Oxidation Kinetics and Strength Degradation of Carbon Fibers in a Cracked Ceramic Matrix Composite

Michael C. Halbig, Army Research Laboratory, Cleveland, OH

Ceramic matrix composites (CMCs) are proposed for use in various high temperature structural applications. Proposed applications for C/SiC materials include leading edges, control surfaces, nozzles, thrusters, integrated blades, cooled panel heat exchangers and combustion chambers, and friction materials for brakes. Two primary benefits of using C/SiC are low weight and high temperature capability compared to other materials. Lighter weight can lead to benefits of increased thrust (performance) and/or increased payload. Higher temperature capability is important for meeting high thermal loads due to combustion gas temperatures in propulsion applications and due to reentry and hypersonic flight conditions in airframe applications. The use of high temperature CMC materials that require little or no cooling can allow for more flexible and simpler designs which can lead to smaller overall vehicle designs and weight savings. Despite the benefits of using C/SiC in certain types of applications, one of the barriers to its use is the degradation of the carbon fiber reinforcement, particularly in oxidizing environments. This leads to strength reduction and potential component failure. For single use or short mission applications in oxidizing environments, the oxidation of the carbon fibers may not be a factor. However, in reusable or long term applications, oxidation protection schemes may be necessary.

The oxidation kinetics of carbon fibers in complex composite systems are not well understood. Many studies involve thermogravimetric analysis (TGA) in which weight loss of the composite is monitored over time. These types of studies provide valuable information, however the oxidation of the composites in unstressed and stressed states can be very different, primarily, due to the presence of pre-existing cracks. The pre-existing cracks are an as-received property of C/SiC. The microcracks form during cool down after high temperature processing due to the coefficient of thermal expansion mismatch between the carbon fiber and the silicon carbide matrix. In an unstressed state at elevated temperatures, the formation of silica and the closing of cracks near the processing temperature can seal the cracks and protect the interior of the composite from the outside oxidizing environment. However in many real application conditions, stresses present can prevent cracks from sealing due to wide crack openings and the relatively slow rate of silica growth. Therefore, fibers are more prone to oxidation when the composite is under stress.

Experimental results and oxidation modeling will be presented to discuss carbon fiber susceptibility to oxidation, the oxidation kinetics regimes, and composite strength degradation and failure due to oxidation. Thermogravimetric analysis (TGA) was used to study the oxidation rates of carbon fiber and of a pyro-carbon interphase. The analysis was used to separately obtain activation energies for the carbon constituents within a C/SiC composite. TGA was also conducted on C/SiC composite material to study carbon oxidation and crack closure as a function of temperature. In order to more closely match application conditions, C/SiC tensile coupons were also tested under stressed oxidation conditions. The stressed oxidation tests show that C/SiC is much more susceptible to oxidation when the material is under an applied load where the cracks are open and allow for oxygen ingress. The results help correlate carbon oxidation with composite strength reduction and failure. Also since the test conditions allow for easy oxygen ingress, the oxidation kinetics of carbon within a C/SiC composite can be studied without the added variable of crack closure.

The results from the experimental analysis were used to provide input for the development of a finite difference model that allows for further analysis of the oxidation kinetics of carbon fibers in a cracked ceramic matrix. Oxygen concentrations and carbon consumption within a cross-section of the composite can be calculated over time during the oxidation process. The effects of such important variables as temperature, diffusion coefficient, reaction rate constant, geometry, and environment can be investigated with the model. The reduction in carbon can be used to predict the composite strength reduction and failure.

As seen from oxidation studies, microstructural analysis, and model development, the oxidation of carbon occurs in two primary regimes, i.e., the diffusion-controlled regime and the reaction-controlled regime. In the reaction-controlled regime, there was a strong temperature dependence. In this regime, component lives were longer and strains to failure were lower in stressed oxidation tests and weight loss rates were lower in TGA tests compared to the trends for the other regime. Microstructural analysis of polished cross-sections tested under stress suggests and the model confirms that the material becomes
saturated in oxygen. Due to the relatively slow oxygen/carbon reactions and the high oxygen concentration within the composite, oxidation occurred throughout the material. In the diffusion-controlled regime, there was less of a temperature dependence. In this regime, component lives were shorter and strains to failure were higher in stressed oxidation tests and weight loss rates were higher in TGA tests. Microstructural analysis of polished cross-sections tested under stress suggests and the model confirms that there was a sharp gradient in oxygen concentration from the edge up to the moving reaction front of oxidizing carbon with very low oxygen concentrations on the interior side of the reaction front. A shrinking core of the carbon fiber reinforcement was seen from the outer perimeter inward as oxidation progressed.

