Development of Engineered Ceramic Matrix Composites

S. V. Raj[1] (PI), R. Bhatt[2] and M. Singh[2]

1) Glenn Research Center, Cleveland, OH

2) Ohio Aerospace Institute, Cleveland, OH

Acknowledgements

Technicians: Mr. Ray Babuder; Mr. Robert Angus; Mr. Ronald Phillips & Mr. Daniel Gorican

Program Manager: Dr. Koushik Datta

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Introduction

- **Advanced aircraft engines require the use of reliable, lightweight, creep-resistant and environmentally durable materials.**
- **Silicon carbide-based ceramic matrix composite (CMC) technology is being developed to replace nickel-based superalloy blades and vanes.**
    - **Near term 1589 K (2400 ºF) (cooled).**
    - **Medium term 1755 K (2700 ºF) (cooled).**

Factors Affecting Composite Properties

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Composites are engineered systems, whose properties depend on:

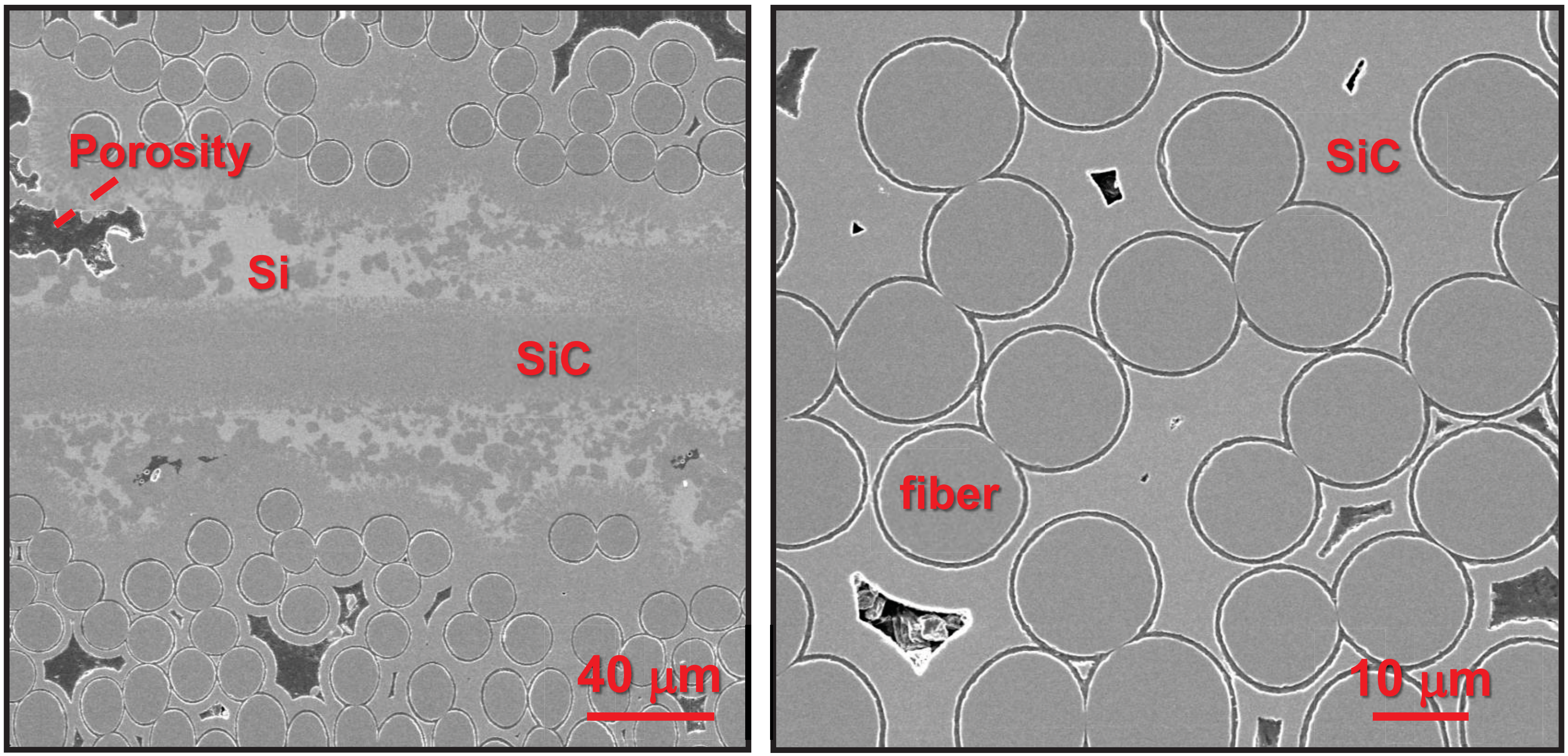
- Fiber properties
- **Matrix properties**
- Interfacial properties
- Volume fractions of the constituents
- Processing
- Fiber weave architecture
- Fiber coatings
- Protective coatings (e.g. EBCs, TBCs)

