# Influence of Constituents on Creep Properties of SiC/SiC Composites

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**Presentation at HTCMC-9,**
**Toronto, Canada, June 26 – July 1, 2016**

# *Presentation Overview*

<u>OBJECTIVE:</u>

- With the overall goal of developing higher temperature SiC/SiC CMC for improved aero-propulsion engines, the objective of this study was to understand the <u>creep-limited upper use temperatures of SiC/SiC CMC</u> with currently available fiber and matrix constituents by measuring and modeling the high-temperature creep behavior of CMC containing two high-performance SiC fibers and various SiC-based matrices.

<u>SiC/SiC CMC CONSTITUENT FOCUS:</u>
- **SiC Fibers:**
  - Hi-Nicalon-S (**HNS**) (current best creep-resistant fiber)
  - Sylramic<sup>TM</sup>-iBN (**iBN**) (slightly less creep-resistance, but higher thermal conductivity and capable of higher temperatures w/o strength loss for matrix improvement by CMC heat treatment)

- **SiC-based Matrices:**

  - Full Reaction-Formed SiC by polymer decomposition + Si Melt Infiltration (**Full RFMI**)

  - Full CVI SiC (**Full CVI**)

  - Partial CVI SiC with partial SiC slurry and Non-Reactive Si Melt Infiltration (Partial **CVI-NRMI**)

  - Full Polymer-derived SiC with CVI $Si_3N_4$/BN fiber coatings (**Full PIP**)

# *Approach*

## EXPERIMENTAL:

- **Focus on 2D-balanced SiC/SiC CMC with both straight and 5HS woven fibers**

- **Measure on-axis creep behavior of CMC at constant stresses and constant temperatures of 1315, 1400, and 1450$^0$C in lab air. CMC stresses were kept below 110 MPa (16 ksi) to assure in most cases no matrix cracking on initial loading.**

## MODELING:
**Use CMC creep data and previously determined empirical models for the creep behavior of the HNS, iBN, and the CVD-derived Ultra SCS fibers to:**
- **Understand the creep-controlling constituent for each CMC type.**
- **Develop an empirical understanding and analytical equations where possible for the creep behavior of the various matrix types.**
- **Develop methodology for predicting the <u>creep-limited upper use temperatures</u> (T*) for each CMC type under constant stress and temperature conditions.**
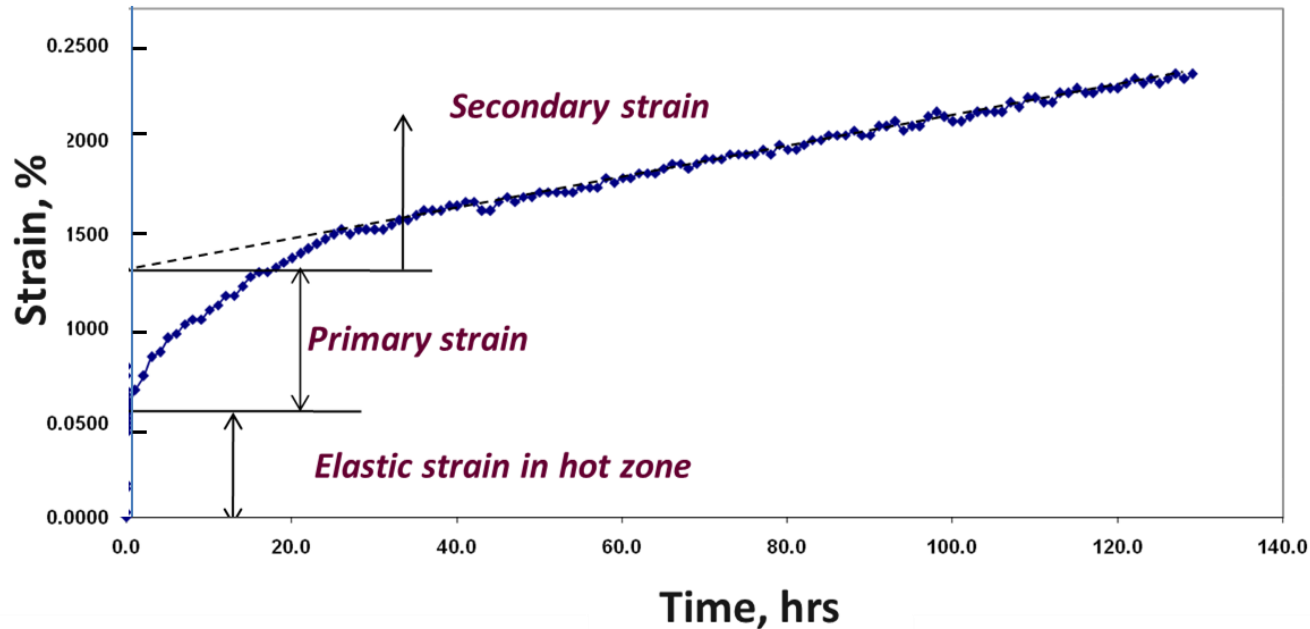
# *Background on NASA Fiber Creep Studies*

