 1700 K were observed, corresponding to CO and Si, and CO₂ and SiO, respectively. The relative lack of change in the background signal observed from FiberForm_B suggests that most of the organic component of the sample had been thermally decomposed by the time this experiment began.

Fig. 9. Fluxes and TOF product distributions from coated FiberForm_B. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. **(a)** Total flux as a function of temperature from $T_s = 1000$ to 1800 K for $m/z = 16, 32, 28$, and 44 products. TOF distributions as a function of temperature, increasing to 1800 K, then decreasing to 1000 K, for **(b)** O and **(d)** CO. Fluxes separated into their IS (O only), TD, and TD_{slow} components shown in **(c)** and **(e)** for O and CO, respectively. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached.

Flux angular distributions from coated FiberForm_B collected at 1600 K are shown in **Fig. 10(left)**. Signal could be detected at $m/z = 16, 32, 28,$ and 44 , corresponding to O, O₂, CO, and SiO, respectively. Because it was known, based on the experiment with uncoated FiberForm as well as the previous study with FiberForm,[50] that CO₂ is not produced in significant quantities above 1200 K from FiberForm, SiO was assigned as the detected species at $m/z = 44$. The O-atom distribution was separated into IS, TD, and TD_{slow} components. The IS O-atom angular distribution was somewhat lobular, and its overall flux calculated from the sum of the IS O fluxes from all measured angles was much smaller than the overall TD O-atom flux. The overall TD_{slow} O flux was around half that of the overall IS O flux. The O₂ distribution was only separated into IS and TD components, with the IS O₂ angular distribution roughly equivalent in shape to the TD O₂ angular distribution. The overall IS O₂ flux was slightly less than the overall TD O₂ flux. The CO distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO flux being around 1/3 that of the overall TD CO flux. The SiO distribution was separated into TD and TD_{slow} components. Compared to the other angular distributions so far mentioned, both the TD SiO and TD_{slow} SiO angular distributions exhibited much higher levels of noise. Thus, a quantitative comparison between the two channels could not be easily made. Flux angular distributions collected at 1000 K for O, O₂, CO, and CO₂ are shown in **Fig. 10(right)**. The O-atom distribution was separated into IS, TD, and TD_{slow} components, with the overall TD_{slow} O flux being less than half that of the overall TD O flux, and the overall IS O flux being slightly greater than the overall TD O flux. The IS O angular distribution had a slightly lobular shape, similar to that of the IS O angular distribution from uncoated FiberForm at 1000 K. The O₂ distribution was separated into IS and TD components. The IS O₂ distribution was also somewhat lobular, and its overall flux was much smaller than the overall TD O₂ flux. The CO distribution was separated into TD and TD_{slow}

components, with the overall TD_{slow} CO flux being around 2/3 that of the overall TD CO flux. The CO_2 distribution was also separated into TD and TD_{slow} components, with the overall TD_{slow} CO_2 flux being less than half that of the overall TD CO_2 flux.

Fig. 10. Flux angular distributions of O, O₂, CO, SiO (1600 K only), and CO₂ (1000 K only) products from coated FiberForm_B at $T_s = 1600$ K (left) and 1000 K (right). Red symbols represent total flux for a particular product. Yellow symbols (O and O₂ only) represent IS flux. Blue symbols represent TD flux. Green symbols (O, CO, SiO, and CO₂ only) represent TD_{slow} flux. Dashed lines show cosine power fits for each product's TD distribution. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer.

Surface analysis of the coated FiberForm samples after heating and O-atom scattering showed both significant morphological changes and changes in the surface chemical environment. Images from the SEM analysis of the coated FiberForm_A surface after O-atom scattering at higher resolution revealed significant damage on the individual fibers (**Fig. S16**), including pitting and fracturing on the fibers, both in the area of O-atom beam impact as well as in areas outside of the impact. The individual pits on coated FiberForm also appeared to be larger than those observed on uncoated FiberForm. XPS analysis of the O-atom beam impact area (**Table 1(e)**) revealed nearly complete carbon coverage (96.9%) along with a small fraction of oxygen coverage (3.1%), but no calcium was detected. Similar phenomena were observed on the surface of FiberForm_B, and there were no discernible differences between the two coated samples. These changes (**Fig. S16**) were very similar to the changes observed on coated FiberForm that was heated without being exposed to the O-atom beam (**Fig. 1(d)**).

3.7. Temperature-Dependent Flux and Angular Distributions from PICA

Product TOF distributions from uncoated PICA as a function of the temperature are shown in **Fig. 11** for O and CO and in **Fig. S17** for O₂ and CO₂. The fluxes, as shown in **Fig. 11(a)**, had all been corrected for the mass-dependent detection sensitivity of the mass spectrometer. The temperature-dependent fluxes of products from uncoated PICA exhibited more complex behavior than those from the surface of uncoated FiberForm. The IS O flux remained relatively constant as the temperature increased to 1800 K (**Fig. 11(c)**), but as the temperature decreased back to 1300 K, the IS O flux began increasing, with approximately double the flux at 1100 K and 1200 K as the temperature was decreasing compared to the flux at 1100 K and 1200 K as the temperature was increasing. The temperature-dependent TD O flux was mostly increased monotonically, though

compared to the TD O flux from uncoated FiberForm it increased more slowly with increasing temperature until the temperature exceeded 1600 K. From 1000 to 1400 K, the CO flux as temperature was increasing remained higher than the CO flux as temperature was decreasing, while the inverse was observed above 1400 K, where the CO flux was lower as temperature was increasing compared to the CO flux as temperature was decreasing. The total CO flux showed a nearly equivalent composition of TD CO and TD_{slow} CO. The TD CO flux was generally higher than the TD_{slow} CO flux, except within the range from 1400 to 1500 K, where TD_{slow} CO flux was higher than that of TD CO flux. Above 1600 K, a divergence between the TD CO and TD_{slow} CO fluxes was observed, with the TD CO flux increasing much more quickly than the TD_{slow} CO flux. The total O₂ flux (**Fig. S17**) remained fairly constant throughout the experiment, though the TD O₂ flux appeared to decrease as the temperature increased to 1500 K, above which the TD O₂ flux increased as the temperature was raised to 1800 K. As temperature decreased, the TD O₂ flux did not significantly vary. The total CO₂ flux was negligible, with signal only detected at lower temperatures up to 1400 K, similar to the behavior observed from uncoated FiberForm. The background signals of the four products exiting the surface of PICA are shown in **Fig. S18**. As the temperature increased, the background signals of O and O₂ decreased. The background signal of CO was relatively high from 1100 to 1800 K as the temperature increased, but as the temperature decreased, its background signal remained low and relatively constant. The elevated CO background signal was likely a signature of continued thermal decomposition as the temperature of the PICA reached 1800 K. The CO₂ background signal was slightly elevated from 1000 K to 1200 K as the temperature increased but remained at a low and relatively constant level for the remainder of the experiment.

