The Pennsylvania State University
The Graduate School
College of Engineering

FIBER-OPTIC RECESSION EMBEDDED IN A TPS MATERIAL

A Thesis in
Aerospace Engineering
by
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Abstract

The work presented in this report represents our efforts to estimate the silica fiber recession rate in the high speed re-entry conditions. A silica fiber would be used to transmit the spectra of the radiating atmospheric gases to the detectors housed on board a reentry payload. Due to the high heat fluxes generated by a strong shock, the fiber will maintain its structural integrity only for a finite length of time. Understanding the exact mechanism of the melting rate of the fiber and the rate of chemical reaction of the fiber with the gas species surrounding it, is important to predict the total time until the fiber fails. This report calculates the change in topology of the fiber due to recession.
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# List of Symbols

\( T \) \hspace{1cm} Temperature of the fiber (K)

\( C \) \hspace{1cm} Reaction constant, an Arrhenius parameter

\( k_f \) \hspace{1cm} Forward rate coefficient (m\(^3\)/s)

\( E_a \) \hspace{1cm} Activation energy of a reaction (J/mol)

\( K_B \) \hspace{1cm} Boltzmann’s constant (J/K)

\( k_e \) \hspace{1cm} Equilibrium constant

\( k_r \) \hspace{1cm} Backward reaction rate (m\(^3\)/s)

\( r \) \hspace{1cm} Reaction rate (s\(^{-1}\))

\( \nu \) \hspace{1cm} Reaction efficiency

\( R \) \hspace{1cm} Ideal gas constant (J/molK)

\( N_A \) \hspace{1cm} Avogadro’s Number (mol\(^{-1}\))

\( \rho \) \hspace{1cm} Mass density (Kg/m\(^3\))

\( M \) \hspace{1cm} Molar mass (gm/mol)

\( m \) \hspace{1cm} Mass of an atom/molecule (Kg)

\( T_w \) \hspace{1cm} Wall temperature (K)

\( Y_i \) \hspace{1cm} Species mass fraction

\( D_i \) \hspace{1cm} Mass diffusion coefficient (m\(^2\)/s)

\( \nu_{nk,i} \) \hspace{1cm} Stoichiometric coefficients of reactants for reaction k, specimen i

\( \nu_{nk,i} \) \hspace{1cm} Stoichiometric coefficients of products for reaction k, specimen i

\( \eta \) \hspace{1cm} Distance from the surface (m)

\( B_i \) \hspace{1cm} Biot Number

\( h \) \hspace{1cm} Convective heat transfer coefficient (W/m\(^2\)K)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$L_c$</td>
<td>Characteristic length (m)</td>
</tr>
<tr>
<td>$k_b$</td>
<td>Thermal conductivity (W/mK)</td>
</tr>
<tr>
<td>$\dot{q}$</td>
<td>Incident heat flux (W/m²)</td>
</tr>
<tr>
<td>$T_{surf}$</td>
<td>Surface Temperature of the body (K)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Initial temperature of the body (K)</td>
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<tr>
<td>$T_o$</td>
<td>Centerline temperature of the body (K)</td>
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<tr>
<td>$T_\infty$</td>
<td>Freestream temperature (K)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity (m²/s)</td>
</tr>
<tr>
<td>$F_o$</td>
<td>Fourier Number</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Forward reaction rate (s⁻¹)</td>
</tr>
<tr>
<td>$A$</td>
<td>Pre-factor (s⁻¹)</td>
</tr>
<tr>
<td>$f$</td>
<td>Fraction of colliding atoms having sufficient energy to cause the reaction</td>
</tr>
<tr>
<td>$P$</td>
<td>Probability of reaction</td>
</tr>
<tr>
<td>$\dot{N}$</td>
<td>Number flux of a specimen (m⁻²s⁻¹)</td>
</tr>
<tr>
<td>$n$</td>
<td>Number density of a specimen, unless specified otherwise (m⁻³)</td>
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<tr>
<td>$\beta$</td>
<td>Inverse of the molecular most probable thermal velocity (s/m)</td>
</tr>
<tr>
<td>$\dot{S}$</td>
<td>Surface regression rate (mm/s)</td>
</tr>
<tr>
<td>$P$</td>
<td>Probability of reaction</td>
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Chapter 1

Introduction

1.1 History and Background

The thermal protection heat shields form an integral part of any re-usable space vehicle. Design and material studies of heat shields take into account the amount of heat flux that is generated when the vehicle re-enters the atmosphere. The tremendous speed of re-entry forms a strong normal shock thereby generating high heat fluxes. An accurate estimate of heat flux requires the knowledge of the gas composition of the re-entry atmosphere. Analysis of spectra is one of the various methods that could be employed to obtain the composition of the re-entry atmosphere. Previous experiments [3] have gathered this data from an aircraft which was recording the spectra of the re-entry of the Stardust capsule from a safe distance. An improvement in this method would be to house the spectroscopic instruments on board of the re-entry vehicle, since this would reduce the loss of spectra due to atmospheric gas absorption. Recording the spectra on board would also allow the heat shield designers to gather data for the entire duration of the flight. A silica fiber, housed flush in the heat shield, would gather the radiation generated by gases in the shock layer. High temperatures generated by the shock and the reaction of the silica fiber with the constitutive gases are among the technical difficulties being studied in this report.
1.2 Objectives

The primary focus of this project was to consider factors that maximize the survivability of the fiber in the TPS wall. We used PICA as the TPS material for this study. Phenolic Impregnated Carbon Ablator or PICA is a pre-formed carbon fiber impregnated in a phenolic resin and was primarily developed by NASA Ames Research Center. When a silica fiber is housed within the TPS wall, we are looking at an unique case where the ablation products of the TPS might react with the fiber and corrode its surface. Chemical attack coupled with silica melting due to high incident heat flux would regress the fiber. The objective of this study is to analyze the causes of fiber recession and estimate the recession rate of the fiber because of chemical and thermal attack.

1.3 Thesis structure

The thesis consists of five chapters and each chapter represents an important step in analyzing the recession rate of the fiber. Chapter 2 deals with designing the TPS geometry and the two configurations selected to house the fiber. Chapter 3 discusses the results of the CFD simulations that were performed for the two configurations. The heat flux results from the CFD simulations are then converted into a melting rate for the fiber in Chapter 4. Chapter 5 is a report of molecular dynamics simulations run for calculating the chemical kinetics of the reaction pertinent to the fiber. In the last chapter, the topology changes of the fiber due to chemical attack and melting is discussed.
Chapter 2

Geometry and Mesh generation using GridPro

2.1 Objectives

Pre-processing of any CFD simulation starts with designing the geometry. For this study, the geometry is designed to simulate the ablation of TPS wall with a silica fiber embedded in it. The primary objective is to ensure the survivability of the fiber for the longest duration of time so that it can transmit the spectra emitted by the gases in the flow field. CFD simulations were performed for two geometries and the GridPro meshing software [4] was used to generate grids for these geometries.