From a better understating of carbon fiber oxidation, ways to protect the fiber can be determined for different application conditions, such as environment, temperature, stress, and duration. The carbon fibers can be protected through several different approaches that target oxidation inhibition at either the fiber, interphase, matrix, external coating or a combination of these. Oxidation inhibited C/SiC materials were evaluated in TGA and stressed oxidation conditions. The inhibiting approaches consisted of boron-containing particulates in the matrix and/or a CBS (carbon-boron-silicon) external coating. The results show that the approaches were effective in prolonging life and retaining strength even when the C/SiC materials were under stress in a high temperature, oxidizing environment. The purpose of these oxidation inhibitors is to form glasses and solid oxides that seal cracks. However the methods were only effective in sealing cracks at the stress of 10 ksi and not at the higher stress of 25 ksi.
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Acknowledgements

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Tensile Test – SoRI

Oxidation Model Development and Theory – J. Cawley and A. Eckel
Outline

- Introduction - GRC Research in CMCs
  - C/SiC Cracks/Oxidation Pathways
  - Oxidation Kinetics
- Oxidation Studies of Carbon Constituents and C/SiC Composites
- Strength Reduction and Lifetime Tests of C/SiC Composites
- Modeling the Oxidation of Carbon Fibers in a Cracked Ceramic Matrix Composite
- Evaluation of Oxidation Inhibited C/SiC Composite Materials
## NASA GRC’s Role in Ceramic Material and Component Development

<table>
<thead>
<tr>
<th>TRL</th>
<th>General NASA Definitions</th>
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<tbody>
<tr>
<td>9</td>
<td>Actual system “flight proven” on operational flight</td>
</tr>
<tr>
<td>8</td>
<td>Actual system completed and “flight qualified” through test and demonstration</td>
</tr>
<tr>
<td>7</td>
<td>System prototype demonstrated in flight environment</td>
</tr>
<tr>
<td>6</td>
<td>System/Subsystem model or prototype demonstrated/validated in a relevant environment</td>
</tr>
<tr>
<td>5</td>
<td>Component and/or breadboard verification in a relevant environment</td>
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<tr>
<td>4</td>
<td>Component and/or breadboard test in a laboratory environment</td>
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<tr>
<td>3</td>
<td>Analytical and experimental critical function, or characteristic proof-of-concept</td>
</tr>
<tr>
<td>2</td>
<td>Technology concept and/or application formulated (candidate selected)</td>
</tr>
<tr>
<td>1</td>
<td>Basic principles observed and reported</td>
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**Notes:**
- **TRL** stands for Technology Readiness Level.
- Each level describes the progression of development and validation of ceramic materials and components.
Potential Applications for CMC Components in Aerospace

AIRFRAME

**Leading Edges:** Blunt, sharp, and cooled leading edges, nose and nose skirt

**Hot Structures:** Control surfaces, elevons, ruddervators, flaperons, body flaps, integrated panels

**Acreage Surfaces:** Windward TPS panels

**Seals:** TPS seals, control surface seals, penetration seals

PROPULSION

**Turbomachinery Components:** Inserted blades, blisks, stators and rotors, gas path ducting, tip seals, and housings

**Actively-cooled Components:** Cooled panel heat exchangers and combustion chambers (hot gas flow path), nozzles (ramps, bells, extensions), and manifolds

**Uncooled Thin Wall Structures:** Nozzles (radiation cooled), combustion chambers, manifolds, thrust cells, and ducts
Cracks Acting As Oxygen Diffusion Paths

Pyro-Carbon Interphase

Carbon Fiber

SiC Matrix Cracks

Oxygen Diffusion Path

550°C (1022°F), 25 ksi (172MPa)
Fracture surface

1454°C (2650°F), 10 ksi (69MPa)
Fracture surface
Oxidation Kinetics Regimes

**Low Temperature Regime**
- Controlled by C/O\textsubscript{2} reactions
- Entire section saturated in O\textsubscript{2}
- Similar reactivity throughout