Fig. 11. Fluxes and TOF product distributions from uncoated PICA. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. **(a)** Total flux as a function of temperature from $T_s = 1000$ to 1800 K for $m/z = 16, 32, 28$, and 44 products. TOF distributions as a function of temperature, increasing to 1800 K, then decreasing to 1000 K, for **(b)** O and **(d)** CO. Fluxes separated into their IS (O only), TD, and TD_{slow} components shown in **(c)** and **(e)** for O and CO, respectively. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached.

Flux angular distributions for the products that scattered from uncoated PICA collected at 1000 K $\uparrow$ are shown in **Fig. 12(left)**. Signal could be detected at $m/z = 16, 32, 28,$ and 44. Signal from $m/z = 17$ (not shown) was also briefly observed when the detector angle of the mass spectrometer was set at $\theta_f = 5^\circ$, but this signal disappeared after roughly 20 minutes. The O-atom distribution was separated into IS, TD, and TD_{slow} components. The overall TD_{slow} O flux, calculated from the sum of the TD O fluxes at all measured angles, was slightly lower than that of the overall TD O flux, and the overall IS O flux was similar to that of the overall TD_{slow} O flux. The IS O angular distribution did not have a clear shape, and in fact, all the O-atom scattering channels exhibited noisy angular distributions. The O₂ distribution was separated into IS and TD components. The IS O₂ angular distribution was too noisy to discern a shape, and its overall signal level was much lower than that of the overall TD O₂ signal. The CO distribution was separated into TD and TD_{slow} channels, with the overall TD_{slow} CO signal being about two-thirds that of the overall TD CO signal. The shape of the TD_{slow} CO angular distribution appeared to follow a cosine distribution. The CO₂ distribution was separated into TD and TD_{slow} channels, with the overall TD_{slow} CO₂ flux being about 3/4 that of the overall TD CO₂ signal. The TD_{slow} CO₂ distribution appeared to follow a cosine distribution. Angular distributions collected at 1000 K $\downarrow$ for O, O₂, CO, and CO₂, are also shown in **Fig. 12(right)**. The O-atom distribution was separated into IS, TD, and TD_{slow} components. The overall TD_{slow} O flux was nearly equal to that of the overall TD O flux, and the overall IS O flux was only slightly greater than the overall TD O flux. The shape of the IS O angular distribution was relatively broad. The IS O₂ distribution had a somewhat lobular shape, while its overall flux was much smaller than that of the overall TD O₂ flux. The CO distribution was separated into TD and TD_{slow} channels, with the overall TD_{slow} CO flux being about three-

fourths that of the overall TD CO flux. The CO₂ distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO₂ flux being around 1/3 that of the overall TD CO₂ flux.

Fig. 12. Flux angular distributions of O, O₂, CO, and CO₂ products from uncoated PICA at $T_s = 1000 \text{ K}\uparrow$ (left) and $T_s = 1000 \text{ K}\downarrow$ (right), with arrows representing whether temperature had been increasing or decreasing before angular distributions were collected. Red symbols represent total flux for a particular product. Yellow symbols (O and O₂ only) represent IS flux. Blue symbols

represent TD flux. Green symbols (O, CO, and CO₂ only) represent TD_{slow} flux. Dashed lines show cosine power fits for each product's TD distribution. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer.

The images from the SEM analysis of the uncoated PICA surface after heating and O-atom scattering showed small pits forming on the individual fibers (**Fig. 1(f)**). These pits were present both in the area where the O-atom beam impacted as well as in areas outside of the impact spot (**Fig. S19**), similar to what was observed for heated uncoated FiberForm (**Fig. 1(b)**). The char surrounding the fibers showed slightly increased porosity compared to fresh uncoated PICA (**Fig. 1(e)**). Data from the XPS analysis (**Table 1(g)**) of the impact spot showed nearly complete carbon coverage along with a small fraction of oxygen. There was also a small fraction of fluorine present that was not detected in pristine uncoated PICA.

3.8. Temperature-Dependent Flux and Angular Distributions from Coated PICA

Product TOF distributions from coated PICA as a function of the temperature are shown in **Fig. 13** for O and CO and in **Fig. S20** for O₂ and products observed at $m/z = 44$. The flux, as shown in **Fig. 13(a)**, had been corrected for the mass-dependent detection sensitivity of the mass spectrometer. Both the fluxes and the shapes of the TOF distributions exhibited strong temperature-dependent changes – especially the O-atom TOF distributions, which were similar to the O-atom TOF distributions observed from coated FiberForm_A. As the temperature increased from 1000 to 1400 K, the O-atom flux was dominated by IS and was very high and relatively constant. As the temperature reached 1500 K, there was nearly equal flux from both the IS and TD O-atom scattering channels (**Fig. 13(c)**). As the temperature reached 1600 K, the behavior of the IS and TD signals changed significantly, with IS O flux decreasing and TD O flux increasing. The total O flux reflected this change, reaching a minimum near 1600 K and increasing again as the temperature increased to 1800 K. As the temperature decreased from 1800 K, the total O flux monotonically decreased, exhibiting a trend observed from every other sample. A corresponding

phenomenon was observed with the total CO flux. From 1000 to 1200 K, total flux was nearly negligible, but as the temperature increased to 1300 K, the total CO flux increased, driven by increasing TD CO flux. As the temperature reached 1500 K, the total CO flux increased more rapidly. There was also a divergence in the TD and TD_{slow} CO fluxes at that temperature, with the TD_{slow} CO flux increasing more slowly than the TD CO flux as the temperature increased to 1800 K. As the temperature decreased from 1800 K, the change in CO flux qualitatively resembled the change in CO flux observed from the uncoated and coated FiberForm samples as their temperatures decreased. As the temperature decreased to 1500 K, the TD and TD_{slow} CO fluxes were nearly equivalent. The total O₂ flux remained relatively constant (**Fig. S20(b)**) throughout the whole experiment, reflecting trends observed from every other sample as well. The individual IS and TD O₂ fluxes showed relatively little variation, though there was a small decrease in the TD O₂ flux as the temperature increased from 1400 to 1600 K. The flux of the products observed at $m/z = 44$ (**Fig. S20(d)**) showed fairly significant changes compared to the $m/z = 44$ flux from the other experiments. As temperature increased from 1000 to 1400 K the total $m/z = 44$ flux was negligible, but as the temperature reached 1500 K, increases in the flux were much greater, especially compared to the $m/z = 44$ signal from the other samples. Because this sample had the oxidized silicone coating, it was assumed that the $m/z = 44$ signal at higher temperatures was SiO. No CO₂ was detected while the temperature increased from 1000 K, but CO₂ was detected at lower temperatures as the temperature decreased to 1000 K. The background signals (**Fig. S21**) were also reflective of the changes observed, showing continued thermal decomposition as the temperature increased to 1800 K. As the temperature increased, the background signals of O-atoms ($m/z = 16$) and products detected at $m/z = 28$ and 44 began increasing at 1100 K, 1100 K, and 1200 K, respectively, with their background signals peaking at 1400 K, 1400 K, and 1300 K,

respectively. The background signals of O-atoms, as well as products at $m/z = 44$, corresponding to SiO and CO₂, reached their minima at 1800 K, and as the temperature decreased to 1000 K, their signals remained relatively constant. In contrast, the background signal of products at $m/z = 28$, corresponding to CO and possibly Si, reached a minimum at 1600 K before increasing again at 1700 K, and a minimum was not reached again until the temperature was decreased to 1600 K, remaining relatively constant as the temperature decreased to 1000 K. The background signal of O₂ decreased with increasing temperature.