2.2 Geometry selection criteria

Material thermal properties play an important role in selecting the topology of the geometry. Since the silica fiber has a lower melting point compared to TPS material, it has to be housed in the geometry in such a way that it transmits the maximum spectral data and remains protected from extreme temperatures and heat fluxes generated by the shock. TPS materials undergo chemical and thermal ablation, products of both, will affect the physical integrity of the fiber as well as the spectra it receives, since the spectra depends on the gas composition. Two geometries are selected which test the fiber optic environment.
2.2.1 Configuration 1: Fiber in a cavity

In 1967, to obtain the radiative heat intensity during re-entry, a radiometer was installed on Apollo 4 [5] and the design of this radiometer installation is shown in Fig. 2.1. The cavity shaped design of the radiometer protected the optical thermopile sensor from high incident heat flux. Based on this approach, a geometry is designed with the silica fiber housed within a cavity similar to Apollo 4 cavity design. The silica fiber traverses the entire length of the cavity, to maximize the time over which spectra potentially could be captured. A three dimension model of this geometry is shown in Fig. 2.2, the corresponding two-dimensional axisymmetric topology of this geometry is shown in Fig. 2.3, and the frontal and lateral surface of the fiber is shown in Fig. 2.4. This geometry is selected as configuration 1 in this study.

![Figure 2.1: Radiometer Cavity used in Apollo 4.](image1)

![Figure 2.2: Geometry of Configuration 1: Fiber in a cavity.](image2)
2.2.2 Configuration 2: Fiber in TPS

Configuration 1 is disadvantageous also because of its peculiar cavity shape. The by-products of ablation may get trapped in this cavity and might lead to reduction in spectra being captured by the fiber due to absorption. This can be avoided by sheathing the fiber directly in the TPS layer. Although the fiber front surface is directly exposed to the shock, the lateral surface of the fiber is well protected by the TPS. The silica fiber length is assumed to be the same as the thickness of TPS layer. The three dimensional geometry is shown in Fig. 2.5, and the two-dimensional axisymmetric topology of this configuration is shown in Fig. 2.6. This geometry is referred as configuration 2 in this study.
2.3 Mesh generation using GridPro

GridPro [4] can be described as a multi-block, object oriented grid generating software. GridPro generates very high quality grids by using a unique algorithm that automates the process of grid generation. It provides an interactive GUI where the user can specify the geometry and design using the Topology template. The unique algorithm of GridPro ensures that the grid elements are smooth and orthogonal throughout the domain of the specified geometry. GridPro was developed for NASA and finds its uses in many CFD simulations.

Good grids require higher discretization in regions such as the boundary layer, shock, etc.
where capturing the physics is important. Hence, for both configurations, generated grids are highly discretized in regions near the TPS walls, fiber and the region where the shock layer occurs. Generated grids are then imported to GASP as 2-dimensional axisymmetric plot-3d mesh.

### 2.3.1 Grid for Configuration 1: Fiber in a cavity

Regions near the fiber and the cavity are important in this configuration. These regions are therefore highly discretized compared to other regions in the flow field. The grid for configuration 1 employs 18,432 cells. The fiber has a diameter of 25 microns and is resolved using 16 cells on its frontal surface and 145 cells on its lateral surface and, the cavity is captured using $145 \times 33$ cells. The grid for configuration 1 is shown in Fig. 2.7. Figure 2.8 shows the grid around the fiber front and its lateral surface.

![Figure 2.7: Mesh for configuration 1: Fiber in a cavity.](image)
Figure 2.8: The grid of configuration 1 near the fiber front and its lateral surface: Fiber in a cavity (16 cells along the fiber front).

2.3.2 Grid for Configuration 2: Fiber in TPS

Configuration 2 is essentially modeled as a vertical wall in the flow. Regions near the TPS wall, the fiber, and a region between the shock and the wall are highly discretized with 27,648 cells being used to capture configuration 2. To control the mesh discretization, GridPro offers the users a ‘wrap’ function. This feature creates a localized discretization in the regions of interest, which in this case, is the fiber and the TPS wall. The wrap and the mesh for configuration 2 is shown in Fig. 2.9. A value of 32 cells are used to capture the region along the frontal face of the fiber and the TPS wall is assumed to be 0.01 m high and 96 cells traverse its frontal surface, as shown in Fig. 2.10.
Figure 2.9: Mesh for configuration 2: Fiber in TPS.
Figure 2.10: Close-up of the fiber region of configuration 2: Fiber in TPS (32 cells along the fiber front).
Chapter 3

CFD calculations using GASP

3.1 Objectives

A CFD analysis of TPS and fiber case is carried out in GASP CFD solver [6]. GASP is a structured/unstructured, multi-block CFD flow solver which solves the Reynolds Averaged Navier Stokes equation. A thermo-chemical database in GASP is used to define relevant chemical reactions for the flow. To understand the influence of geometry on flow field conditions, CFD simulations were run for the two geometries discussed in the previous chapter. Surface reactions were then modeled for the optimal geometry, by assigning reactions to each surface. Results from these simulations provide a description of the flow field conditions such as temperature, pressure, gas composition and incident heat flux, within the context of the GASP thermo-chemical equilibrium databases and models. Each case was first run without simulating surface reactions. Heat flux values from the CFD results then help in determining the optimal geometric configuration.

The Apollo 4 [1] flight experiment data was used to determine the free stream conditions, which are tabulated in Table 3.1. A constant wall temperature of 2500 K is assumed from the work of Park [5].

3.2 Thermo-Chemical database for CFD calculations

A thermo-chemical database was developed for CFD calculations in order to simulate the complex chemical reactions that occur in the hot gas regime in the strong shock created during atmospheric
reentry to the Earth. Eleven species (N$_2$, O$_2$, N, O, NO, N$_2^+$, O$_2^+$, N$^+$, O$^+$, NO$^+$, e$^-$) for air and 10 carbonaceous and hydrogen species (C, CO, CN, C$_2$H, C$_2$, C$_3$, H, H$_2$, C$^+$, H$^+$) generated from ablative surface reactions and pyrolysis gas blowing are considered. The chemical reactions of significance and their corresponding Arrhenius reaction rate coefficients used in the present work are listed in Table 3.2 and were obtained from Ref. [2]. The total number of chemical reactions for 21 gas species is 154 and the forward reaction rate coefficients are expressed as

$$k_f = CT^n \exp(-E_a/K_B T)$$  \hspace{1cm} (3.1)$$

where $E_a$ is the reaction activation energy, $T$ is the temperature controlling the reactions, and $K_B$ is the Boltzmann’s constant and $C$, $n$ and $E_a/K_B$ are reaction specific rate coefficient constants. The Arrhenius parameters $C$, $n$, and $E_a/K_B$ associated with each chemical reactions are tabulated in Table 3.2. To calculate the backward reaction rates, the equilibrium constants are calculated for each reaction at 3000, 6000, 9000, 12,000, and 15,000 K. The final values for a given temperature are fitted by an expression of the form,

$$K_e = \exp[A_1/Z + A_2 + A_3 \ln(Z) + A_4 Z + A_5 Z^2]$$  \hspace{1cm} (3.2)$$

where $Z = 10,000/T$. The parameters $A_1$-$A_5$ for each reaction are listed in Table 3.3 and are based on values given in Refs. [2] and [7]. Finally, the backward reaction rates, $k_r$, are calculated by assuming,

$$k_r = k_f/K_e$$  \hspace{1cm} (3.3)$$

The chemical reaction equations and the equilibrium constants discussed above are databased and used in the hypersonic commercial CFD software, GASP [8]. The internal energy of the gaseous species is modeled by Gordon-McBride curve fits [9] and the thermal conductivity and viscosity transport properties of the gas mixture are calculated by NASA CEA data originally developed by Svehla [10].