**High Temperature Regime**
- Controlled by oxygen supply
- Large gradient in O\textsubscript{2} conc.
- Moving reaction front, shrinking core

Starting Matrix

6x6 Fiber Tow Array

750°C
25 ksi

1250°C
25 ksi

Reaction Controlled

Diffusion Controlled

\( t_0 \) \quad \rightarrow \quad \rightarrow \quad \rightarrow

\( t_1 \) \quad \rightarrow \quad \rightarrow \quad \rightarrow

\( t_2 \)
Oxidation of Carbon Constituents at 800°C in Oxygen
– Failure under a stress of 20 ksi (polished cross-section)
Oxidation of Carbon Constituents at 1200°C in Oxygen
– Failure under a stress of 20 ksi (polished cross-section)
Thermogravimetric Analysis of Uncoated T300 Carbon Fiber
Percent Weight Loss in Oxygen Versus Time

Time (sec.)

Weight Loss (%)

-100

-75

-50

-25

0

left to right
1400°C, 1300°C

500°C

550°C

600°C

650°C

700°C

left to right
1100°C, 1200°C, 900°C
750°C, 1000°C, 800°C

Ln k (g/sec)

-9.5

-9.0

-8.5

-8.0

-7.5

7.7 kJ/mol

-7.0

64.4 kJ/mol

10,000/T(K)
Additional TGA Data of Uncoated T300 Carbon Fiber
Percent Weight Loss Versus Time (oxygen flowing at 100ccm)
SiC/SiC coupons with machined edges: the pyro-carbon interphase is oxidized in a flowing oxygen environment. The interphase is 3 wt % of the composite (approximately 0.08 grams).

Note: rates are also dependant on the amount of interphase exposed to the environment (i.e. at cracks, voids, and pores)

The graph shows the percent weight loss versus time for different temperatures: 500°C, 550°C, 600°C, 800°C, 900°C, 1000°C, and 1100°C. The graph also includes plots for the log of the rate constant (k) versus 10,000/T(K) for temperatures of 68.9 kJ/mol and 16.3 kJ/mol, with a correlation coefficient R² = 0.9919.
Thermogravimetric Analysis of C/SiC Coupons
Percent Weight Loss Versus Time (oxygen flowing at 100ccm)

- CTE mismatch closes cracks at high T

Graph showing weight loss percentage versus time at different temperatures:
- 350°C-600°C
- 650°C-800°C
- 900°C-950°C
- 1000°C-1400°C

Inset images showing oxidized fiber regions and matrix cracks.
Crack Opening Determined by Thermal and Load Strain

Strains adjusted for crack closure at the processing temp.

\[ y = -0.00043x + 0.48968 \]

- Thermal strain
- Thermal strain plus load strain at 10 ksi
- Thermal strain plus load strain at 25 ksi

Oxidized Fiber Regions

Matrix Cracks

Tensile Load

Temp (°C)

Processing Temp.

Strain (%)
Fractured Test Coupons From Stressed Oxidation Tests in Air

800°C 35 MPa / 69 MPa / 138 MPa
(1498°F 5 ksi / 10 ksi / 20 ksi)

1200°C 35 MPa / 69 MPa / 138 MPa
(2218°F 5 ksi / 10 ksi / 20 ksi)
<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>35</th>
<th>69</th>
<th>138</th>
</tr>
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<tbody>
<tr>
<td>Time to Failure (hr)</td>
<td>5.07</td>
<td>2.33</td>
<td>0.48</td>
</tr>
<tr>
<td>Failure Location</td>
<td>TG</td>
<td>Thermal Gradient (TG)</td>
<td>Gage</td>
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</tbody>
</table>
In Air at 1200°C

Edges of Polished Cross-Sections

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<th>138</th>
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<tr>
<td>Failure Location</td>
<td>TG</td>
<td>Thermal Gradient (TG)</td>
<td>Gage</td>
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In Air at 800°C
Polished Cross-Section from Gage (section width ~ 0.13”)

