C/SIC LIFE PREDICTION FOR PROPULSION APPLICATIONS

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ABSTRACT

Accurate life prediction is critical to successful use of ceramic matrix composites (CMC). The tools to accomplish this are immature and not oriented toward the behavior of carbon fiber reinforced silicon carbide (C/SiC), the primary system of interest for many reusable and single mission launch vehicle propulsion and airframe applications. This paper describes an approach and progress made to satisfy the need to develop an integrated life prediction system that addresses mechanical durability and environmental degradation of C/SiC. Issues such as oxidation, steam and hydrogen effects on material behavior are discussed. Preliminary tests indicate that steam will aggressively remove SiC seal coat and matrix in line with past experience. The kinetics of water vapor reaction with carbon fibers is negligible at 600°C, but comparable to air attack at 1200°C. The mitigating effect of steam observed in fiber oxidation studies has also been observed in stress rupture tests. Detailed microscopy of oxidized specimens is being carried out to develop the oxidation model. Carbon oxidation kinetics are reaction controlled at intermediate temperatures and diffusion controlled at high temperatures (~1000°C). Activation energies for T-300 and interface pyrolytic carbon were determined as key inputs to the oxidation model. Crack opening as a function of temperature and stress was calculated. Mechanical property tests to develop and verify the probabilistic life model are very encouraging except for residual strength prediction. Gage width is a key variable governing edge oxidation of seal coated specimens. Future efforts will include architectural effects, enhanced coatings, biaxial tests, and LCF. Modeling will need to account for combined effects.
C/ SiC Life Prediction
For Propulsion Applications

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C/SiC Life Prediction For Propulsion Applications

OUTLINE

♦ Introduction
♦ Oxidation Model
♦ Stress Rupture
  • Gage width
  • Enhanced materials
  • Effect of Environment
♦ Probabilistic Model
♦ Steam Effects on SiC
  Seal Coat and Matrix
♦ Concluding Remarks
Demanding Environments Push CMC Materials Limits

**PROPULSION**
- High temperatures (~ 3500R)
  - Low and intermediate temperatures can also be a problem
- High pressures (e.g. to ~ 6000psi)
- Severe chemical environments
  - Steam
  - Oxygen rich or fuel rich
  - Hydrogen
- High velocity
- Exposure cycles from minutes in rockets to ~ hours in some combined cycle approaches
- Severe thermal transients and gradients

**AIRFRAME**
X-38 Reentry Profile for Body Flap Windward Surface Location

<table>
<thead>
<tr>
<th>Time, s</th>
<th>Temperature, °C</th>
<th>Pressure, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>1800</td>
<td>80</td>
</tr>
<tr>
<td>1000</td>
<td>1600</td>
<td>80</td>
</tr>
<tr>
<td>1500</td>
<td>1400</td>
<td>80</td>
</tr>
<tr>
<td>2000</td>
<td>1200</td>
<td>80</td>
</tr>
</tbody>
</table>

Temperature: red line
Pressure: blue line
Task Objectives

♦ Primary goal:
  • Develop and verify a robust methodology for confident determination of the reusable life capability of C/SiC space propulsion hardware.

♦ Secondary goals:
  • To ground the methodology with mechanism-based descriptions of mechanically and environmentally induced damage.
  • To expand the database for C/SiC.
  • To directly support flight experiments which use CMC propulsion components.
Materials

- Plain weave C/SiC with seal coat
- Enhanced with seal coat
  - plain weave
  - 5 harness satin weave
  - w/wo CBS coating
C/SiC Life Controlled by Complex, Interactive Mechanisms

- Environmental
  - surface recession due to moisture
  - interface and fiber oxidation

- Mechanical
  - strains due to thermal and mechanical loads
  - cycling of loads (LCF, HCF)
  - creep
Crack Opening Determined by Load and Thermal Strain

Reference Temperature
Cracks closed under no load

Oxidized Fiber Regions

Matrix Cracks

Tensile Load

Composite Strain, %

\[ y = -0.00044x + 0.48937 \]

\( \varepsilon_t + \varepsilon_2 \)

\( \varepsilon_t + \varepsilon_1 \)

\( \varepsilon_t \)

\( \varepsilon_1 \) at 69 MPa (10 ksi)

\( \varepsilon_2 \) at 173 MPa (25 ksi)

\( \Delta \) thermal strain
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Temperature Dependent Carbon Fiber Oxidation Mechanism