### 3.2.1 Surface reaction modeling in CFD

Neglecting heat transfer from vibrational non-equilibrium, a partially catalytic wall assumes that the species concentrations approach equilibrium at a finite rate. Surface reactions differ for TPS
and fiber surfaces but the reaction mechanism for both the surfaces is the same.

Reactions on TPS wall

The oxidation and nitridation reactions at the wall are expressed by

$$O + C(s) \xrightarrow{r_1} CO$$ (3.4)

$$N + C(s) \xrightarrow{r_2} CN$$ (3.5)

where C(s) is assumed to come from the ablative char surface material. Given the local gas equilibrium assumption at the wall temperature, the flux of atoms to the wall can be computed as follows:

$$N = \frac{N_A \rho}{4M} \sqrt{\frac{8K_B T_w}{\pi m}}$$ (3.6)

where $\rho$ and $m$ is the density and mass of either an O or N atom, $T_w$ is the wall temperature (or local flow temperature in the case of temperature jump at the wall), $K_B$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, and $M$ is the molar mass in kg/mol. When $N$ is multiplied by the surface reaction efficiency, $\gamma$, this expression translates into a reaction rate. The rates for oxidation and nitridation are

$$r_1 = \frac{\gamma_{CO} \rho O}{M_O} \sqrt{\frac{R_O T_w}{2\pi}}$$ (3.7)

$$r_2 = \frac{\gamma_{CN} \rho N}{M_N} \sqrt{\frac{R_N T_w}{2\pi}}$$ (3.8)

Park[11] used the values of $\gamma_{CO} = 0.63 \exp(-1160/T_w)$ and $\gamma_{CN} = 0.3$ for surface oxidation and nitridation reaction efficiencies, respectively, for Stardust re-entry calculations performed with a viscous shock layer (VSL) code. [12]. The value of $\gamma_{CN} = 0.3$ was originally obtained from Park’s shock-tube measurement [13] and has been used to estimate the efficiency of the surface nitridation efficiency ($\gamma_{CN}$) in Refs. [12, 14, 15]. However, the surface nitridation efficiency of Park was measured on a metal wire grid coated with carbon. In addition, the efficiency of surface reactions strongly depends on the roughness of the ablating material [12, 16] and especially, for the PICA ablator, accurate efficiency of surface oxidation and nitridation is not well established. Suzuki et al. obtained new temperature-dependent nitridation efficiencies for graphite test pieces exposed
in a plasma heated wind tunnel. The new nitridation efficiency was estimated to be \( \gamma_{CN} = 8.441 \times 10^{-3} \exp(-2232/T_w) \) for surface temperatures ranging from 1,351 to 1,723 K, which was found to be two orders of magnitude lower than Park’s efficiency (\( \gamma_{CN} = 0.3 \)). Furthermore, surface nitridation efficiency was also assumed to be negligibly small in the PICA ablator in the work of Milos et al. [16] and Driver et al. [18]. Although the chemical efficiency values of the surface nitridation and oxidation for the PICA ablator still need to be evaluated and updated, Park’s efficiency value, 0.4, which was calculated based on \( T_w = 2500K \) for CO and Driver’s value, 0.005 for CN formation are chosen, in this work.

Atomic oxygen and nitrogen formed due to dissociation in the shock layer undergo atomic recombinations reactions at the wall. These reactions are given as[12]

\[
\begin{align*}
O + O & \rightarrow O_2 + 5.08 \text{ eV} \quad (3.9) \\
N + N & \rightarrow N_2 + 9.8 \text{ eV} \quad (3.10)
\end{align*}
\]

The reaction rates for first-order recombination of oxygen and nitrogen atoms are

\[
\begin{align*}
r_3 &= \frac{\gamma_O \rho_O}{M_O} \sqrt{\frac{R_O T_w}{2\pi}} \\
r_4 &= \frac{\gamma_N \rho_N}{M_N} \sqrt{\frac{R_N T_w}{2\pi}}
\end{align*}
\]

and the recombination coefficients, \( \gamma_O \) and \( \gamma_N \), are input as user-defined constants in GASP.

Efficiency of catalytic recombination processes depends on thermal properties and roughness of material. In Refs. [12] and [19], it was assumed that catalytic recombination could be ignored because the nitridation and oxidation processes on a highly rough surface dominate compared to catalytic recombination. However to investigate the effect of the recombination surface reactions, values of 0.01 are specified for \( \gamma_O \) and \( \gamma_N \) in this work.

Mass balance at the wall is enforced by,

\[
-\rho D_i \frac{\partial Y_i}{\partial \eta} = \sum_{k=1}^{N_k} (\nu''_{k,i} - \nu'_{k,i}) r_k M_i
\]

where \( D_i \) is the mass diffusion coefficient and \( Y_i \) is the species mass fraction. \( \nu''_{k,i} \) and \( \nu'_{k,i} \) are
the stoichiometric coefficients of the reactants and products of species $i$ in reaction $k$ for the $N_k$ reactions. Conservation of mass at the surface means that the rate of diffusion away from the surface equals the rate of production of species caused by catalytic surface reactions. As previously mentioned, a total of 21 species chemical model is considered and CO and CN species are initially produced by oxidation and nitridation process, respectively, at the wall. The remaining carbonaceous species, C$_2$, C$_3$, C, are created from the gaseous chemical reactions. Finally, there are recombination reactions for N and O in Eqs. (3.9) and (3.10) and two more reactions for chemical ablation according to Eqs. (3.4) and (3.5). Therefore, the mass-conservation equations are as follows[8]

\[ -\rho D_{N_2} \frac{\partial Y_{N_2}}{\partial \eta} = 0 \]  
(3.14) 

\[ -\rho D_{O_2} \frac{\partial Y_{O_2}}{\partial \eta} = 0 \]  
(3.15) 

\[ -\rho D_{NO} \frac{\partial Y_{NO}}{\partial \eta} = 0 \]  
(3.16) 

\[ -\rho D_N \frac{\partial Y_N}{\partial \eta} = (-1) M_N (r_2 + r_4) \]  
(3.17) 

\[ -\rho D_O \frac{\partial Y_O}{\partial \eta} = (-1) M_O (r_1 + r_3) \]  
(3.18) 

\[ -\rho D_{CN} \frac{\partial Y_{CN}}{\partial \eta} = (1) M_{CN} (r_2) \]  
(3.19) 

\[ -\rho D_{CO} \frac{\partial Y_{CO}}{\partial \eta} = (1) M_{CO} (r_1) \]  
(3.20) 

A first-order discretization would therefore yield the following for $N$:

\[ \frac{(Y_N)_2 - (Y_N)_1}{\frac{1}{2} \Delta \eta} = \frac{\gamma_N}{D_N} \sqrt{\frac{R_N T_w}{2\pi}} (Y_N)_1 \]  
(3.21) 

**Reactions on Fiber surface**

Quartz (silica) was the material of choice for the fiber in this simulation. Because of thermal and chemical ablation of the TPS, there is presence of carbonaceous species in the region around the fiber.