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<th>69</th>
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<tbody>
<tr>
<td>Time to Failure (hr)</td>
<td>5.70</td>
<td>2.48</td>
<td>0.83</td>
</tr>
<tr>
<td>Failure Location:</td>
<td>Gage</td>
<td>Gage</td>
<td>Gage</td>
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</table>
In Air at 800°C

Edges of Polished Cross-Sections

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Strength Retained and Strain to Failure After Tensile Coupon Oxidation Exposures

- Residual Strength - 600C
- Residual Strength - 800C
- Strain to Failure - 600C
- Strain to Failure - 800C

Strength Retained (%)

Composite Weight Loss (%)
Stressed Oxidation/Creep Rupture of C/SiC in Air
Temperatures from 750°C-1500°C,
Stresses of 69 and 172 MPa (10 and 25 ksi)

Acknowledgements to David N. Brewer (ARL) and Ralph J. Pawlik (QSS) at NASA GRC for conducting stressed oxidation tests.
Approach:

Use a 2-D finite difference model that is physics based to simulate the oxidation of carbon fiber cross-sections in a cracked ceramic matrix composite.

Use theoretically and experimentally based variables in the model to keep track of oxygen concentrations and carbon recession and the time for carbon reactions.

Product:

A model that predicts a composite’s strength reduction and/or time to failure based on the oxidation of load bearing fibers for such application variables as environment, temperature, and stress.
One crack throughout the section is bridged by fiber tows and runs parallel to the gray plane. Also cracks perpendicular to the overall crack run through the individual fiber tows.
\[
\frac{x^2}{k_p} + \frac{x}{k_1} = t
\]

\[
k_1 = \left(\frac{1}{N}\right) \left(\chi C_T\right) (K)
\]

\[
k_1 = \left(\frac{1}{N}\right) \left(\chi \frac{P}{RT}\right) \left\{ k_0 \exp\left(\frac{-Q}{RT}\right) \right\}
\]

\[
k_p = \frac{2DC_T}{N}
\]

\[
k_p = \left(\frac{4DC_T}{N}\right) \ln \left\{ \frac{\left(1+\chi\left(D_k/D\right)+1\right)}{\left[D_k/D\right]+1} \right\}
\]

\[
D = \frac{5.9543 \times 10^{-24} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{\left( P \sigma_{AB}^2 \Omega_{AB} \right)} T^{3/2}
\]

\[
D_k = 8.575T^{1/2}d
\]


- Linear and Parabolic Contributions
- Linear Rate Constant
- Parabolic Rate Constant
- \(O_2 + 2C \Rightarrow 2CO\) and Knudsen Diff.
- Diffusion Coefficient
- Knudsen Diffusion Coefficient
Model Representation

Model ¼ section

\[ D_{\text{eff}} = \epsilon D_{AB} \frac{k_t}{k_t^2} \]

- \( D_{\text{eff}} \) = effective diffusion coefficient
- \( \epsilon \) = open void fraction (porosity)
- \( D_{AB} \) = interdiffusion coefficient
- \( k_t \) = tortuosity factor

Representation allows for recession at both edges to be modeled. Use different tortuosity factors for diffusion in the x and y directions. Also allows for layout to be easily changed for different specimen geometries (volume and edge effect studies).

Quarter section is 161 x 509 grids, Tow array is 8 x 13, Cracked elliptical tows are 8 x 80 grids.
Results from the Oxidation Model
- Oxidation Patterns

800°C
1000 ppm Oxygen
25% Carbon Reacted
Time: 79.1 hr.
39.6% of the carbon grids are flawed.