Low Temperature Regime:
- Controlled by C/O₂ reactions
- Entire section saturated in O₂
- Similar reactivity throughout

High Temperature Regime:
- Controlled by oxygen supply
- Large gradient in O₂ conc.
- Moving reaction front, shrinking core

Starting Matrix
6x6 Fiber Tow Array

- t₀
- 750°C 172 MPa (25 ksi)
- 1250°C 172 MPa (25 ksi)
Status of the Oxidation Model

FY'03 effort:

- Activation energy and a pre-exponential constant for the Arrhenius reaction rate equation were obtained.
  - Thermogravimetric analysis (TGA) tests were conducted for T-300 carbon fiber in flowing oxygen focusing on 6 temperatures in the reaction controlled regime (450°C - 600°C).
  - Values are used as inputs into the model.

- Strength reduction correlated with a quantified loss of carbon.
  - 12 C/SiC tensile coupons were exposed to furnace oxidation exposures in air at temperatures of 600°C and 800°C.
  - Coupons were allowed to oxidize until 4-20% composite weight loss.
  - Residual tensile strength tests were conducted.

- Oxidation Model has been optimized.
  - More accurate inputs: geometry and tortuosity factors to match tensile coupons, to allow for different edge effects, and oxygen ingress into individual carbon fiber tows.
  - Current efforts focus on matching the model to the experimental results.
Reaction controlled model predicts greater differences between 600 and 800°C weight loss results than observed.
Exponent of 0.25 fits strength loss data, but rate constant difference is smaller than expected from model.
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Summary of Mechanical Testing of C/SiC in Support of Life Model Development

Tests performed to date on plain weave C/SiC

- Stress-rupture tests under various environments (steam, air, vacuum).
- Rupture and tensile tests at 800 and 1200°C:
  - Twenty tensile tests at in a reduced partial pressure of oxygen.
  - Twenty-six stress-rupture tests in a reduced partial pressure of oxygen.
  - Twenty stress-rupture tests at a single stress.
  - Twenty interrupted stress-rupture tests to measure residual strength.
  - Stress-rupture testing of wide specimens to assess dependency of specimen area on life.

Testing under way or completed in CY 2003

- Test thick specimens under rupture conditions
  - Quantify specimen volume effects in material that is 2X thicker than material tested to date.

- Testing of Enhanced C/SiC and CBS coated materials and 5 HS weave Enhanced C/SiC.
  - Compare to standard C/SiC.
  - Determine rupture behavior of Enhanced C/SiC and CBS-coated materials in different environments (air, steam, 1000ppm O₂/Ar).
Stress Rupture Life Is a Function of Specimen Width for C/SiC

207 MPa (30 ksi), 1000 ppm O₂/Ar

Material volume effects need to be incorporated in life prediction models.

Average life at 800°C is about 1.5 times longer than at 1200°C.

17.8 mm wide specimens resulted in about a 2.5 increase in life compared to 10.1 mm wide specimens.

- Standard (10.1 mm wide gage)
- Chubby (17.8 mm wide gage)
- Extra chubby (25.4 mm wide gage)
C/SiC Oxidation Damage Rates

1200 °C, 207 MPa (30 ksi), 1000 ppm O₂/Ar

Edge Rate = 0.0084 mm/hr
Fiber Consumption rate: 0.0084 X thickness

Surface Rate = 0.0028 mm/hr
Fiber Consumption rate: 0.0028 X gage width

(average thickness of one ply)

- Surface damage penetration rate is 1/3 edge penetration rate
- Highest volume of carbon fiber is consumed by surface penetration
Edge Damage Effects Insignificant for Large Panels

1200°C Damage, Edge volume / surface volume

Specimen Gage Width, mm

Edge area oxidized
Unoxidized core
Surface area oxidized

Set to 1 at gage width = thickness
Stress Rupture Lives of Various C/SiC Materials

(stress = 207 MPa (30 ksi), 1000 ppm O₂/Ar)

<table>
<thead>
<tr>
<th>Material Type</th>
<th>800 °C</th>
<th>1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard C/SiC</td>
<td>65.41</td>
<td>26.84</td>
</tr>
<tr>
<td>enhanced C/SiC</td>
<td>113.18</td>
<td>49.15</td>
</tr>
<tr>
<td>enhanced C/SiC with CBS</td>
<td>13.68</td>
<td>318.99</td>
</tr>
</tbody>
</table>
Effect of Environment on Stress Rupture of C/SiC