At temperatures above 1000 C, the TPS generated carbon residue begins to react with SiO$_2$. 

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Work by Henderson and Tant [20] showed the following exothermic reactions can occur,

\[
\text{SiO}_2\text{solid} + 3C \rightarrow \text{SiC} + 2\text{CO} \quad (3.22)
\]
\[
\text{SiO}_2\text{solid} + 2C \rightarrow \text{Si} + 2\text{CO} \quad (3.23)
\]
\[
\text{SiO}_2\text{solid} + C \rightarrow \text{SiO} + \text{CO} \quad (3.24)
\]

Additionally, work by Miller, Lee and Cutler [21], showed that the most important reaction is Eq. 3.24. The catalytic efficiency of this reaction was assumed \(\gamma = 0.73\) in thermo-chemical database for silica carbon surface reaction.\(^1\)

Work by Yang, Shan Janssen, Schneider, Ohji and Kanzai [22] have noted that molecular nitrogen reacts with silica. Most of the nitrogen molecules from the free stream are dissociated in the shock region. This leads to lower concentration of molecular nitrogen as compared to atomic nitrogen. Hence, this reaction was not modeled for gas surface reaction simulations.

### 3.3 CFD Results from GASP

**3.3.1 Configuration 1: Fiber in a cavity**

The TPS material as well as the fiber, will undergo ablation because of high temperatures generated by the shock. Because the fiber has a lower melting point of around 1800 K, it will ablate much quicker than the TPS. Initially, the fiber will span the entire length of the cavity but the fiber tip will melt and partially recede in the cavity. The cavity shape could possibly protect the fiber until the cavity material ablates. If so, the fiber would have more time to transmit the spectra, as compared to the case when the fiber is embedded in the TPS and its tip is flushed with the TPS surface. Temperatures reach high values in the shock region, but are comparatively lower in the cavity.

Temperature contours for this case are shown in Fig. 3.1. Stagnation line temperature values seen in Fig. 3.2 show a peak temperature of 20,000 K. High heat flux values, shown in Fig. 3.3 are incident on the lateral surface of the fiber (see Fig. 2.4) and to protect the fiber from melting,

\(^1\)This value was assumed after discussions with Dr. Adri Van Duin, who provided this estimate based on his previous analysis.

The Pennsylvania State University.
the initial length of the fiber can be shortened, hence reducing the heat flux on the lateral surface. Because of the shape of the cavity, ablation products tend to accumulate in the cavity, which eventually affects the quality of the incident radiation being captured by the fiber. Thus, to ensure the longevity of the fiber and to have optimum levels of spectra reaching the fiber, the fiber has to be sheathed within the TPS layer.

![Temperature contour of configuration 1: Fiber in a cavity](image)

Figure 3.1: Temperature contour of configuration 1: Fiber in a cavity

### 3.3.2 Configuration 2: Fiber in TPS

Because of the TPS cladding surrounding, the fiber is protected for a longer time as compared to the first configuration. Heat flux to the fiber is incident only on the frontal surface. CFD simulations on this configuration are run in two steps. The first case of this configuration was run without simulating the surface reactions and the second simulation was run with surface reactions coupled to the respective surfaces.
Figure 3.2: Stagnation line temperature plot of configuration 1: Fiber in a cavity

Figure 3.3: Heat flux incident on lateral surface of fiber of configuration 1: Fiber in a cavity

Figure 3.4: Temperature contour of configuration 2: Fiber in TPS without surface reactions
Configuration 2: Fiber in TPS without surface reactions

Temperature contours for configuration 2, without surface reaction modeling are shown in Fig. 3.4. The temperature along the stagnation line is shown in Fig. 3.5 and the heat flux values along the frontal surface of the fiber are shown in Fig. 3.6. Total species concentration along the stagnation line is shown in Fig. 3.7. The absence of recombination reactions on the surfaces results in a strong concentration of atomic N and O accumulates near the surface. A contour plot of atomic nitrogen in Fig. 3.8, shows high number density of atomic nitrogen along the surfaces.

Configuration 2: Fiber in TPS with surface reactions

Gas-surface reactions are simulated for the TPS surface and silica fiber in this final case. Temperatures contours for this configuration are shown in Fig. 3.9, and overall gas composition along the stagnation line is shown in Fig. 3.10. CO formation at the TPS wall starts when atomic oxygen, formed due to dissociation of oxygen molecule in the shock, collides with the carbon surface of the wall. Similarly, atomic nitrogen, formed due to dissociation of nitrogen molecules, reacts with the carbon surface and forms CN.

Surface emitted CO and CN molecules then undergo dissociation forming atomic carbon, atomic
Figure 3.7: Stagnation line gas number density plot of configuration 2: Fiber in TPS, without surface reactions

Figure 3.8: Number density contour of atomic nitrogen for configuration 2: Fiber in TPS, without surface reactions

Figure 3.9: Temperature contour of configuration 2: Fiber in TPS, with surface reactions
oxygen and atomic nitrogen. The concentration of gaseous atomic carbon in the flow can be seen from the number density plot of carbon shown in Fig. 3.11. Fiber reactions with atomic carbon will start only after there are sufficient carbon atoms near the fiber. Thus, the CO number density will tend to be higher near TPS wall than near the fiber, as seen from Fig. 3.12. From the number density contour of CN, it is verified that the reactions are indeed assigned to the correct surfaces in the GASP software. The CN number density presented in Fig. 3.13 shows that CN forms only along the TPS wall since there is no N – SiO$_2$ gas surface reaction.

As mentioned earlier, the surface recombination reactions are not modeled along the fiber surface and this leads to a higher concentration of dissociated atomic oxygen and nitrogen atoms in front of the fiber. This is shown in Figs. 3.14 and 3.15.

The gas-surface reaction simulations were modeled without any user defined blowing condition.

A peak stagnation temperature of 20,000 K is seen in Fig. 3.16. Heat flux values along the frontal face of the fiber can be seen in Fig. 3.17 and a heat flux value of $\dot{q} = 2.5 \times 10^7$ (W/m$^2$) is used to calculate the burn rate of the fiber. Fore-body heat-shield qualification work on stardust PICA by Tran et al. [23] reported similar working heat flux values. The atomic carbon density near the fiber and the atomic oxygen density along the TPS wall will be used to calculate the surface number flux and consequently the regression rate of both surfaces due to chemical attack.
Figure 3.12: CO number density contour of configuration 2: Fiber in TPS, with surface reactions.