Modeled Composite Cross-Section

1200°C
1000 ppm Oxygen
25% Carbon Reacted
Time: 35.6 hr.
28.9 % of the carbon grids are flawed (at least 5% oxidized).
Results from the Oxidation Model

- Oxygen Concentrations (at 1000 ppm)
Comparison of the Model to the Microstructure from Experimentation at 1200°C (at 1000 ppm)

9.7 hrs

10.1 hr

8% carbon oxidized
C/SiC Material Descriptions

All 4 materials have the following characteristics:
- Manufactured by Honeywell Advanced Composites Inc. (HACI, now General Electric Power System Composites)
- 2D Plain weave fiber architecture
- Pyro-Carbon Alpha-3 interphase coating
- SiC matrix processed through isothermal CVI

The 4 materials have the following differences:

<table>
<thead>
<tr>
<th></th>
<th>Treatment</th>
<th>Inhibitor in Matrix</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard C/SiC</td>
<td>none</td>
<td>none</td>
<td>SiC</td>
</tr>
<tr>
<td>standard C/SiC w/cbs</td>
<td>none</td>
<td>none</td>
<td>SiC, C-B-Si</td>
</tr>
<tr>
<td>enhanced C/SiC</td>
<td>1750°C</td>
<td>yes</td>
<td>SiC</td>
</tr>
<tr>
<td>enhanced C/SiC w/cbs</td>
<td>1750°C</td>
<td>yes</td>
<td>SiC, C-B-Si</td>
</tr>
</tbody>
</table>
TGA of CVI C/SiC Materials in Flowing Oxygen (100ccm) at Temperatures of 600°C and 800°C – out to 25 hr

- **Temperature**
  - 600°C
  - 800°C

- **Material**
  - Standard (S)
  - Standard w/cbs (SC)
  - Enhanced (E)
  - Enhanced w/cbs (EC)

- **Complete Carbon Burnout**
TGA of CVI C/SiC Materials in Flowing Oxygen (100ccm) at Temperatures of 1000°C, 1200°C, and 1400°C – out to 25 hr

- **TEMPERATURE**
  - 1000°C
  - 1200°C
  - 1400°C

- **MATERIAL**
  - Standard (S)
  - Standard w/cbs (SC)
  - Enhanced (E)
  - Enhanced w/cbs (EC)
Composite Weight Loss After 25 hr in TGA
(oxygen flowing at 100ccm)

- std. C/ SiC
- std. C/ SiC w/cbs
- enh. C/ SiC
- enh. C/ SiC w/cbs

Temperature (°C): 600, 800, 1000, 1200, 1400
Composite Weight Loss (%): 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50

Complete Carbon Burnout
Composite Weight Loss After 50 hr in TGA

(oxygen flowing at 100ccm)
Stressed Oxidation at 1454°C/10 ksi in Air
Strain Versus Time for Stressed Oxidation of HACI C/SiC Materials - Tests at 1454°C/69MPa (2650°F/10 ksi)

- std. C/SiC
- enh. C/SiC, 25 hr. run out
- enh. C/SiC w/cbs, 25 hr. run out
Stressed Oxidation at 1454°C/25 ksi in Air

Note: DLC enh. C/SiC and enh. DLC C/SiC w/cbs failed in the thermal gradient region.
Stressed Oxidation at 800°C in Air

800°C/10 ksi in Air

800°C/25 ksi in Air
Summary/Conclusions

Oxidation of the carbon constituents within C/SiC occurs in two primary regimes.

- Reaction controlled regime: lower temperatures, oxygen saturates into the interior, oxidation rate is slower but oxidation is more widespread, embrittlement effect and low strains to failure.
- Diffusion controlled regime: higher temperatures, oxygen and carbon reactions occur quickly, reaction front moves inward, shrinking core, high strains to failure.

The T300 carbon fiber and the pyrolytic carbon interphase have different oxidation rates. In the lower temperature regime, the pyro-C has a slower reaction rates. Resulting activation energies suggest further testing is necessary.

Stress has a significant effect in opening cracks especially at high temperatures.

- In unstressed conditions: crack closure near processing temperature due to CTEs and silica formation. Cracks remain open at low temperatures.
- Under stress at high temperatures and at low temperatures, cracks are open and allow for oxygen ingress. Oxidation patterns according to kinetic regimes are observed.
The oxidation model is a useful tool for studying the oxidation kinetics, the effect of different variables (temperature, environment, porosity and tortuosity), and edge effects. With additional adjustment of the model (effective diffusion coefficients) to match experimental results, the model can be used to determine oxidation damage over time and determine strength reduction and failure.

Oxidation inhibitors can significantly improve the oxidation resistance of carbon in C/SiC composites at intermediate (800°C) and high temperatures (1454°C). However, the approaches investigated in this study were only effective at low stress levels.