# *Relevant to the*

# *Creep Behavior for the Various*

# *SiC/SiC CMC Types*
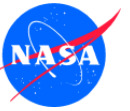
# Typical Tensile Creep Behavior
## of Near-Stoichiometric Polymer-derived SiC Fibers



Hi-Nicalon-S: *Single fiber, 1400°C, 270 MPa, air*

- **Near stoichiometric polymer-derived SiC fibers with ~ equiaxed grains, like HNS and iBN, show elastic behavior followed by a small primary (transient) stage and a secondary (steady-state) creep stage.**
- **The primary stage increases linearly with stress, whereas the typically larger steady-state stage increases to the third power with stress, but decreases linearly with increasing grain size.**

# *Typical Tensile Creep Behavior of the Near-Stoichiometric CVD-derived Ultra SCS Monofilament SiC Fiber*
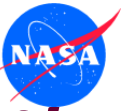
**Ultra Fiber Creep in air at 1400⁰C and 278 MPa (40 ksi)**
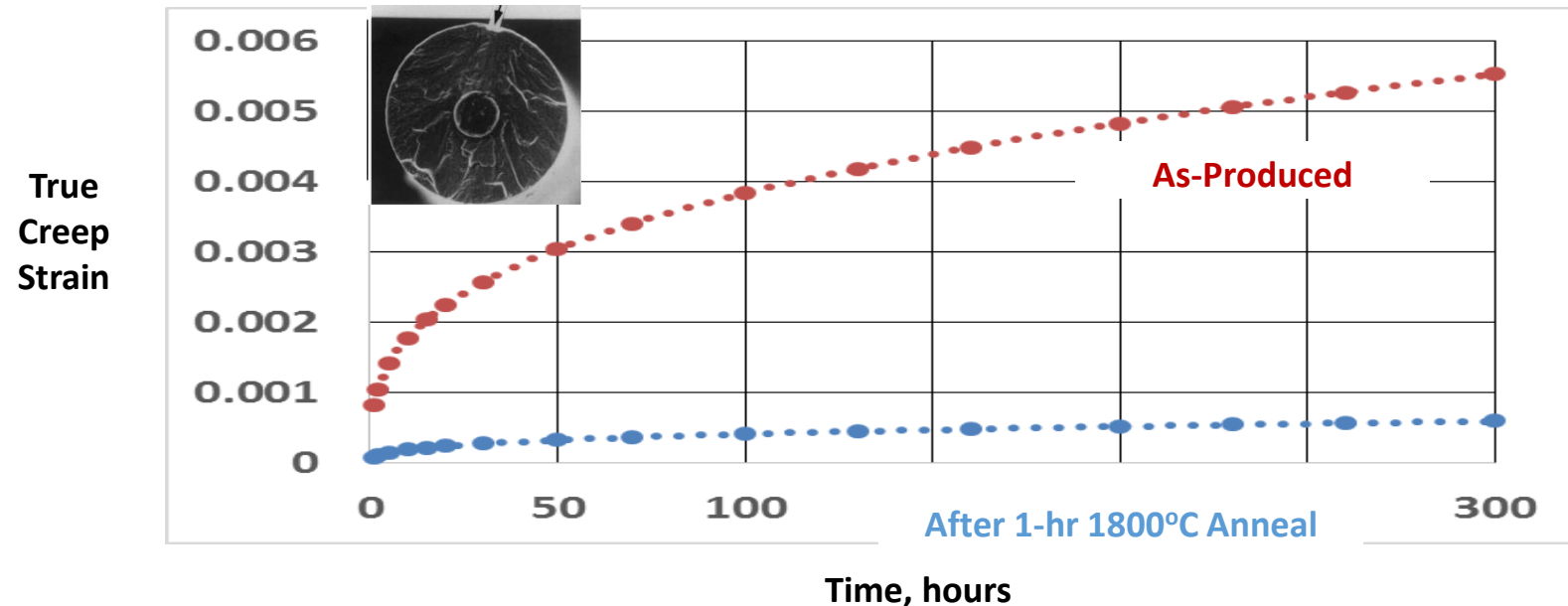


- **Because of microstructural similarities, it is assumed that the stress-time-temperature creep behavior of the CVD-derived Ultra fiber should be useful in understanding the creep behavior of a CVI SiC matrix constituent.**