Fig. 13. Fluxes and TOF product distributions from coated PICA. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer. (a) Total flux as a function of temperature from $T_s = 1000$ to 1800 K for $m/z = 16, 32, 28$, and 44 products. TOF distributions as a function of temperature, increasing to 1800 K, then decreasing to 1000 K, for (b) O and (d) CO. Fluxes separated into their IS (O only), TD, and TD_{slow} components shown in (c) and (e) for O and CO, respectively. Arrows indicate whether temperature had been increasing or decreasing when temperature was reached.

Flux angular distributions for the coated PICA collected at 1000 K $\uparrow$ are shown in **Fig. 14(left)**. At 1000 K $\uparrow$, product signal could only be detected unambiguously for $m/z = 16, 32$, and 28, corresponding to O, O₂, and CO. The O-atom distribution was only separated into IS and TD components, with the overall IS O flux, calculated from the sum of the IS O fluxes from all measured angles, slightly higher than the overall TD O flux. The IS O angular distribution had a narrower shape than a cosine distribution, peaked along the surface normal. The overall IS O₂ flux was around two-thirds that of the overall TD O₂ flux, with the IS O₂ angular distribution directed more towards the surface normal. The CO distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO flux being around one-third that of the overall TD CO flux. The TD_{slow} CO angular distribution was also relatively noisy. Flux angular distributions collected at 1000 K $\downarrow$ at $m/z = 16, 32, 28$, and 44, corresponding to O, O₂, CO, and CO₂, are shown in **Fig. 14(right)**. The O-atom distribution was separated into IS, TD, and TD_{slow} components, with the overall TD_{slow} O flux being less than half that of the overall TD O flux. The IS O-atom distribution had a somewhat lobular shape, and its overall flux was larger than that of the overall TD O flux. The overall IS O₂ flux was much smaller than the overall TD O₂ flux. The IS O₂ angular distribution also had a maximum towards the surface normal. The CO distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO flux being around two-thirds that of the overall TD CO flux. The CO₂ distribution was separated into TD and TD_{slow} components, with the overall TD_{slow} CO₂ being less than half that of the overall TD CO₂ signal.

Fig. 14. Flux angular distributions of O, O₂, CO, and CO₂ (1000 K↓ only) products from coated PICA at $T_s = 1000\text{ K}\uparrow$ (left) and $T_s = 1000\text{ K}\downarrow$ (right), with arrows representing whether temperature had been increasing or decreasing before angular distributions were collected. Red symbols represent total flux for a particular product. Yellow symbols (O and O₂ only) represent IS flux. Blue symbols represent TD flux. Green symbols (O, CO, and CO₂ only) represent TD_{slow} flux. Dashed lines show cosine power fits for each product's TD distribution. All fluxes shown have been corrected for the mass-dependent detection sensitivity of the mass spectrometer.

Images from the SEM analysis of the coated PICA surface after heating and O-atom scattering showed major pitting and fractures forming on the individual fibers (**Fig. 1(d)**). These fractures were present both in the area where the O-atom beam impacted as well as in areas outside of the impact spot (**Fig. S22**). Compared to the surface of coated FiberForm after heating (**Fig. 1(d)**), the fractures on the fibers of the coated PICA appeared to be even more extensive. The char surrounding the fibers appeared to be slightly more porous after annealing compared to pristine coated PICA, with more pronounced porosity compared to uncoated PICA. Data from the XPS analysis of the impact spot (**Table 1(i)**) showed major carbon coverage (92.8%) as well as a small fraction of oxygen (5.2%), silicon (1.3%), and calcium (0.7%). Compared to pristine coated PICA (**Table 1(h)**), the fraction of oxygen and silicon decreased significantly, but the fraction of calcium had remained relatively unchanged.

4. Discussion

Two primary factors affected the differences in the temperature-dependent reactivity and in the scattered product angular distributions between the various samples and their experimental conditions. The first was the addition of CV-1144-0 silicone (pretreated with exposure to atomic oxygen) coating onto the uncoated FiberForm. The second was the impregnation of phenolic resin into the fiber structure to form a carbon/carbon composite. In this section, how these two factors interact in different ways to explain the differences in behavior between the samples will be discussed. One additional minor factor to be discussed will be the effect of residual impurities within the FiberForm structure and how O₂ might affect the overall oxidation behavior.

4.1. Thermal Decomposition without the O-atom Beam

The parameters of the overall experiment meant that the saturation that was observed in the signal during the thermal decomposition of the materials as their temperatures were increased to 1000 K or 1600 K could not be easily adjusted. The presence of the saturation also meant that neither accurate quantification of the pyrolyzed species leaving the sample nor accurate identification of the products could be conducted. Nevertheless, the mass spectra did provide some useful insights into what was contained within the samples and how the coatings affect the decomposition. The detection of products from uncoated FiberForm as it was heated from room temperature to 1000 K indicated that the pristine uncoated FiberForm sample was not fully carbonized. At lower temperatures, in the range of 300 to 500 K, the presence of several higher mass species was likely indicative of various hydrocarbons adsorbed onto the surface, which was to be expected. However, at higher temperatures, species continued to desorb, with CO₂ and CO (corresponding to $m/z = 44$ and 28, respectively) being released in the 700 to 900 K range, as well as the CO product signal rising as the temperature approached 1000 K. From silicone-coated FiberForm, despite the persistent saturation of signal at $m/z = 73$, the overwhelming prevalence of $m/z = 73$ signal meant that the silicone coating was likely not completely oxidized. While the data from the XPS analysis of coated FiberForm showed that the Si2p peak was present within the binding energy region for SiO₂, if the silicone were completely oxidized, it would not be possible for signal to be detected at $m/z = 73$ from the decomposition of SiO₂. From searches of the NIST database[52] and other literature,[53] it was found that $m/z = 73$ could fragment from a number of disiloxane or disilane compounds. In addition, there also appeared to be some variation in the coating application between the two different coated FiberForm samples that were tested. While special care was taken to prepare the sample slabs and oxidize them in as consistent a means as