Figure 3.13: CN number density contour of configuration 2: Fiber in TPS, with surface reactions.

Figure 3.14: Atomic oxygen number density contour of configuration 2: Fiber in TPS, with surface reactions.

Figure 3.15: Atomic nitrogen number density contour of configuration 2: Fiber in TPS, with surface reactions.
Figure 3.16: Stagnation line temperature plot of configuration 2: Fiber in TPS with surface reactions.

Figure 3.17: Heat flux incident on frontal surface of fiber for configuration 2: Fiber in TPS with surface reactions.
Table 3.1: Freestream conditions of flow calculation [1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m$^3$)</td>
<td>$3.41 \times 10^{-4}$</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>238.47</td>
</tr>
<tr>
<td>Velocity (km/s)</td>
<td>10.252</td>
</tr>
<tr>
<td>$N_2$ mole fraction (%)</td>
<td>79</td>
</tr>
<tr>
<td>$O_2$ mole fraction (%)</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3.2: Reaction rate coefficient, $k_f = C T^n \exp(-E_a/K_B T)$ [2]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$C^{n}$</th>
<th>$n$</th>
<th>$E_a/K_B$ (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2 + M \rightarrow N + N + M$</td>
<td>7.0$^{18}$</td>
<td>-1.6</td>
<td>113,200</td>
</tr>
<tr>
<td>$N_2 + A \rightarrow N + N + A$</td>
<td>3.0$^{19}$</td>
<td>-1.6</td>
<td>113,200</td>
</tr>
<tr>
<td>$O_2 + M \rightarrow O + O + M$</td>
<td>2.0$^{18}$</td>
<td>-1.5</td>
<td>59,360</td>
</tr>
<tr>
<td>$O_2 + A \rightarrow O + O + A$</td>
<td>1.0$^{19}$</td>
<td>-1.5</td>
<td>59,360</td>
</tr>
<tr>
<td>$C_2 + M \rightarrow C + C + M$</td>
<td>3.7$^{11}$</td>
<td>0</td>
<td>69,900</td>
</tr>
<tr>
<td>$CN + M \rightarrow C + N + M$</td>
<td>2.5$^{11}$</td>
<td>0</td>
<td>87,740</td>
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<td>$H_2 + M \rightarrow H + H + M$</td>
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<td>48,300</td>
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<td>3.0$^{21}$</td>
<td>-1.6</td>
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<td>$O + e \rightarrow O^+ + e + e$</td>
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<td>-3.78</td>
<td>158,500</td>
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<tr>
<td>$N + e \rightarrow N^+ + e + e$</td>
<td>2.5$^{31}$</td>
<td>-3.82</td>
<td>168,200</td>
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<tr>
<td>$C + e \rightarrow C^+ + e + e$</td>
<td>3.7$^{28}$</td>
<td>-3.00</td>
<td>130,720</td>
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<tr>
<td>$H + e \rightarrow H^+ + e + e$</td>
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<td>-2.80</td>
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<td>$NO + O \rightarrow O_2 + N$</td>
<td>8.4$^{9}$</td>
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<td>$CO + C \rightarrow C_2 + O$</td>
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<td>58,000</td>
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<td>$CO + N \rightarrow CN + O$</td>
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<td>38,600</td>
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<td>0.1</td>
<td>14,600</td>
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<td>$CN + C \rightarrow C_2 + N$</td>
<td>5.0$^{10}$</td>
<td>0</td>
<td>13,000</td>
</tr>
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<td>$CO + C_2 \rightarrow C_3 + O$</td>
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<td>0</td>
<td>41,200</td>
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<td>$C_3 + N \rightarrow CN + C_2$</td>
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<td>$C_3 + C \rightarrow C_2 + C_2$</td>
<td>1.0$^{9}$</td>
<td>0</td>
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<td>$C_2H + H \rightarrow C_2 + H_2$</td>
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<td>$O + N \rightarrow NO^+ + e$</td>
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<td>31,900</td>
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<td>$N + N \rightarrow N_2^+ + e$</td>
<td>4.4$^{14}$</td>
<td>1.5</td>
<td>67,500</td>
</tr>
</tbody>
</table>

$^a$ $C$ has the units of $(m^3/s)$
Table 3.3: Parameters for equilibrium constants [2]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$A_5$</th>
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<tbody>
<tr>
<td>$N_2 + M \rightarrow N + N + M$</td>
<td>-3.293682</td>
<td>0.998998</td>
<td>-8.237028</td>
<td>-5.526183</td>
<td>-0.582174</td>
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<tr>
<td>$O_2 + M \rightarrow O + O + M$</td>
<td>1.578640</td>
<td>2.688744</td>
<td>4.215573</td>
<td>-8.091354</td>
<td>0.174260</td>
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<tr>
<td>$C_2 + M \rightarrow C + C + M$</td>
<td>2.538863</td>
<td>1.782394</td>
<td>5.753987</td>
<td>-10.296164</td>
<td>0.296264</td>
</tr>
<tr>
<td>$CN + M \rightarrow C + N + M$</td>
<td>1.360714</td>
<td>0.958930</td>
<td>2.726324</td>
<td>-9.879787</td>
<td>0.044408</td>
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<td>$H_2 + M \rightarrow H + H + M$</td>
<td>1.817328</td>
<td>1.202335</td>
<td>4.427498</td>
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<td>0.185211</td>
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<td>$N_2 + e \rightarrow N + N + e$</td>
<td>-3.293682</td>
<td>0.998998</td>
<td>-8.237028</td>
<td>-5.526183</td>
<td>-0.582174</td>
</tr>
<tr>
<td>$O + e \rightarrow O + O + e$</td>
<td>0.614124</td>
<td>-6.755241</td>
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<td>-16.003456</td>
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<td>$N + e \rightarrow N + N + e$</td>
<td>0.200588</td>
<td>-3.965871</td>
<td>-0.041731</td>
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<td>$N_2 + O \rightarrow NO + N$</td>
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<td>-7.693047</td>
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<td>$NO + O \rightarrow O_2 + N$</td>
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<td>-1.768215</td>
<td>-4.759554</td>
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<tr>
<td>$CO + C \rightarrow C_2 + O$</td>
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<td>1.852541</td>
<td>-5.069929</td>
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<td>$CO + O \rightarrow O_2 + C$</td>
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<td>$CO + N \rightarrow CN + O$</td>
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<td>1.776403</td>
<td>-4.373308</td>
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<tr>
<td>$C_3 + N \rightarrow CN + C_2$</td>
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<td>-5.060829</td>
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<td>0.035551</td>
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<td>-7.434149</td>
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<td>$N + N \rightarrow N_2^+ + e$</td>
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<td>-5.822935</td>
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<td>0.188105</td>
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</table>
Chapter 4

Heat Flux calculations

4.1 Objectives

Even with due precautions taken in designing the topology, the fiber will undergo recession because of melting and chemical attack. The fiber receives heat from the incident heat flux, values of which are shown in Fig. 3.17 and quartz fiber has a melting point of around 1700 K. A mathematical model is generated to calculate the fiber melting rate due to incident heat flux by using a transient heat transfer calculation.