- **Unlike the polymer-derived SiC fibers with ~ equiaxed grains, the CVD-derived Ultra fiber only displays a primary (transient) stage with $t^{1/3}$ and linear stress dependences. This is probably related to the elongated transverse grains in these fibers, which grow in size with annealing above 1400⁰C along with free Si removal, thereby increasing fiber creep resistance.**

# Best-Fit <u>Creep</u> Parameters for <u>Straight</u> SiC Fiber Types under constant Stress and Temperature

Polymer-derived:  $\varepsilon_s$ (%) = $A \cdot \theta / d$ (T)   where $\theta = \sigma^3 \cdot t \cdot \exp(-B/T)$,

CVD-derived:        $\varepsilon_p$ (%) = $C$ (T) $\cdot \theta^{1/3}$

$d$ = grain size (nm), $\sigma$ = stress (MPa), t = hours, T = Kelvin

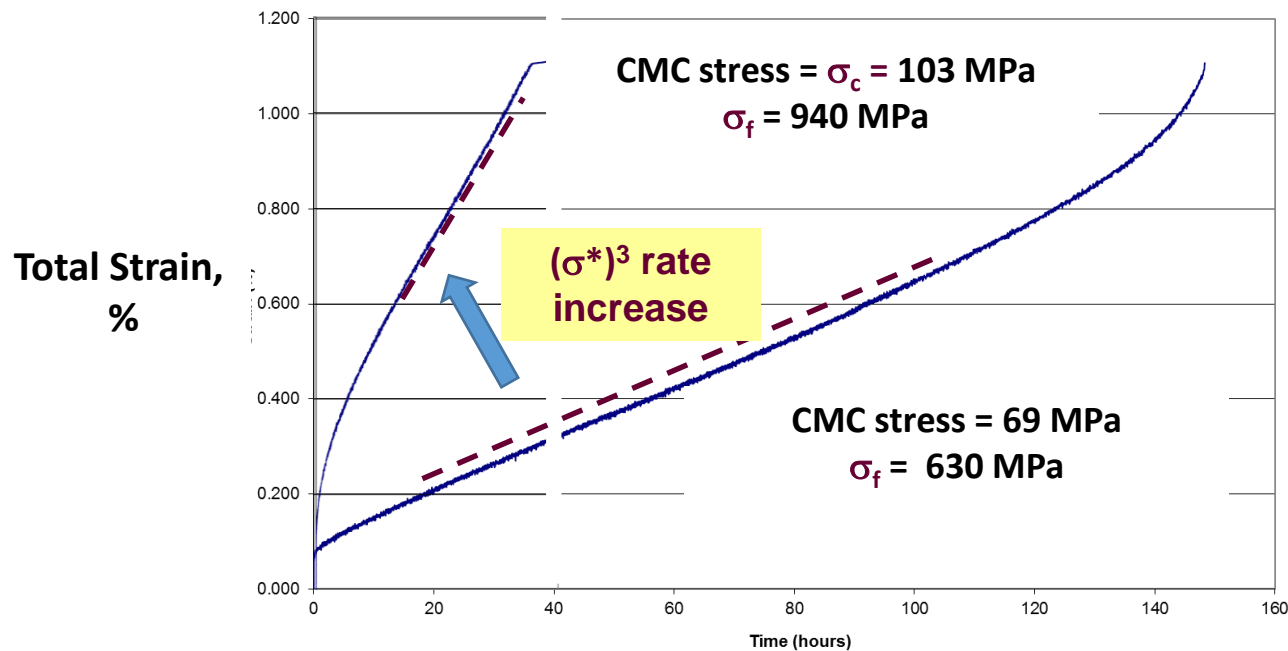| | d (nm) | A (%.K. nm/MPa$^3$.hr) | B (K) | C (%/ MPa. hr$^{1/3}$) |
|---|---|---|---|---|
| HNS | 20 | 2.2 x 10$^{16}$ | 97900 | |
| iBN | ~ 200 | 4.5 x 10$^{17}$ | 97900 | |
| Advanced SiC Fiber | 400 | 2.2 x 10$^{16}$ | 97900 | |
| Ultra (as-produced) | | | 97900 | 9 x 10$^4$ |
| Ultra (1600$^0$C anneal) | | | 97900 | 2 x 10$^4$ |
| Ultra (1800$^0$C anneal) | | | 97900 | 9 x 10$^3$ |

- The theoretical <u>Advanced polymer-derived SiC fiber</u> is projected to mimic the Hi-Nicalon-S fiber, but with reduced oxygen content and ~400 nm grains distributed uniformly in the fiber to increase creep resistance.
- The B parameter for all fiber types corresponds to a steady-state creep activation energy of Q = 8.31 B = <u>814 kilo-joules</u> (diffusion of C in SiC).
- For 2D-woven architectures with stress-riser bends in small-diameter fibers, the A constants increase by ~ 2 to 3 depending on fiber diameter and weaving angle.
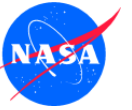
# *Creep Data for the Various SiC/SiC CMC Types*