possible, it was very likely that the process of box coat application of the silicone had inherent uncertainties in how evenly it was sprayed. Despite this inconsistency, the mass spectra collected from the thermal decomposition of coated FiberForm_B, up to 1600 K, provided far more important data at high temperatures, especially in the range from 1200 to 1600 K. In this range, the signal showed no saturation, which allowed relatively accurate quantification of the amount of product at every significant peak detected. In particular, SiO was found. As discussed by Chen, et al. (2021),[29] when oxide-covered silicon carbide was heated above 1600 K, SiO product was released that was directly associated with the breakdown of the oxide layer. Though the oxide decomposition from FiberForm occurred around 1400 K instead of the 1700 K seen from SiC, the oxide layer on FiberForm remained after the temperature surpassed 1000 K even while the underlying silicone had decomposed. The presence of this oxidized silicone coating had a major effect on FiberForm even in the absence of the O-atom beam. After a sample of coated FiberForm was heated at 1800 K for 30 minutes the surface of the coated FiberForm (**Fig. 1(d)**) showed extensive fractures and pits on its surface that were not present on the uncoated FiberForm (**Fig. 1(b)**) after it was heated. Similar to the thermal decomposition of the oxide layer from silicon carbide, most of the oxide decomposition observed from coated FiberForm likely occurred at the interface between the silicon oxide layer and either the surfaces of the individual carbon fibers or the unoxidized silicone remnant. Similar changes were observed on the uncoated FiberForm and coated FiberForm samples after their experiments with the O-atom beam. At least within the parameters of this experiment, this suggests that the coating had a far more significant effect on the fibers compared to the O-atom beam itself as the samples were heated. While a much higher O-atom flux could have a more noticeable impact on the fibers, the SEM analysis conducted was unable to reveal any erosion solely because of the O-atom beam.

The thermal decomposition of PICA was far more complicated compared to that of FiberForm. Because of the overwhelming saturation of so many peaks, there was no way to properly quantify the decomposition at most of the m/z ratios within the temperature range surveyed. A few insights could be drawn from the data, however. In comparing the thermal decomposition mass spectra between the coated PICA (**Fig. S5**) and the uncoated PICA (**Fig. S4**), the primary difference appeared to be the addition of signal at $m/z = 73$ from the coated PICA, with no significant differences observed with any of the other peaks. This suggests that the silicone coating did not significantly affect the pyrolysis chemistry of the PICA bulk. This makes sense when considering the multilayer thermal decomposition model[6] of PICA, in which the vast majority of the pyrolysis products originate from deep within the PICA bulk. As the depth of the silicone coating did not surpass 300 μm , the vast majority of the PICA decomposition products likely did not directly interact with the silicone.

4.2. Atomic Oxygen Oxidation of FiberForm

From uncoated FiberForm, the flux of desorbing O-atoms and CO species as the temperature increased to 1800 K followed monotonic trends similar to the trends observed in previous studies of O-atom scattering from the surfaces of both FiberForm[50] and vitreous carbon.[22, 24] The temperature-dependent CO flux could be attributed to increased carbon reactivity at high temperatures. As with the previously-conducted studies, hysteresis was again present between the flux as the temperature increased and the flux as the temperature decreased. The temperature-dependent flux for the O-atom signal is unusual, however. One might imagine that the temperature-dependence of the O-atom and CO fluxes to be inverse to each other; for example, as the temperature increased, if the CO flux increased and the O-atom flux decreased, it could be surmised that more O-atoms are consumed as they react with the FiberForm in order to

produce more CO. Instead, what was observed was that both O-atom flux and CO flux increased concurrently with the temperature. Thus, while it can be deduced that FiberForm reactivity with O-atoms increased with increases in the temperature to produce more CO, there is no satisfactory explanation for why O-atom flux also increased. Speculation in work from Murray et al. (2020)[24] surmised that surface-adsorbed O-atoms may migrate out of the scattering detection area faster at lower temperatures than at higher temperatures such that at higher temperatures a higher fraction of adsorbed O-atoms will leave the surface instead of remaining to migrate. One other possibility they raised was that more O-atoms are absorbed into the bulk of the material at lower temperatures than at higher temperatures, meaning that the higher O-atom flux at higher temperatures was an apparent effect from the release of absorbed O-atoms from the bulk. A final possibility raised in the original vitreous carbon study from Murray et al. (2015)[22] was speculation that the porosity of their vitreous carbon sample increases with the temperature, thus allowing more collisions at the surface and possibly enhancing O-atom trapping. The limitations of the experiment presented in this study prevent a way to verify this hypothesis. However, there has been a recent study that has used transmission electron microscopy (TEM) to study a glassy carbon surface *in situ* as their samples were slowly ramped up to 1200°C.[54] A very recent study from Cochell et al. (2021)[55] used *in-situ* scanning TEM to observe real-time oxidation of different microstructures of FiberForm. Unfortunately, neither of these two studies reported on their respective materials' porosities. As for the other species, the O₂ flux showed negligible temperature dependencies as FiberForm was heated compared to the temperature-dependent flux of O-atoms and CO. This behavior was similar to that observed in the study from Poovathingal et al. (2021).[22, 50]. They attribute this temperature-independent O₂ flux to nonreactive scattering of incident O₂ arising from multiple bounces within the porous structure of FiberForm. While the recent vitreous carbon study

from Murray et al. (2020),[24] which found a slight increase in O₂ flux as temperature increased, might contradict this explanation, the vitreous carbon study from Murray et al. (2015),[22] which used a similar O-atom beam utilized in this present study, did not show any temperature dependence of the O₂ product flux. As the beam used in Murray et al. (2020)[24] was a high-flux continuous O-atom beam instead of the low-flux pulsed O-atom beam utilized in present, this is likely the source of the difference in the temperature-dependent O₂-behavior observed. Poovathingal et al. (2021)[50] speculates that the continuous O-atom beam allowed higher surface coverage of O-atoms on the vitreous carbon surface, which promoted O-atom recombination and thus higher O₂ product flux. Finally, with regards to CO₂, its temperature-dependent behavior was also very similar to that observed from previous O-atom beam-surface scattering studies on vitreous carbon and FiberForm, with significant product flux only observed at lower temperatures and product flux becoming negligible as the temperature surpassed 1100 K.

Except for O₂, the TOF distributions for all scattered species from FiberForm showed slow signal that could not be fit with a Maxwell-Boltzmann distribution and had to be fit with a TD_{slow} function. As with many of the results observed from O-atom scattering of FiberForm, this phenomenon was also observed and remarked upon by Poovathingal et al. (2021).[50] The lack of TD_{slow} signal within any of the O₂ TOF distributions was likely related to its lack of interaction with the FiberForm, acting similar to argon as mentioned above. The presence of TD_{slow} signal in the O-atom TOF distributions, however, may be related directly to its high interactivity with the carbon fibers. As Poovathingal et al. stated, O-atoms that chemisorb onto the carbon fibers can desorb and then re-adsorb onto a different fiber with a finite residence time. The accumulation of these residence times can result in TD_{slow} signal appearing in the TOF distributions of O-atoms desorbing from FiberForm. TD_{slow} signal observed in the TOF distributions of CO and CO₂ may

also be related to this phenomenon. While not every O-atom chemisorption event will result in CO or CO₂ formation, a fraction of the O-atoms bouncing and re-adsorbing within the carbon fiber structure will form CO or CO₂ products, likely represented as TD_{slow} within their TOF distributions.