4.2 Transient Heat Transfer calculation

4.2.1 Biot Number

Heat transfer to any solid body will encounter resistance at its surface and within the body. The ratio of heat transfer resistance inside the body to the resistance at the surface of the body is known as the Biot number. This number provides an estimate of the temperature gradients within the solid body when it heats up or cools down due to convection. Mathematically, the Biot number can be defined as,

\[ B_i = \frac{hL_c}{k_b} \]  

where, \( h \) is the convective heat transfer coefficient, \( L_c \) is the characteristic length and \( k_b \) is the thermal conductivity of the body.
The convective heat transfer coefficient is calculated from the heat flux by the following equation,

\[
\dot{q} = h dT
\]  

(4.2)

where, \(dT\) is the difference between the flow and surface temperatures, and \(\dot{q}\) is heat flux incident on the surface.

For the silica fiber, a typical value of heat flux incident on the fiber was found to be, \(\dot{q} = 2.5 \times 10^7 \text{ (W/m}^2\text{)}\) from the CFD simulations, \(T_{surf} = 300 \text{ K}\) was the initial temperature of the fiber and a free stream temperature of, \(T_\infty = 2500 \text{ K}\) was considered. Substituting these values into Eq. 4.2, the value of the convective heat transfer coefficient is, \(h = 11.363 \times 10^3 \text{ (W/m}^2\text{K)}\).

Since heat transfer is considered only along the long axis of the fiber and the heat flux is incident only on the fiber tip, the characteristic length of the fiber is considered to be its diameter, \(L_c = 4.8 \times 10^{-4} \text{ m}\). The thermal conductivity of selected materials was documented by Powell et al. [24] and the thermal conductivity of high quality quartz at high temperatures is provided as, \(k_b = 4.0 \text{ (W/mK)}\). Substituting the values of the convective heat transfer coefficient, the thermal conductivity and the characteristic length into Eq. 4.1, we calculate the value of the Biot number, \(B_i = 1.3\).

### 4.2.2 Melting time calculation

Heat transfer problems having a Biot number less than 0.01 can be approximated using the lumped capacitance method which assumes that the temperature distribution is uniform within the solid. For larger Biot number, such as what we obtained, it is necessary to solve the transient heat transfer equation.

The transient heat transfer equation, with constant thermal conductivity and without internal heat generation is given as,

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}
\]  

(4.3)

where, \(\alpha = \text{thermal diffusivity of the fiber}\), which is given by,

\[
\alpha = \frac{k_b}{\rho C_p}
\]  

(4.4)

In order to non-dimensionalize the governing equation 4.3, relevant variables are arranged in suitable
groups. Temperature difference is considered as a separate group and is given as, \( \theta = T - T_{\infty} \). The maximum possible temperature difference group is given as, \( \theta_i = T_i - T_{\infty} \), where, \( T_i \) = initial temperature of the solid and \( T_{\infty} \) = surrounding temperature. A dimensionless form of these dependent variables is defined as,

\[
\theta^* = \frac{\theta}{\theta_i} = \frac{T - T_{\infty}}{T_i - T_{\infty}}
\]

using a non-dimensionalization for length as,

\[
x^* = \frac{x}{L}, \text{ dimensionless spatial coordinate}
\]

and a non-dimensionalized time is given as,

\[
t^* = \frac{\alpha t}{L^2} = F_o
\]

where, substituting \( F_o \) = Fourier number in Eq. 4.3, the heat equation becomes,

\[
\frac{\partial^2 \theta^*}{\partial x^*^2} = \frac{\partial \theta^*}{\partial F_o}
\]

Assuming that the heat flow occurs only along the centerline of the fiber, an approximate one term solution to Eq. 4.8 is given by Incropera et al. [25]. The non-dimensionalized centerline temperature expression for Eq. 4.5 is given as,

\[
\theta^*_{o} = \frac{T_o - T_{\infty}}{T_i - T_{\infty}} = C_1 \exp (-\zeta_1^2 F_o)
\]

For \( Bi = 1.3 \), coefficients \( C_1 = 1.1275 \) and \( \zeta_1 = 0.9201 \) radian are given by Incropera [25]. The rate of fiber melting is the same as the time it takes the fiber to reach a centerline temperature of \( T_o = 1700 \) K from its initial temperature of \( T_i = 300 \) K for a given length.

Substituting these values into Eq. 4.9, we obtain a Fourier number \( F_o \) of 1.3366. The specific heat capacity of quartz is provided by Hemingway [26], \( C_p = 74.45 \) J/mol – K. Dividing by the molecular weight of quartz, \( m = 60.08 \times 10^{-3} \) Kg/mol, the value of the specific heat of quartz is, \( C_p = 1.2391 \times 10^3 \) J/KgK. The value of the quartz density is assumed as, \( \rho = 2650 \) Kg/m\(^3\). From the values of \( C_p, \rho \) and \( k_b \) in Eq. 4.4, we get \( \alpha = 1.2181 \times 10^{-6} \) m\(^2\)/s.
A relationship between the melting length and the time is derived by substituting values of $F_o$ and $\alpha$ into Eq. 4.7,

$$L = \sqrt{\frac{\alpha t}{F_o}} = \sqrt{9.1134 \times 10^{-7} \times t}$$

(4.10)

From Eq. 4.10, we can estimate that assuming the fiber remains in the flow for 1 second, it will lose 0.9546 mm length because of melting.
Chapter 5

ReaxFF MD simulations

5.1 Objectives

At temperatures above 1500 K, the silica fiber is susceptible to reactions with the gas species present in its vicinity. Among these gas species, atomic carbon has a strong presence in the flow field. Work by Miller, Lee and Cutler [21] shows that this reaction is possible

$$\text{Si}_x\text{O}_{2x}(s) + \text{C}(g) \rightarrow \text{Si}_x\text{O}_{2x-1}(s) + \text{CO}(g) \quad (5.1)$$

This gas-surface reaction removes surface material from the quartz fiber and has the potential to introduce new chemical species into the region surrounding the fiber. The value of the forward reaction rate $k_c$ and the equilibrium constant for reaction 5.1 is calculated using molecular dynamics package known as ReaxFF [27]. Since this was first such study to consider the use of silica fibers in hypersonic shock layers, molecular dynamics calculation are necessary because, to the best of author’s knowledge, reaction rates for gas-surface carbon-silica reaction have not been measured or calculated prior to this work. The ReaxFF molecular dynamics package can be used to simulate collision of atoms and molecules of carbon species on a silica lattice in real time. The ReaxFF simulations thus provide reaction rates which are then translated into a macroscopic recession rate for the silica fiber.
5.2 Determination of the Forward Rate Coefficient