# Creep Behavior at 1400$^0$C for CMC with _Full RFMI matrix_ and 2D-balanced non-woven HNS architecture ($f_o = 0.11$)



CMC stress = $\sigma_c$ = 103 MPa
$\sigma_f$ = 940 MPa

$(\sigma^*)^3$ rate increase

CMC stress = 69 MPa
$\sigma_f$ = 630 MPa

Total Strain, %

Time (hours)

- **CMC creep strain before rupture is linear with time and increases with CMC stress to the third power indicating that although this material is not cracked, <u>its creep is controlled entirely by the Hi-Nicalon-S fiber</u> even though it has a low on-axis fraction of ~11%.**
- **Thus the RFMI matrix is very creep prone at 1400$^0$C and the creep-limited upper use temperature for this CMC type is controlled entirely by the fiber creep behavior under a stress based on the total CMC stress.**

# *Calculating Creep-Limited UUT (T\*) for SiC/SiC CMC containing highly Creep-Prone Matrices like Full RFMI*

- **Using steady-state creep equations and associated parameters for the creep-controlling polymer-derived SiC fiber, one can then calculate the CMC T\* with this fiber by:**

$$T^* \text{ (kelvin)} = B/\ln\{( A/d )\cdot\sigma_f^{\ 3}\cdot t/\varepsilon^*\}$$

   **Where $\sigma_f = (\sigma_c / f_o)$ = fiber initial stress, t = desired CMC component service life, and $\varepsilon^*$ = max strain (%) that CMC component can tolerate.**

- **As an example, assume $\sigma_f$ = 400 MPa ($\sigma_c$ = 100 MPa, $f_o$ = 0.25), t = 1000 hr, and $\varepsilon^*$ = 0.2%, a value often quoted for metal turbine components. Then ~T\* for <u>straight</u> polymer-derived SiC fibers are:**

|  | Hi-Nicalon-S | Sylramic-iBN | Advanced |
|:---:|:---:|:---:|:---:|
| **T\*** | **$1330^0$C** | **$1310^0$C** | **$1410^0$C** |