4.3. Impurities and O₂ Reactivity

The presence of a peak around 3 ms within the CO TOF distribution from uncoated FiberForm at temperatures of 1300 and 1400 K was unexpected. While the temperature-dependent product flux of CO from the uncoated FiberForm still followed the general monotonic trend observed in the previous FiberForm study from Poovathingal et al., subtle differences were discovered that ended up being attributed to the heating of the FiberForm to 1800 K. From 1300 to 1500 K, there was a noticeable decrease in the rate of increase of the product flux as the temperature was increasing compared to the product flux when the temperature was decreasing, such that at these temperatures the product flux as the temperature was increasing was lower than the product flux as the temperature was decreasing. Poovathingal et al.[50] observed that their CO product flux as the temperature was increasing was always lower than the CO product flux as the temperature was decreasing. The investigation described in this present study not only found that this trend reverted to that seen in Poovathingal's study after heating the sample to 1800 K, but anomalous peaks were also discovered at 3 ms in the product TOF distributions of CO at 1300 K and 1400 K that disappeared after annealing. Increasing amounts of CO products as the temperature of O₂-adsorbed carbons approached 1300 K has been observed in a number of prior studies.[56, 57] Previous studies that have looked at O₂ scattering from graphite[7] and graphene[9] have shown etching at high surface temperatures of 1375 K localized within defect sites on the material. However, these studies were focused on the use of relatively clean carbon samples, whereas the FiberForm in the present study is not assumed to be free of impurities. One possibility

for the identity of the impurities could be adsorbed hydrocarbons. As S1(b) shows, during the thermal decomposition of uncoated FiberForm products at $m/z = 28$ and 44 are still being produced up to 1000 K. However, since it was found that the FiberForm O_2 was scattered from contained calcium, the presence of this impurity was the likely cause of both the reduction in the CO product flux around 1300 and 1400 K as well as the appearance of the 3 ms peak within the product TOF distribution of CO. FiberForm oxidation studies from Panerai et al. (2013)[39] and Lachaud et al. (2011)[38] found calcium carbonate deposits left over after their high temperature oxidation experiments. The fact that their experiments only reached 1300 K may be why they were still able to detect impurities, whereas the FiberForm samples in the present study were heated to 1800 K, removing everything from the surface except for carbon and a small fraction of oxygen. The presence of this phenomenon in the product TOF distributions from coated FiberForm_A (raised to 1000 K), PICA, as well as coated PICA, may be responsible for some of the behavior observed from these samples, with the leveling of the temperature-dependent CO product flux from uncoated PICA at 1400 to 1500 K being a prime example. From coated PICA, 3 ms peaks are even observed within the SiO ($m/z = 44$) product TOF distributions above 1500 K. While this type of reactivity has not been directly observed before, one possible explanation for this is described below. In general, unlike O-atoms, which are highly reactive and react directly with their target species, molecular oxygen must first dissociate before it is available to participate in a reaction.[58] As Chen and Yang (1998) describe,[58] this dissociated atomic oxygen can form an epoxide group with the surface carbons, helping to weaken the C—C and promoting the desorption of carbon oxide species like carbon monoxide. This higher barrier to reaction resulting from dissociative chemisorption of O_2 having to first dissociate may be the reason behind the comparatively slow desorption of O_2 -induced CO products. In addition, a study from Schrader (1978)[59] had found

that the presence of calcium catalytically increases the chemisorption rate of molecular oxygen onto gold. This catalytic effect may be why the O₂-induced CO product was observed on the TOF distribution at 3 ms, while on non-catalytically enhanced carbon, O₂-induced CO desorption may occur over a much longer time scale, if at all. Why there is a reduction in the CO product flux from pristine FiberForm compared to the CO flux from pre-heated FiberForm, however, is far from clear. There is certainly the possibility that calcium may have been interacting with the incident atomic oxygen, though the nature of the interaction is something that is unclear. Because of the limitations of XPS, the exact chemical nature of the calcium, whether it was in the form of CaCO₃, CaC₂, CaO, etc., cannot be determined, though because CaCO₃ had been found in prior studies and that because it has the relatively lowest vapor pressure of those listed, it was more than likely in the carbonate form.

4.4. Atomic Oxygen Oxidation of Uncoated PICA

Temperature-dependent product fluxes from PICA exhibited more complicated behavior compared to temperature-dependent fluxes from uncoated FiberForm, with overall much reduced relative fluxes of O-atoms and CO in relation to O₂. This was not necessarily expected, as it was assumed that the majority of the PICA was charred once the temperature reached 1000 K; thus, the temperature-dependent behavior was expected to be similar to that from uncoated FiberForm. The presence of an elevated CO background signal (**Fig. S18**) showed this assumption to be misguided, with overall high CO background signal all the way up to 1800 K, representative of continued thermal decomposition. This was suggestive of residual species contained within the PICA continuing to decompose. Bessire et al. (2018)[6] discovered continued production of CO up to 1200°C and hypothesized that much of the CO production comes from the decomposition of oxygen-containing phenyl groups. The flux as the temperature increased also provided clues, with

the O-atom flux as the temperature increased being relatively lower compared to O-atom flux from uncoated FiberForm, indicative of increased O-atom adsorption or absorption into the charring material, and quite possibly into the remains of the charred phenolic resin. A recent study from He et al. (2019)[60] investigated the atomic oxygen oxidation mechanisms of epoxy resins used in low-Earth orbit and found abstraction of hydrogen to form volatile –OH groups as well as formation of these same hydroxyl groups onto the epoxy polymers. Both of these mechanisms of either abstraction of a hydrogen or the addition of an O-atom to phenylic species have been previously determined from the atomic oxygen attack on benzene.[61] Within this present study, the transient observation of $m/z = 17$ product at the beginning of the uncoated PICA scattering experiment was evidence for possible O-atom abstraction of hydrogen from these lingering polycyclic aromatic hydrocarbons species still present during the experiment. Thus, it is likely that the relatively low O-atom product flux up until 1500 K could be because of the residual aromatic hydrocarbons absorbing and reacting with the incident O-atoms. Indeed, as the temperature increased, the CO product flux was overall higher in comparison to the O-atom product flux. The images from the SEM analysis of uncoated PICA after the experiment show erosion within the char region compared to pristine uncoated PICA (**Fig. 1(e)**), with more of the carbon fibers exposed, and this erosion was likely related to the higher CO production. This char erosion was also observed in previous oxidation and pyrolysis studies of PICA-like materials.[62] This phenomenon corroborates a common assumption made when developing oxidation models involving carbon/carbon fiber composites, in which the matrix of the materials erodes more quickly than the reinforcing carbon.[8, 63] The presence of the matrix was likely also related to the relatively higher proportion of TD_{slow} signal in the TOF distributions of O-atoms, CO, and CO_2 , as compared to their total signals, though it is unclear how it contributes. Perhaps, similar to the

structure on uncoated FiberForm, the roughness of the char matrix provided a large surface area onto which incoming O-atoms could adsorb and re-adsorb.