The forward reaction rate for Eq. 5.1 is expressed in Arrhenius form as,

\[ k_c = A \exp \left( -\frac{E_a}{K_B T} \right) \]  

(5.2)

where \( E_a \) is an activation energy of the chemical reaction, \( T \) is the temperature controlling the reactions, and \( K_B \) is the Boltzmann constant. \( A \) is known as the pre-factor and it represents the frequency of collision of the reacting gas species onto a surface. Treating Eq. 5.1 reaction as first order, the rate of gaseous carbon monoxide concentration, \([CO(g)]\) may be expressed as the function of time by,

\[ \frac{d[CO(g)]}{dt} = k_c[CO(g)] \]  

(5.3)

The rate of reaction can be determined by studying the number of CO molecules formed as a function of time. This reaction is simulated at five temperatures, ranging from 1500 to 2500 K to provide gas-surface reaction rates for the conditions predicted by the CFD results. Also, the rate of reaction is a function of time as well as temperature. Using the ReaxFF MD program, simulations at 2500 K, seven unique lattices were generated from the original energy minimized lattice. Silica lattice structure is different in each of the seven cases, thus making these cases unique and independent, even though the number of atoms in each lattice is the same. Atomic carbon collisions on these seven lattices are simulated at each temperature to ensure that the simulations cover all different carbon atom impingement angles, thereby giving us a good statistical prediction of the reaction products. A plot of the natural logarithm of the CO molecules formed as a function of time gives \( k_c \) at each temperature. Equation 5.2 shows that if the logarithm of the rate coefficient is plotted as a function of inverse temperature, the intercept and slope of the straight line gives \( \ln A \) and \( \frac{E_a}{K_B} \) respectively. Thus Arrhenius parameters are known and can be used in the macroscopic recession rate calculations.

5.3 Specific information about simulations in ReaxFF

The ReaxFF molecular dynamics software simulates reactions using the reactive force fields method [27]. The starting point of each simulation is the base lattice geometry on which atomic and molecular
interactions are simulated. For this case, the simulation models the interaction of carbon atoms on the silica lattice. The silica lattice can be made using a molecule building software such as MOLDEN [28] or Accelrys Material Studio. The lattice file is used by the ReaxFF software in the geometry biograph file format. The interactions and collisions of atoms and molecules are controlled by force field files. Velocity and structure of the colliding particle is provided to ReaxFF by addmol.vel and addmol.bgf files respectively. The control file dictates the temperature of the system, it supplies the software with information regarding the ensemble to be used for a particular simulation, the size of each time step, and the number of iterations.

There are two steps in simulating collisions for a gas-surface reaction. The lattice of silica generated by the molecule building software, will have many anomalies since the lattice structure is not optimized for lowest possible energy. In order to achieve the lowest possible energy of the lattice, we perform energy minimization of our lattice using ReaxFF. The energy minimized structure is then heated up to a temperature of 2500 K. Heating the lattice structure will modify the configuration of the silica lattice to produce a more randomized structure. This step is configured to generate seven different structure files, which are then used for the final NVT MD simulation. An NVT simulation means that the number of particles, volume, and temperatures of the system are maintained at constant values. The selected temperature of the system is maintained using a Berendsen thermostat. The time step for every iteration is 0.25 pico seconds and the simulations are run for $5 \times 10^5$ iterations.

There are three primary outputs of every ReaxFF simulation. The main output file is called xmolout and it contains the Cartesian co-ordinates of each particle at every time step. This file is viewed using MOLDEN. The mole fraction of the products are given as an output in the molfra.out file and energy of the entire system along with the temperature at every time step is printed out in the summary.txt file.

Figure 5.1 shows a screen shot from one of the simulations. Red, golden, and gray spheres represent the oxygen, carbon, and silicon atoms respectively.

### 5.4 Simulation Results

Due to the lattice differences in the seven structures, the rate of CO molecule formation varies even for an NVT-MD simulations at the same temperature. For each temperature, the number of
CO molecules formed is therefore averaged over seven simulations. The natural logarithm of the number of CO molecules formed is plotted as a function of time at five temperatures in Fig. 5.2. From the figure, we can see that this is not a linear curve and there are two possible explanations for the non-linearity. First order chemical reactions will exhibit linear profile, which means that Eq. 5.1 might not be a first order reaction. Also, after observing the simulations, we notice that in the first 70 ps of the simulated time, the impinging carbon atom either reacts with the silica surface to form a CO molecule or it attaches to the silica surface. After this initial period, most of colliding carbon atoms react to form the CO molecule. This could be another plausible explanation for the linearity in the curve between 70 to 125 ps, shown “linear fit 2” in Fig. 5.2. For the purpose of the reaction rate analysis, we are interested in the region where the reaction has achieved steady
state and hence we take the slope values from the “linear fit 2” region of the curves. The slope of the linear fit of each curve will represent the reaction rate at that temperature. The values of the reaction rates are provided in Table. 5.1.

Figure 5.2: Natural logarithm of the number of CO molecules created versus simulated time.

The natural logarithm of the calculated slope is then plotted versus the inverse of system temperature. The linear fit relation of the data points, as shown in Fig. 5.3, will provide us with the Arrhenius parameters of Eq. 5.1. From Fig. 5.3, we get the linear fit relation as $y = -796.11x + 22.93$ where the logarithmic form of Arrhenius equation is given as:

$$\ln (k_c) = -\frac{E_a}{R \cdot T} + \ln A \quad (5.4)$$

Comparing the linear fit relation with Eq. 5.4, at $T = 1500$, the computed value of pre-factor is $A = 9.085 \times 10^9 \text{ s}^{-1}$ and the activation energy of the reaction is $E_a = 6.618 \text{ KJ/mol} - K$. Substituting computed values of the pre-factor and the activation energy into Eq. 5.2, the forward reaction rate for the reaction is $k_c = 5.341 \times 10^9 \text{ s}^{-1}$. 
Of all the impinging carbon atoms on the silica lattice, only a fraction will result in reaction 5.1. This fraction is calculated from Eq. 5.5 as \([29]\),

\[
    f = \exp\left(\frac{-E_a}{RT}\right)
\]

This represents the fraction of sufficiently energetic collisions that actually result in a reaction and for Eq. 5.1, \(f\) has a value of 0.588 at 2500 K. The main reaction products predicted by the ReaxFF are provided in Table 5.2. Based on this table, it can be seen that the reaction given by Eq. 5.1 is the dominant process and the probability of CO formation for every colliding carbon atom is roughly about 50 percent.
Table 5.1: Slope of the linear fit of the logarithm of number of CO molecules created. (see Fig. 5.2)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Reaction rate$^b$</th>
<th>Constant of integration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>5.565 × 10^{-3}</td>
<td>2.962</td>
</tr>
<tr>
<td>1750</td>
<td>6.354 × 10^{-3}</td>
<td>2.995</td>
</tr>
<tr>
<td>2000</td>
<td>6.871 × 10^{-3}</td>
<td>2.886</td>
</tr>
<tr>
<td>2250</td>
<td>5.510 × 10^{-3}</td>
<td>3.083</td>
</tr>
<tr>
<td>2500</td>
<td>6.248 × 10^{-3}</td>
<td>3.054</td>
</tr>
</tbody>
</table>

$^b$ Units of reaction rate are (ps)$^{-1}$.