- **These T\* values for RFMI matrices should also hold for a fully cracked CMC at t = 0, but such a case may be undesirable due to fiber environmental attack. Also beneficially, these T\* do not take the CMC above $1414^0$C where melting and diffusion of the free silicon in the matrix can cause internal CMC damage.**
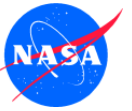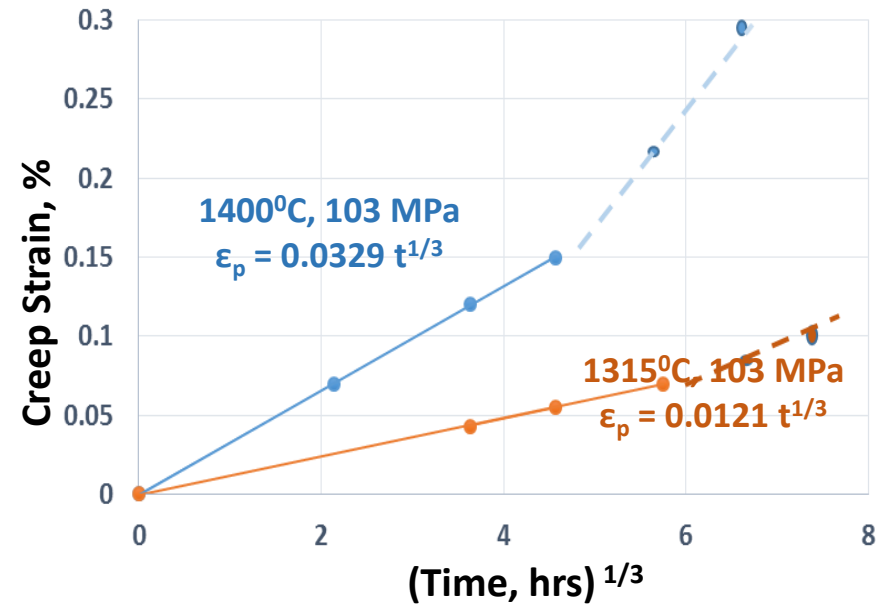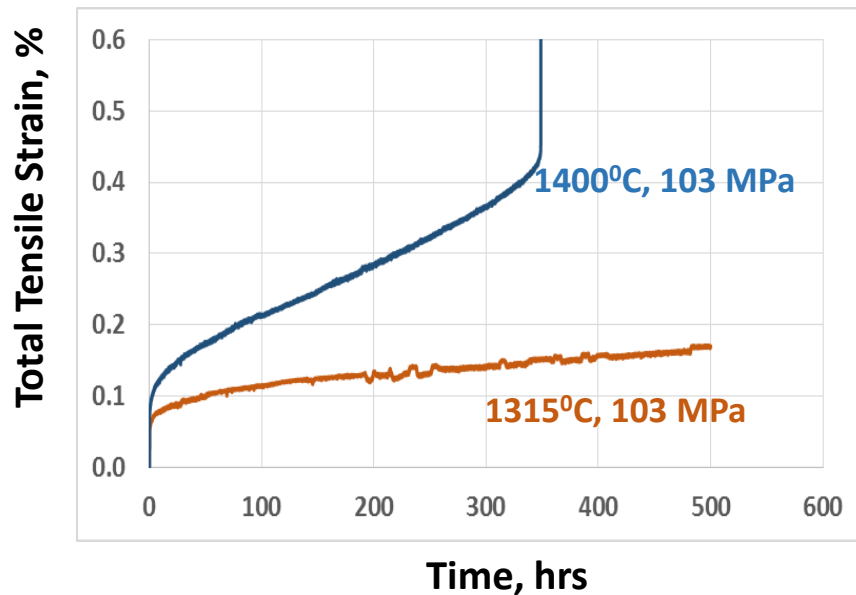
# Creep Behavior at 1315 and 1450⁰C for CMC with _Full CVI matrix_ (~50%) and 2D-balanced 5HS-woven HNS fiber architecture ($f_o$ = 0.17)
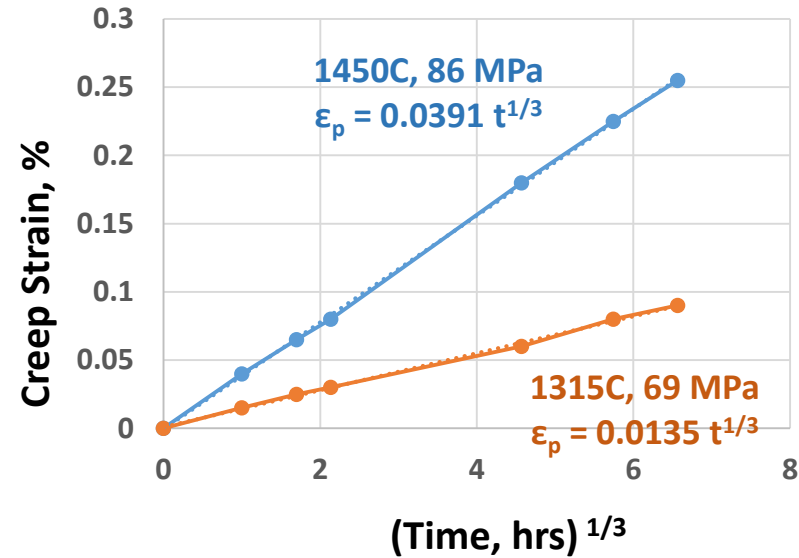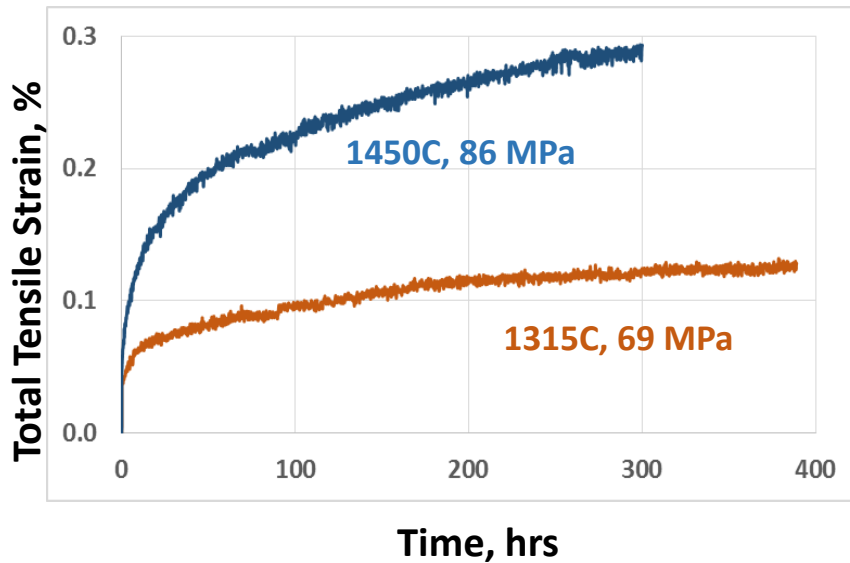