As the temperature decreased from 1800 K, the CO product flux decreased monotonically, and the O-atom product flux followed similar behavior except at 1200 K, increasing slightly before decreasing again at 1100 K, which suggests that the behavior of O-atom scattering from PICA as temperature decreased more closely follows that of O-atom scattering from uncoated FiberForm. This makes sense, because as more char was eroded, the temperature-dependent scattering behavior was going to more resemble that of its carbon fiber substrate. In addition, similar to what happens to uncoated FiberForm after heating, there were pits found on the carbon fibers of charred PICA, while pristine PICA did not have any of these pits. Like with uncoated FiberForm, it was likely that these pits on charred PICA are due primarily to heating the sample to 1800 K, but because an experiment with a sample of PICA heated without O-atom exposure was not conducted, it is unclear how much the O-atoms contributed to the pits. The erosion of the char with and without O-atom exposure also could not be compared. One other small factor that may also affect the behavior of PICA is the presence of impurities. Data from the XPS analysis of pristine PICA only revealed the presence of carbon and oxygen on the surface, but PICA heated and scattered with O-atoms also showed the presence of fluorine. The presence of this fluorine could be anomalous contamination, but the presence of only carbon and oxygen on pristine PICA could also reflect the dominance of the phenolic resin accessible by the XPS instrument, with the phenolic resin matrix mostly shielding any resident impurities in the material from detection. One way to investigate this would be to anneal PICA to only 1000 K and then use XPS analysis to examine its surface for more of its embedded impurities. Another possibility would be to heat the PICA up to 1800 K,

then use the atomic oxygen beam-surface scattering apparatus to collect temperature-dependent data similar to what was done with all the samples in this present study.

4.5. Effects of Oxidized Silicone Coating

The addition of silicone onto FiberForm and PICA caused the results of O-atom scattering from both sample types to exhibit remarkably similar behavior. The temperature-dependent product flux from both silicone-coated FiberForm and silicone-coated PICA showed greatly increased O-atom flux from 1000 to 1500 K, along with a corresponding suppression of CO flux within this temperature range. This greater flux of O-atoms from the surface was because of the passivating effect of the oxide coating on the FiberForm fibers. Instead of adsorbing onto and reacting with the fiber surfaces, a large fraction of incident O-atoms scattered from the oxide layer through both IS and TD channels. Results from Chen et al. (2021)[29] and from Murray et al. (2017)[51] show the vast majority of the O-atom flux from SiO_2 leaving through IS channels. In contrast, the TD O-atom flux from coated FiberForm was higher compared to that in those previous studies, constituting ~30% on average of the total O-atom flux at each temperature, while the TD O-atom flux from coated PICA was even greater, constituting almost half of the total O-atom flux. Because this is the first study to use this specific atomic oxygen beam-surface scattering technique with silicone-coated FiberForm and silicone-coated PICA, there are no prior oxidation studies with silicon-containing C/C composites to elucidate why the TD O-atom signal was so high. However, since CO flux was very low in this temperature range, it can be reasonably assumed that the fibers to which the O-atom beam has access are mostly coated with the silicone and thoroughly oxidized such that very little carbon was exposed to the O-atom beam. Thus, this proportionally higher TD O-atom signal compared to the TD O-atom signal from oxidized SiC was attributed to the fibrous and porous structure of the surface. The presence of porosity meant

multiple bounces of the incident O-atoms between the fibers of FiberForm, driving a larger proportion of the incident atoms into thermal equilibrium, which meant a higher proportion of TD O-atom scattering, especially compared to scattering from a flat, crystalline layer of SiO₂. This general phenomenon was observed with argon scattering from FiberForm.[50] Despite the porosity, however, there was no TD_{slow} component observed in the O-atom TOF distribution from coated FiberForm. This was likely because of the general lack of reactivity O-atoms have towards SiO₂ compared to carbon, with the incident O-atoms bouncing within the fiber in an analogous manner to argon scattering,[50] or directly scattering from the silicon-oxide covered char. Around 1500 K this trend broke down, and upon reaching 1600 K, the O-atom and CO product fluxes from both coated FiberForm_A and coated PICA reverted to a trend resembling that of scattering from uncoated FiberForm. It is known from Chen et al. (2021)[29] that for oxide-covered silicon carbide under high vacuum ($\sim 5 \times 10^{-7}$ torr), the oxide layer began to break down around 1673 K. While this present study suggested an oxide layer breakdown beginning around 300 K lower compared to the oxide layer of the silicon carbide wafer, it was clear from examining the background of the different species that the breakdown of the SiO₂ was the proximal cause of the change in reactivity for both O and CO. Starting at 1200 K, background signals at $m/z = 16$, 28, and 44 from both coated samples all increased significantly, with $m/z = 28$ and 44 likely corresponding partly to Si and SiO, respectively. The mass spectra from the pyrolysis of coated FiberForm_B from 1200 to 1600 K corroborated this data, showing a significant contribution from SiO in this range as well as a much smaller contribution from Si. This breakdown was most evident when examining the images from the SEM analysis of the surfaces of both coated samples after they were heated and exposed to O-atoms. In fact, the primary contribution for much of the erosion observed on these samples appeared to be because of the thermal decomposition of the silicone layer, a process that

appeared to erode much of the underlying carbon away as the layer decomposed, whether the carbon was in the form of the carbon fibers, or from the char in regard to coated PICA. Quantitative differences in erosion were difficult to ascertain between uncoated PICA and coated PICA, as shown in **Fig. 1**, and additional experiments were not conducted to heat and examine the surface of coated PICA without O-atom exposure. The differences in the product fluxes of O-atoms and CO from coated PICA (**Fig. 13(a)**) and coated FiberForm (**Fig. 7, Fig. 9**) as the temperature decreased from 1800 K could be explained as follows. As coated PICA would contain the charred matrix, the incident O-atom beam will preferentially react with the charred carbon, forming CO, whereas in coated FiberForm, only the carbon fibers were remaining, reducing the amount of reactive scattering. This could be why the product fluxes of O-atoms and CO from coated PICA were closer to each other compared to the product fluxes of O-atoms and CO from coated FiberForm_A and coated FiberForm_B. The CO background signal at 1800 K from coated PICA, however, suggests that, especially compared to uncoated PICA, there was still a significant amount of residual aromatic hydrocarbons even at that temperature. A reason for this lingering presence could be explained when examining the data from the XPS analysis of coated PICA after the experiment, which showed residual silicon on the surface as well as a small fraction of calcium. Analogous to uncoated PICA, the presence of the phenolic resin, even in its charred form, appeared to provide a shielding effect that prevented further loss of impurities through decomposition. One other reason for the lingering presence of hydrocarbons could also be that the PICA was coated with 1.5 box coats of CV-1144-0 instead of just 1 box coat. A coating of 150-300 μm instead of 100-200 μm may mean that more energy was needed to decompose the silicone layer on the samples completely. Fluorine was also not found on coated PICA, while on uncoated PICA a peak

for it was observed in the XPS analysis. Further studies will need to be conducted with coated PICA, like uncoated PICA, to be able to address these discrepancies.