600°C, 69 MPa (10 ksi)

<table>
<thead>
<tr>
<th>Test Environment</th>
<th>Time to rupture, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>10</td>
</tr>
<tr>
<td>20% steam/80% Ar</td>
<td>100</td>
</tr>
</tbody>
</table>

1200°C, 69 MPa (10 ksi)

<table>
<thead>
<tr>
<th>Test Environment</th>
<th>Time to rupture, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1</td>
</tr>
<tr>
<td>80% steam/20% Ar</td>
<td>10</td>
</tr>
<tr>
<td>50% steam/50% Ar</td>
<td>10</td>
</tr>
<tr>
<td>20% steam/80% Ar</td>
<td>100</td>
</tr>
<tr>
<td>vacuum</td>
<td>600</td>
</tr>
</tbody>
</table>
Weight loss in inert environment (argon) is negligible.
- At 1200°C, carbon fiber weight loss kinetics in air and steam due to oxidation are rapid; fibers are consumed in 1.5 hours.
- At 600°C in steam, weight loss is negligible, while in air, rapid weight loss occurs.
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Probabilistic Residual Strength (PRS) Modeling Approach

\[ \log(s_{\text{app}}) \]

\[ \log(t_f) \]

\[ s_r[(s_{\text{app}})_1, t] \]

\[ s_r[(s_{\text{app}})_2, t] \]

Deterministic strength degradation law

\[(s_{\text{app}})_1\]

\[(s_{\text{app}})_2\]

\[(t_f)_1\]

\[(t_f)_2\]
PRS Model Predicts Behavior at 1200°C

1200°C, 207 MPa (30 ksi)

Time to Failure, hours

Probability of Occurrence

Experimental Data
PRS - Power Law
PRS - Kachonov

Residual Strength, MPa

1200°C, 207 MPa (30 ksi), 15 h exposures and RT tensile test.
PRS Model Predictions at 800°C

- Time to Failure, hours
  - Probability of Occurrence
  - Graph showing experimental data and model predictions for 800°C, 207 MPa (30 ksi)

- Residual Strength, MPa
  - Probability of Occurrence
  - Graph showing experimental data and model predictions for 800°C, 207 MPa (30 ksi), 15 h exposure and tensile test
Power Law Behavior for Stress Rupture Strength and Residual Strength

\[ s = -25 \times t^{1/4} + 100 \]

Exponent of 0.25 fits stress rupture and residual strength loss data.
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Status of Steam Environment Model

- Objective: Determine SiC recession rate as a function of P, T, gas velocity, gas chemistry
  - 3 O/F’s between 1 and 2
  - 3 pressures: 100, 500, 1000 psi
  - Thin film thermocoupled samples
  - Gas velocity ~ 180 m/s (600 ft/s)
  - Weight, recession measured at intervals for a total exposure time of up to 1 hour at each condition.
- FY’03: Studied recession of SiC coated C/SiC under simulated rocket engine environments.
- FY’04:
  - Complete recession study
  - Compare results to SiC recession model predictions developed for aircraft engine applications
Subsonic High-pressure Coupon Test Configuration
Used for Determination Of SiC Recession
Due to Moisture Generated by Combustion of H₂ and O₂
SiC Coated C/SiC After Exposure to H₂ / O₂ Combustion

0.625 mm (25 mil) thick SiC seal coat
Total pressure: 6.8 atm
Gas velocity: ~ 180 m/sec

100 psi
55 min
60 min
10 min
1210°C
1380°C
1540°C

500 psi
47 min
23 min
1.75 min

flow direction

1 cm
SiC Coated C/SiC Recession Measured As Thickness at Leading Edge After Specimen Exposure to Products of H₂/O₂ Combustion
Concluding Remarks

- Fiber oxidation dominates C/SiC behavior
- Stress makes fibers accessible
- Edge effects diminish as specimen width increases
- Coatings and inhibitors greatly extend life
- Water vapor oxidizes carbon like air at high temperature, but is less aggressive at low temperature
- Water vapor strips protective silica scale rapidly at high temperature and water vapor partial pressure. Environmental barrier coating is required.
- Much more effort will be required to develop a physics based life prediction model, and the physics will be unique to a given set of fiber coating, matrix, and external coating constituents
Acknowledgements

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♦ John Zima for conducting the mechanical tests
♦ Dr. John R. Ellis for his many helpful comments during the life of this effort