- **CMC creep strain follows $t^{1/3}$ time dependence, indicating that its creep is primarily controlled by the Full CVI SiC matrix.**
- **Assuming a CVI SiC content of 50%, the transient creep equation for the Ultra fiber,** $\varepsilon_p \,(\%) = (C)[\sigma_m]\,[\,t \times \exp(-B/T)\,]^{1/3}$ **,**
**and $\sigma_m$ equal to the full CMC stress on the matrix, above CMC curves yields C parameters at 1315 and 1450⁰C that match those measured for the Ultra fiber at these temperatures, indicating that the Ultra fiber creep equation and parameters can be used to predict SiC/SiC CMC on-axis creep with Full CVI matrices and current polymer-derived SiC fibers.**

# CMC Creep Behavior at 1315 and 1400$^0$C for CMC with Partial CVI-NRMI matrix and 2D-balanced 5HS-woven iBN architectures ($f_o$ = 0.21)



Left chart — Total Tensile Strain, % vs Time, hrs: curves labeled "1400$^0$C, 103 MPa" and "1315$^0$C, 103 MPa"

Right chart — Creep Strain, % vs (Time, hrs)$^{1/3}$:
- 1400$^0$C, 103 MPa: $\varepsilon_p = 0.0329\, t^{1/3}$
- 1315$^0$C, 103 MPa: $\varepsilon_p = 0.0121\, t^{1/3}$

- CMC Creep data with Partial CVI-NRMI also follows a $t^{1/3}$ dependence indicating initial control by CVI SiC matrix with content of only ~22%.
- For longer times the data starts to bend upward, suggesting either matrix cracking or MI silicon diffusing into CVI SiC making it more creep prone.
- At 1315$^0$C, CMC with Partial CVI-NRMI matrix is initially more creep resistant (reduced **C** parameter) than the CMC with <u>as-produced</u> Full CVI matrix, which can be explained by the Partial CVI matrix being <u>annealed</u> during the NRMI process near 1400$^0$C.

# Creep Behavior at $1454^0$C for CMC with Full PIP matrix and 2D-balanced 5HS-woven iBN architecture ($f_o$ = 0.25%)
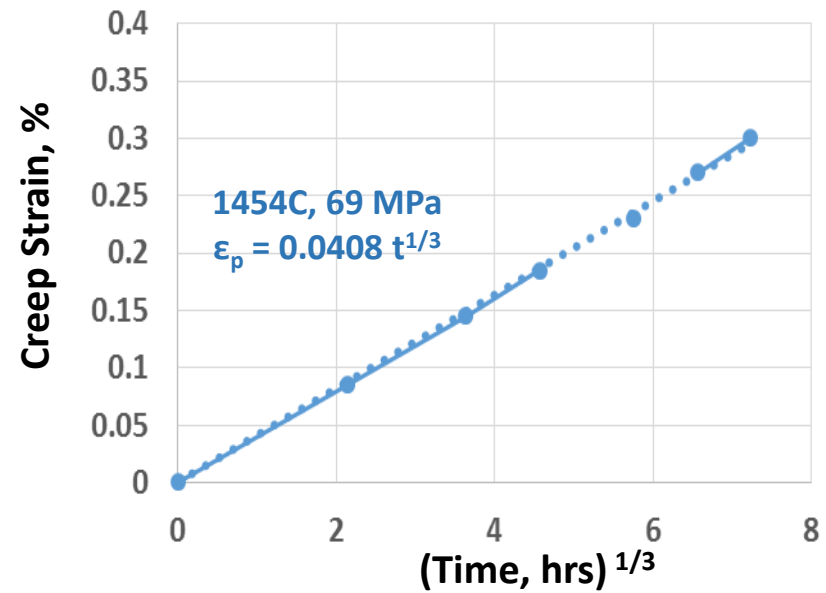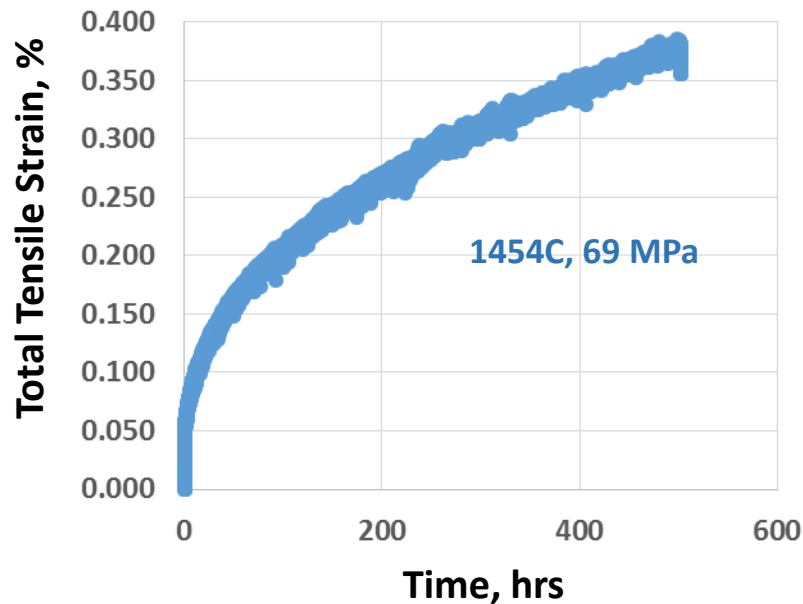