4.6. Angular Distributions

In comparing the angular distributions between uncoated FiberForm (**Fig. 5**) and coated FiberForm, both A and B (**Fig. 8, 10**), at 1000 K, significant differences were observed. Between the O-atom and O₂ product flux angular distributions between uncoated FiberForm (**Fig. 5 (left)**) and coated FiberForm (**Fig. 8 (left)**) at 1000 K[†], the angular distributions from coated FiberForm were broader in shape and generally of much higher intensity compared to those of uncoated FiberForm. In addition, TD_{slow} signal was not observed in the TOF distributions of O-atoms from coated FiberForm, while it was present in the O-atom TOF distributions from uncoated FiberForm. These differences were representative of the presence of the silicon oxide on the fibers. A significant difference in the power of the cosine distribution fit for the TD O-atom distributions between uncoated FiberForm at 1000 K (**Fig. 5 (right)**) and coated FiberForm_A at 1000 K after the silicone coating had decomposed (**Fig. 8 (right)**) was observed (1.5 and 2.5, respectively). It is unclear precisely how this change occurred, but there was likely a change in the overall orientation of the fibers in the local region upon which the beam impinged. As described in Poovathingal et al. (2021),^[50] thermal desorption from a planar surface ought to follow a $\cos^1(\theta_f)$ distribution. Deviations from this unit power are likely because of the many individual carbon fibers at the apparent surface of the FiberForm, with the fiber surfaces not necessarily parallel to the apparent surface of the FiberForm. Thus, the orientation distribution of the fibers may have changed as the silicone coating decomposed from the FiberForm, causing the change in the powers of the cosine distribution fit. A different cosine distribution power was observed from the 1000 K TD O-atom distribution from FiberForm_B, however (**Fig. 10 (right)**), and it was unclear why this

value was different from that of FiberForm_A (1.6 vs 2.5, respectively). As for the effects of the silicone coating on the CO and CO₂ product flux angular distributions, the similar shapes of the angular distributions between coated and uncoated FiberForm suggest that their product formation was representative of scattering from the underlying carbon fibers within the FiberForm, with the primary effect of the oxide layer being reduced product flux, the overall product flux of reactive products from coated FiberForm being around half that from uncoated FiberForm.

At 1600 K, the similarities in the angular distributions between uncoated FiberForm and coated FiberForm suggested a very similar surface structure between the two samples. The main difference, other than the overall higher product flux from coated FiberForm, was the presence of a very small $m/z = 44$ signal on coated FiberForm as opposed to uncoated FiberForm, where there was no detectable signal. As CO₂ production had repeatedly been observed to be negligible above 1200 K from carbon, it was highly unlikely that the detected signal was CO₂. Instead, it was likely that residual silicon still left behind on the surface was the actual cause of the signal. This was not confirmed using the naturally occurring isotopic ratio of silicon, though, as signal at $m/z = 45$ or 46 were not checked. The TD O-atom product flux angular distributions from coated FiberForm_B had a noticeably different cosine power compared to TD O-atom angular distributions from uncoated FiberForm as well as itself at 1000 K (both 2.2 vs 1.6, respectively). As previously stated, these changes were likely due to the local fibers' orientation distribution changing.

Because this was the first O-atom beam-surface scattering study of PICA, there are no clear data within the literature with which to compare the product flux angular distributions from PICA in this present study. Regardless, the behavior of scattering from PICA exhibits a number of similarities to O-atom scattering from the FiberForm samples, including in how the O₂ product flux could be fully fit with only Maxwell-Boltzmann distributions, while all the other species show

significant TD_{slow} flux. Previous studies of carbon/carbon composite oxidation have all observed preferential oxidation of the carbon matrix as opposed to the carbon fiber FiberForm base.[64] Interestingly, no $m/z = 44$ flux was observed from the coated PICA at 1000 K before annealing. This could be because of the higher box-coat application of silicone used for coated PICA compared to coated FiberForm that ensured more complete coverage of the surface. It is difficult to draw concrete conclusions from this, however, and more studies will need to be done to elucidate the meanings behind the differences in behavior observed, including additional angular distributions at 1600 K.

5. Conclusion

A comparative study was conducted on how the presence of CV-1144-0 silicone coating and phenolic resin matrix affects the atomic oxygen reactivity of FiberForm-based heat shields. The introduction of CV-1144-0 silicone coating onto the fibers of both FiberForm and PICA changed the behavior of the O-atom scattering dynamics of both materials in similar ways, with greatly reduced, yet not completely suppressed, reactive scattering, along with an enormous increase in nonreactive O-atom scattering, reflective of the protective and passivating effect of the silicon-oxide coating on the sample surface. This protection, however, only remains up until the passive-to-active oxidation transition, when the silicon oxide coating began to decompose, after which the oxidation behavior started to resemble that of its uncoated form, whether FiberForm or PICA. The addition of the phenolic resin matrix into the FiberForm to form PICA resulted in far more complicated O-atom beam-surface scattering, where even the changes in flux of products leaving the surface as the temperature decreased were dissimilar to that of FiberForm, whether coated or uncoated, though the pattern of coated PICA oxidation as the temperature decreased was

more similar to that of uncoated FiberForm than that of uncoated PICA. In addition, it was discovered that the presence of impurities may cause minor changes in the reactivity of the samples. When pristine uncoated FiberForm contained impurities such as calcium, its atomic oxygen reactivity will show slight differences compared to atomic oxygen oxidation of FiberForm that had been previously heated to 1800 K. This difference was revealed in the slightly reduced flux of CO from 1300 to 1500 K from uncoated FiberForm as well as the presence of a 3 ms peak in the CO TOF distribution, a peak position that was also observed in CO and SiO TOF distributions from uncoated and coated PICA. This peak was observed to appear with only an O₂ beam scattering against the impurity-filled sample, suggesting that O₂, even at such a low proportion of the O-atom beam, had a more significant effect on reactivity than was anticipated. Furthermore, it was discovered that, whether because the phenolic resin matrix contains more impurities, and/or because the matrix prevents the carbon fiber impurities from escaping the surface, the PICA, both coated and uncoated, still retained detectable fractions of impurities and trace amounts of silicon on coated PICA, even after heating to 1800 K with O-atom scattering. Overall, the dynamics of atomic oxygen molecular beam-surface scattering from samples of FiberForm, PICA, and their silicone-coated equivalents were able to be characterized. This new data will be used by NASA to develop improved oxygen ablation models. Further investigations, however, will still need to be conducted in order understand the atomic oxygen oxidation of these materials further. In particular, studies will need to be conducted on the charred PICA material.