Table 5.2: Primary reaction products predicted by ReaxFF at 2500 K after 0.5 × 10^6 iterations

<table>
<thead>
<tr>
<th>Lattice number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Carbon atoms</td>
<td>101</td>
<td>101</td>
<td>101</td>
<td>101</td>
<td>101</td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon stuck on silica surface</td>
<td>10</td>
<td>24</td>
<td>19</td>
<td>22</td>
<td>13</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>CO molecules</td>
<td>47</td>
<td>42</td>
<td>48</td>
<td>42</td>
<td>42</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>CO$_2$ molecules</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C$_2$ molecules</td>
<td>14</td>
<td>9</td>
<td>9</td>
<td>6</td>
<td>13</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Unreacted C atoms</td>
<td>15</td>
<td>13</td>
<td>15</td>
<td>13</td>
<td>11</td>
<td>11</td>
<td>9</td>
</tr>
</tbody>
</table>
Chapter 6

Regression Rate calculations

6.1 Objectives

An assessment of the recession rate of the silica fiber and the TPS wall was made from surface number flux values of the chemical attack species from CFD results and their respective probability of reaction. A short code was written to calculate the topology of the recessed surface as a function of elapsed time.

6.2 Recession rate: TPS wall

The TPS wall will undergo recession due to chemical ablation by atomic oxygen. This chemical reaction is given as,

\[ \text{C}(_{\text{s}}) + \text{O} \rightarrow \text{CO} \]  \hspace{1cm} (6.1)

where, \( \text{C}(_{\text{s}}) \) is a carbon atom at the wall surface and the atomic oxygen and CO species are gaseous. Previous work on gas-surface collision by Titov et al. [30] showed that a simple calculation can be used to estimate the mass loss due to this gas-surface reaction. Atomic oxygen in the flow field collides with the TPS wall with a number flux normal to the wall, \( \dot{N} \), which is given as,

\[ \dot{N} = \frac{n_o}{2\sqrt{\pi\beta}} \]  \hspace{1cm} (6.2)
where, \( n_o \) is atomic oxygen number density and \( \beta \) is reciprocal of the molecular most probable thermal velocity, given as,

\[
\beta = \sqrt{\frac{m}{2K_B T}} \quad (6.3)
\]

where, \( K_B \) is the Boltzmann constant and \( m = 16 \times 1.6605 \times 10^{-27} \text{ kg/mol} \) is the mass of an oxygen atom.

The surface regression rate is related to mass loss by this relation,

\[
\dot{S} = \left( \frac{\dot{N}}{n_c} \right) P \quad (6.4)
\]

where, \( n_c = 1.575 \text{ gm/cc} \) is carbon mass density and \( P \) is the fraction of total collisions resulting in Eq. 6.1. Using typical values of oxygen number density in the boundary layer as seen in Fig. 3.10, \( n_o \approx 1.5 \times 10^{23} \text{ m}^{-3} \), at a temperature of \( T = 2500 \text{ K} \) and the probability of Eq. 6.1 as \( P = 0.9 \), an approximate regression rate of, \( \dot{S} \approx 0.6 \text{ mm/s} \), is calculated.

### 6.3 Recession rate: Silica Fiber

As was shown in Eq. 5.1, carbon atoms collide with the fiber front and erode the silica surface. The atomic carbon gaseous specimen is created in the flow due to dissociation of CO and CN. The number flux of atomic carbon normal to the fiber can be calculated by using an analysis similar to that for the TPS wall regression. The number flux of carbon is given by,

\[
\dot{N} = \frac{n_c}{2\sqrt{\pi \beta}} \quad (6.5)
\]

where, \( n_c \) is the number density of atomic carbon, \( \beta \) is given by Eq. 6.3, where now, \( m = 12.011 \times 1.6605 \times 10^{-27} \text{ kg/mol} \) is mass of a carbon atom. The recession rate for silica fiber is given by,

\[
\dot{S} = \left( \frac{\dot{N}}{n_{si}} \right) P \quad (6.6)
\]

The probability of carbon silica gas surface reaction was calculated as \( P = 0.5 \), in section 5.4. Assuming an approximate carbon number density value from Fig. 3.10, \( n_c = 1 \times 10^{22} \text{ m}^{-3} \) near the fiber and the density of silica as, \( n_{si} = 2.65 \text{ gm/cc} \), the calculated silica recession rate is
\( \dot{S} \approx 0.3 \text{ mm/s}. \) This recession rate represents recession by chemical attack only and does not include recession due to melting caused by the incident heat flux.

### 6.4 Changes in Topology due to recession

By employing an axisymmetric grid, a three-dimensional CFD analysis of the flow, was simplified to a two-dimensional model. Hence, a section of the right edge of the grid for configuration 2 represents the fiber and the TPS wall boundaries, as seen in Fig. 6.1. Each highlighted cell corresponds to a small flow field region adjacent to the surface of the fiber and the TPS wall. Due to recession, the location of the fiber and the TPS surface points will change as function of time. The recession rate for the TPS wall is modeled using Eq. 6.4, where \( \dot{S} \) is a function of the surface temperature and the local atomic oxygen mass density. Similarly, the recession rate of the fiber is modeled using Eq. 6.6, where \( \dot{S} \) is a function of the surface temperature and local atomic carbon mass density. The temperature and the mass density of atomic oxygen and atomic carbon at each node of the highlighted cell is provided in a data file format from the GASP CFD simulations.

Figure. 6.2 shows the effects of recession on the topology over 5 seconds. Fiber melting due to incident heat flux is also modeled in this figure, by using the recession rate calculated in Sec. 4.2.2.
Figure 6.1: Cells along Fiber and TPS boundary in configuration 2 grid.

Figure 6.2: LHS: Regression of TPS and Fiber surfaces RHS: Close-up view of Fiber regression.
Chapter 7

Conclusions and recommendations

The objective of this study was to understand the exact mechanisms by which the fiber will recess and how it will affect the transmitted spectra. High incident heat flux due to a strong normal shock causes the most damage to the fiber. A separate cooling sleeve made up of copper can be used to cover the fiber before it is placed within the TPS layer. This will conduct the heat away from the fiber and keep it cool for a longer duration. It was seen that the gas composition of the flow field changed due to gas-surface reactions taking place on the fiber. The reaction mechanisms for this reaction were modeled based on the results of the ReaxFF molecular dynamics simulation. Although we ran these simulations on seven different lattices, running these simulations on more lattices would improve the statistical results. This analysis was carried out specifically for the quartz (silica) fiber, but a similar analysis could also be done for sapphire fibers.

This project can be carried forward to estimate of the spectra viewed by the fiber. A radiation code could be used to model the spectra, based on the gas composition predicted by GASP CFD code.
Bibliography


The Pennsylvania State University.