- **Like CMC with CVI SiC, creep data for CMC with Full PIP matrix produced at ~$1600^0$C also follows a $t^{1/3}$ dependence at low stress for long time at $1454^0$C.**
- **Mechanism for similar behavior with CVI matrices is uncertain since porous PIP matrix is expected to carry little load and behave like the creep-prone fine-grained polymer-derived SiC fibers.**
- **One possible mechanism is that the iBN fibers are coated with a dual layer of CVI $Si_3N_4$ over BN (Mod-1 coating) with the CVI $Si_3N_4$ coating having significant volume fraction and potentially high creep resistance like CVI SiC.**

# Temperature Dependence for "C" parameter in the Primary Creep Equation for CVI-derived Fibers and Matrices

Assuming the creep of uncracked SiC/SiC CMC with CVI-derived matrices is controlled entirely by the matrix, the CMC creep behavior can be closely predicted from primary creep strain equation for the CVI-derived Ultra fiber,

$$\varepsilon\ (\%) = C(T)[\ \sigma_m\ t^{1/3}\ \exp\ (-\ B/3T)$$

its "C" dependence on max anneal or creep temperature, and a stress on the matrix based on the total CMC stress, $\sigma_m = (\sigma_c / V_m)$



Free Si in CVI Product ⟵

Grain growth plus free Si Leaves CVI Product ⟶

CVI C Parameter, $10^4\ \%/\ MPa.\ hr^{1/3}$

Creep or Pre-Anneal Temperature, °C

△ Ultra Fiber (anneal T)
■ Full CVI Matrix (creep T)
● Partial CVI Matrix (anneal T)
★ Full PIP Matrix (anneal T)
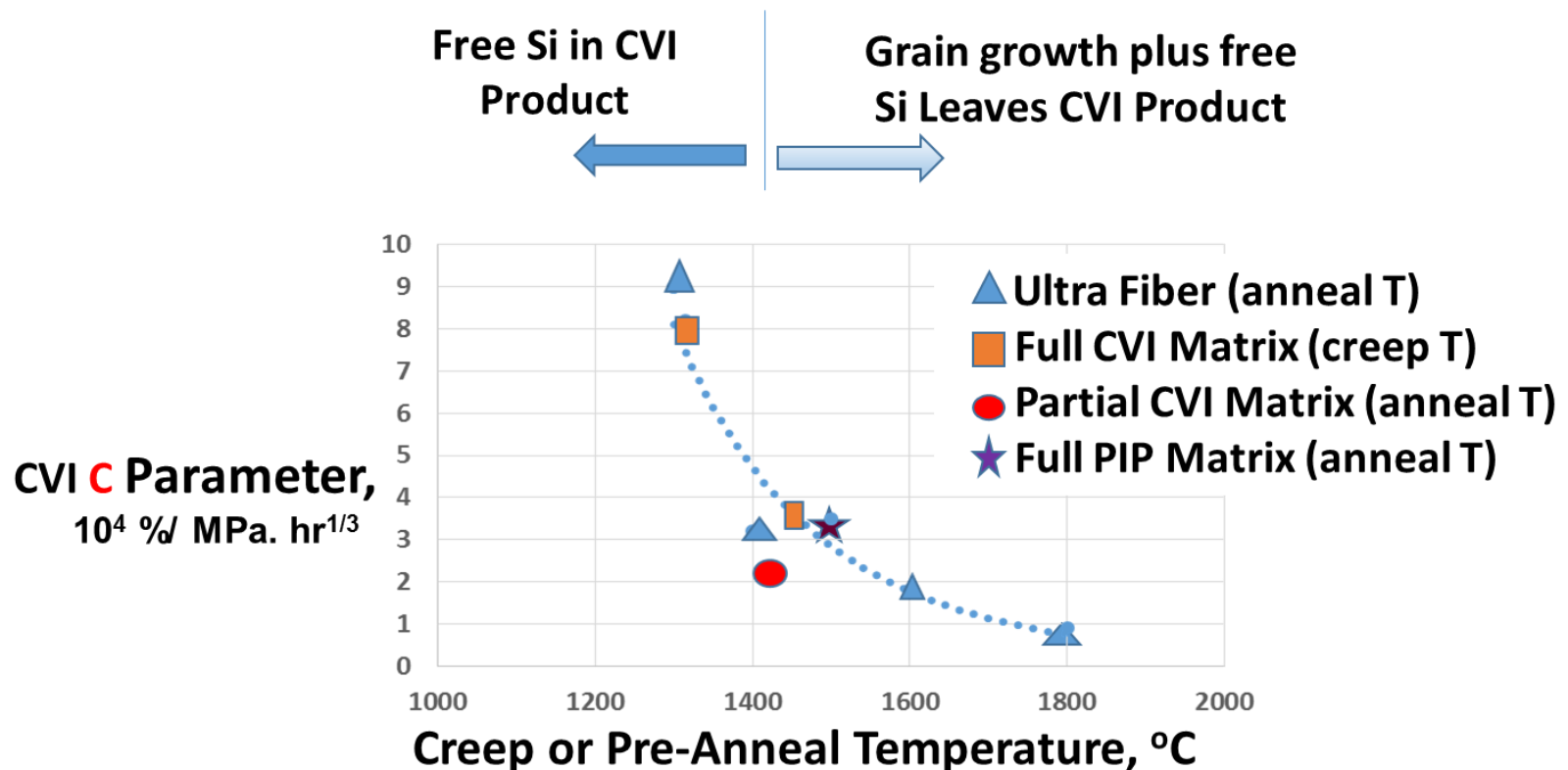
# *Calculating Creep-Limited UUT (T\*) for SiC/SiC CMC containing Full or Partial CVI Matrices*