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Supporting Information

S1. Translational energy distributions of the O/O_2 hyperthermal beams used for the different scattering experiments. For **(a)** uncoated FiberForm, **(b)** coated FiberForm_A, **(c)** coated FiberForm_B, **(d)** uncoated PICA, **(e)** coated PICA, **(f)** uncoated FiberForm for O_2 reactivity experiment.

S2. Mass spectral results from products released from pristine FiberForm as it was heated from room temperature to 1000 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Integrated intensities of peaks corresponding to specific m/z ratios as a function of sample temperature.

S3. Mass spectral results from products released from coated FiberForm_A as it was heated from room temperature to 1000 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Selection of largest integrated intensities of peaks corresponding to specific m/z ratios as a function of sample temperature. **(c)** Selection of smaller integrated intensities of peaks corresponding to specific m/z ratios as a function of sample temperature.

S4. Mass spectral results from products released from uncoated PICA as it was heated from room temperature to 1000 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Selection of largest integrated intensities of peaks corresponding to specific m/z ratios as a function of sample temperature.

S5. Mass spectral results from products released from coated PICA as it was heated from room temperature to 1000 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Selection of largest integrated intensities of peaks corresponding to specific m/z ratios as a function of sample temperature.

S6. Mass spectral results from products released from coated FiberForm_B as it was heated from room temperature to 1600 K, with a detector viewing angle of $\theta_f = 5^\circ$ with respect to the normal of the macroscopic surface. **(a)** Mass spectra as a function of sample temperature. **(b)** Intensities of signals detected at $m/z = 73$, 74, and 75 represented as percentages of the total signal at these three m/z ratios, as a function of sample temperature.

S7. Additional SEM of **(a)** uncoated and **(b)** coated FiberForm annealed to 1800 K for 30 minutes without the O-atom beam.

S8. TOF product distributions and fluxes of O_2 and CO_2 from uncoated FiberForm. TOF distributions as a function of temperature increasing up to 1800 K, then decreasing to 1000 K, for (a) O_2 and (c) CO_2 . Fluxes separated into their IS (O_2 only), TD, and TD_{slow} (CO_2 only) components shown in (b) and (d) for O_2 and CO_2 , respectively. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S9. Integrated intensities of background TOF distributions for $m/z = 16$, 32, 28, and 44 products from uncoated FiberForm as a function of surface temperature from 1000 K to 1800 K. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S10. SEM of uncoated FiberForm in areas (a) out-of-beam, and (b) in-beam after experiments with hyperthermal O/O₂ beam.

S11. Additional results from O_2 reactivity experiment. TOF product distributions for CO product from uncoated FiberForm, scattered with O-atoms, as a function of temperature (a) before annealing once from 1000 K to 1800 K, and (b) after annealing. TOF distributions plotted out to 5,000 μs to reveal slow signal. (c) Individual TOF distributions for CO products from pristine FiberForm, scattered with O_2 , at 1400 K $\uparrow$ and 1400 K $\downarrow$. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S12. TOF product distributions and fluxes of O_2 and $m/z = 44$ from coated FiberForm_A. TOF distributions as a function of temperature increasing up to 1800 K, then decreasing to 1000 K, for (a) O_2 and (c) $m/z = 44$, corresponding either to CO_2 or SiO. Fluxes separated into their IS (O_2 only), TD, and TD slow ($m/z = 44$ only) components shown in (b) and (d) for O_2 and $m/z = 44$, respectively. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing. For $m/z = 44$, fluxes at lower temperatures reflect CO_2 product, while fluxes at higher temperature likely reflect SiO.

S13. Integrated intensities of background TOF distributions for $m/z = 16, 32, 28$, and 44 products from coated FiberForm_A as a function of surface temperature from 1000 K to 1800 K. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S14. TOF product distributions and fluxes of O_2 and $m/z = 44$ from coated FiberForm_B. TOF distributions as a function of temperature increasing up to 1800 K, then decreasing to 1000 K, for (a) O_2 and (c) $m/z = 44$, corresponding either to CO_2 or SiO . Fluxes separated into their IS (O_2 only), TD, and TD_{slow} ($m/z = 44$ only) components shown in (b) and (d) for O_2 and $m/z = 44$, respectively. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing. For $m/z = 44$, fluxes at lower temperatures reflect CO_2 product, while fluxes at higher temperature likely reflect SiO .

S15. Integrated intensities of background TOF distributions for $m/z = 16, 32, 28$, and 44 products from coated FiberForm_B as a function of surface temperature from 1000 K to 1800 K. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S16. SEM of coated FiberForm after experiments with hyperthermal O/O₂ beam.

S17. TOF product distributions and fluxes of O_2 and CO_2 from uncoated PICA. TOF distributions as a function of temperature increasing up to 1800 K, then decreasing to 1000 K, for (a) O_2 and (c) CO_2 . Fluxes separated into their IS (O_2 only), TD, and TD $_{slow}$ (CO_2 only) components shown in (b) and (d) for O_2 and CO_2 , respectively. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S18. Integrated intensities of background TOF distributions for $m/z = 16, 32, 28$, and 44 products from uncoated PICA as a function of surface temperature from 1000 K to 1800 K. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S19. SEM of uncoated PICA after experiments with hyperthermal O/O₂ beam, within its out-of-beam area.

S20. TOF product distributions and fluxes of O_2 and $m/z = 44$ from coated PICA. TOF distributions as a function of temperature increasing up to 1800 K, then decreasing to 1000 K, for (a) O_2 and (c) $m/z = 44$, corresponding either to CO_2 or SiO . Fluxes separated into their IS (O_2 only), TD, and TD_{slow} ($m/z = 44$ only) components shown in (b) and (d) for O_2 and $m/z = 44$, respectively. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing. For $m/z = 44$, fluxes at lower temperatures reflect CO_2 product, while fluxes at higher temperature likely reflect SiO .

S21. Integrated intensities of background TOF distributions for $m/z = 16, 32, 28$, and 44 products from coated PICA as a function of surface temperature from 1000 K to 1800 K. Arrows indicate signal at the temperature collected when temperature was either increasing or decreasing.

S22. SEM of coated PICA after experiments with hyperthermal O/O₂ beam, within its out-of-beam area.