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Theoretical study on the micro-scale oxidation of resin-infused carbon ablators

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ABSTRACT

When subjected to high enthalpy air, phenolic-impregnated carbon-based ablative thermal protection systems undergo oxidation of their carbon fiber substrate and carbonized phenolic matrix. The oxidation process is governed by the competition between reaction and diffusion within the porous material and occurs at a range of depths depending on the flow conditions, the material chemical composition, and the material micro-structure. This study aims to examine the effects of the distribution of carbonized phenolic matrix on the oxidation behavior of carbon fiber materials, with the goal of guiding future material design. The oxidation is simulated on ideal geometries and on representations of actual fibrous carbon preforms obtained from X-ray microtomography. Diffusion is simulated using a random walk technique with a linear interpolation method for surface collisions. Oxidation reactions are simulated using a sticking probability law. It is shown that the oxidation characteristics, particularly the oxidation depth, are strong functions of the Thiele number and that the effect of the matrix distribution within the fibers is more pronounced at low Thiele regimes.

1. Introduction

Atmospheric entry missions require the use of thermal protection systems (TPS) to mitigate the aerothermal loads experienced at hypersonic conditions. One successful class of TPS materials are light-weight carbon phenolic ablators, built upon a carbon fiber preform and impregnated with phenolic resin. The phenolic impregnation improves mechanical properties [1] and limits oxygen penetration into the material. During entry, the phenolic resin pyrolyzes [2], causing a blow back of pyrolysis gases into the boundary layer. During pyrolysis, the phenolic resin undergoes carbonization, also referred to as charring, which produces a structure of pseudo-graphitic carbon left within the carbon fiber substrate. Depending on the impregnation and curing process of the phenolic resin, as well as the pyrolysis conditions, the carbonized resin can have a variety of distributions, densities, and mass fractions [3]. After full pyrolysis, the remaining carbonaceous material, composed of carbon fiber substrate and carbonized phenolic matrix, undergoes mass loss due to oxidation, sublimation, and spallation [4] (mass loss due to mechanical forces of friction and shear).

Many current ablation material response models, based on the work of Kendall et al. [5], rely on a surface ablation hypothesis. Heritage models do not account for the micro-structure of the material and the in-depth oxidation that can occur due to the diffusion of reactants into the material. Because of the high porosity and range of oxidation depths, the micro-scale oxidation behavior must be understood and incorporated into the next generation of volume averaged models [6] in order to guide material design.

A micro-scale oxidation model was first proposed by Lachaud and Vignoles [7] and applied to ideal representations of carbon fiber substrates [8]. Our research group then studied the inclusion of a phenolic phase on ideal representations of carbon fiber substrates in order to develop a preliminary understanding of the effects of resin distribution on the oxidation process [9]. However,

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Nomenclature

Greek

ε	Porosity, –
Ω	Molar volume, $m^3\ mol^{-1}$
Φ	Thiele number, –
ρ	Density, $kg\ m^{-3}$
θ	Average cylinder pitch angle, rad

Symbols

A	Reactivity contrast, –
$\vec{e}$	Unit vector, –
C	Concentration, $mol\ m^{-3}$
D	Diffusion coefficient, $m^2\ s^{-1}$
d	diameter, m
J	Molar oxidation flux, $mol\ m^{-2}\ s^{-1}$
k	Reactivity, $m\ s^{-1}$
n	Surface normal, –
r	Radius, m
S	Surface function, –
s	Specific surface area, m^{-1}
t	Time, s
v	Recession velocity, $m\ s^{-1}$
x	Mass fraction, –
z	Matrix recession depth, m

Subscripts

eff	effective
f	fiber
m	matrix
p	pore

such ideal geometries do not adequately capture the complex fiber clusters and structures evidenced in real carbon fiber substrates under a scanning electron microscope [10]. An effort was made to obtain a realistic representation of carbon fiber substrates through the use of hard X-ray micro-tomography [10,11]. The resulting tomography images, with sub-micron voxel sizes, provide a digital representation of the real material that can be used to calculate material properties or simulate material response [12,13]. A computational framework, called Porous Materials Analysis (PuMA) [14] was developed at the NASA Ames Research Center to handle these large micro-tomography datasets. PuMA includes an implementation of the oxidation method proposed by Lachaud and Vignoles [7], modified to oxidize large datasets using parallel computing.

Using the PuMA framework, this study aims at understanding the effects of the micro-scale structure on the overall oxidation of resin-infused carbon fibers in order to guide material design. To this goal, we examine the effects of two carbonized phenolic distributions, shown in Fig. 1, on the micro-scale oxidation response. These two distributions, representing extreme cases, were selected: (a) carbon fiber substrate coated with a high density char and (b) carbon fiber substrate filled with a low density char. The overall mass of the charred material is the same in each case. The resulting materials, built upon the same carbon fiber substrate, have different porosity, but have the same constituent mass fractions, density, and chemical composition. These distributions are not intended to represent those of existing materials, but rather to serve as a theoretical model, capturing the extreme cases, to study the micro-scale oxidation and guide future material development.

Simulations are performed on ideal geometries as well as on micro-tomography representation of a carbon fiber preform material at various diffusion/reaction regimes for both the phenolic-coated (Fig. 1a) and phenolic-filled (Fig. 1b) cases.

Section 2 provides an overview of the simulation tools used in this study. We describe the oxidation model and the numerical method used to solve the diffusion/reaction problem. We also provide details on the use of 3D micro-tomography within the PuMA framework. Section 3 details analytical and numerical studies on ideal geometries, as well as numerical simulations on tomographic representations of a carbon fiber material available commercially (in this case FiberForm®). Section 4 contains the conclusion and outlook.

2. Methods

2.1. Physical model

For carbon/resin composites, the oxidation reaction of the carbonaceous char is a main source of material recession during ablation at temperatures below the sublimation regime. In an oxygen-rich entry plasma, oxidation primarily occurs via the reaction pathway $C(s) + O \rightarrow CO$ and, to a lesser extent, via $C(s) + O_2 \rightarrow CO_2$ [15,16]. Other decomposition mechanisms may also occur under certain conditions, e.g. sublimation, nitridation, decomposition via reactions with CO_2 and material removal by shear stresses. For a fibrous char, the local motion of the carbon/gas interface can be modeled using a differentiable surface function $S(x, y, z, t)$ [7,8], as:

$$\frac{\partial S}{\partial t} + \vec{v} \cdot \nabla S = 0, \tag{1}$$

where the recession velocity, $\vec{v}$, of the surface is

$$\vec{v} = \Omega J \vec{n} \tag{2}$$

Here, Ω is the solid molar volume and $\vec{n}$ is the unit normal vector from the surface. J is the molar oxidation flux. Assuming Fickian mass diffusion and first order oxidation reactions, J is given by

$$J = -D \nabla C \cdot \vec{n} = k_f C \tag{3}$$

where D is the diffusion coefficient of the reactant in the bulk fluid phase, k_f is the intrinsic reactivity [17] of the carbon fiber,[1] and $C = C(x, y, z, t)$ is the local concentration of oxygen.

The conservation of oxygen in the gas phase assuming negligible convection is given by

$$\frac{\partial C}{\partial t} - \nabla \cdot (D \nabla C) = 0 \tag{4}$$

An analogous expression to Eq. (3) can be written for the carbonized matrix, with the intrinsic reactivity of the matrix k_m

[1] The intrinsic reactivity of the carbon fiber is not to be confused with the effective reactivity, k_{eff}, which describes, instead, the reactivity of the bulk porous material.