- **Using the primary stage creep equations and associated parameters for the CVD-derived Ultra SCS fiber, one can then calculate T\* for the SiC/SiC CMC with a CVI matrix content $V_m$ by:**

$$T^* \text{ (kelvin)} = B/3 \ln (C \, \sigma_m \, t^{1/3} / \varepsilon^* )$$

**Here $\sigma_m = (\sigma_c / V_m) =$ matrix stress, t = desired CMC component service life, and $\varepsilon^* =$ max creep strain (%) that CMC component can tolerate.**

- **Assuming $\sigma_c = 50$ MPa to avoid initial matrix cracking, $V_m = 0.20$ (Partial) to 0.50 (Full), t = 1000 hr, and $\varepsilon^* = 0.2\%$, T\* for as-produced and $1800^0$C-annealed CVI SiC matrices are estimated as follows:**

|  | As-produced $V_m = 0.20$ | As-produced $V_m = 0.50$ | $1800^0$C Annealed $V_m = 0.20$ | $1800^0$C Annealed $V_m = 0.50$ |
|---|---|---|---|---|
| **T\*** | **$1290^0$C** | **$1365^0$C** | **$1490^0$C** | **$1580^0$C** |

- **Note that if the CMC with CVI matrix should crack at the high T\*, the crack-bridging creep-prone polymer-derived fibers within a short time will probably cause undesirable CMC deformation and/or rupture.**

# Summary and Conclusions

- For the current SiC/SiC CMC types addressed in this study, it was determined that at high temperatures no close creep match between the fiber and matrix existed in order that both could carry the on-axis CMC load for long times. For example, for CMC with Full RFMI matrices, the HNS and iBN fibers controlled CMC creep; and for CMC with Full CVI, Partial CVI-NRMI, and Full PIP matrices, the matrix controlled CMC creep.

- At high temperatures, it was shown that obtaining a fiber-matrix creep match with the best creep-resistant polymer-derived SiC fibers may not be possible since they display creep strain that follows <span style="color:red">time to the first power</span>; while the CVI-derived SiC matrices follow <span style="color:red">time to the 1/3 power</span>.

- Using previously determined fiber creep equations, it was also shown that for a CMC 1000 hour service life and a 0.2 % creep strain limit, the creep-limited upper use temperature $T^*$ for Full RFMI composites was ~1300$^0$C for the HNS and iBN fibers and at best 1400$^0$C if an Advanced polymer-derived SiC fiber could be developed.

- Likewise, using a previously determined creep equation for the large-diameter CVI-derived Ultra fiber, it was shown that for un-cracked CMC with CVI-derived matrices under the same service requirements, the $T^*$ could be as high as 1600$^0$C dependent on the CMC creep or pre-anneal temperature.

- All these results support the need for development of <u>small-diameter CVI-derived SiC fibers</u> to match the creep behavior of CVI-derived matrices, and thus obtain SiC/SiC CMC with highest creep resistance and $T^*$.