MMCs & IMCs

CMCs

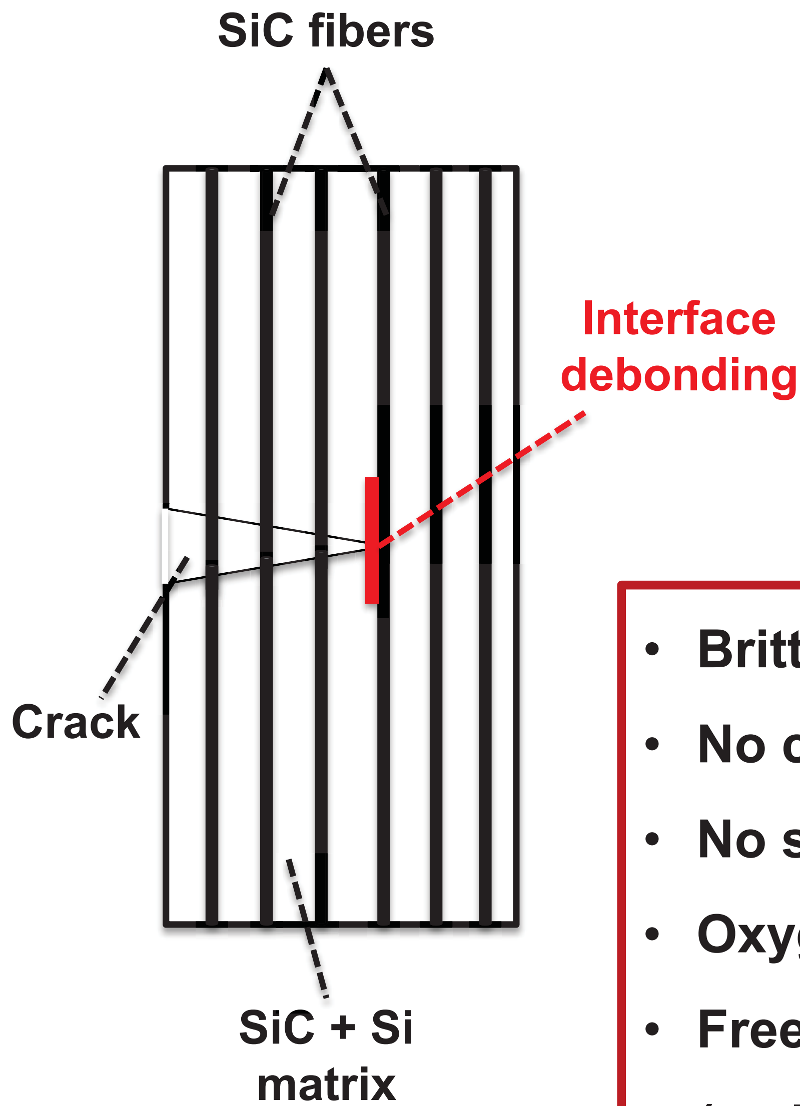
Typical Microstructures of As-Processed BN-Coated Hi-Nicalon MI SiC Composites

(Courtesy M. Singh)



Density ~ 96-97 %

Current SiC/SiC CMC Matrix Capabilities



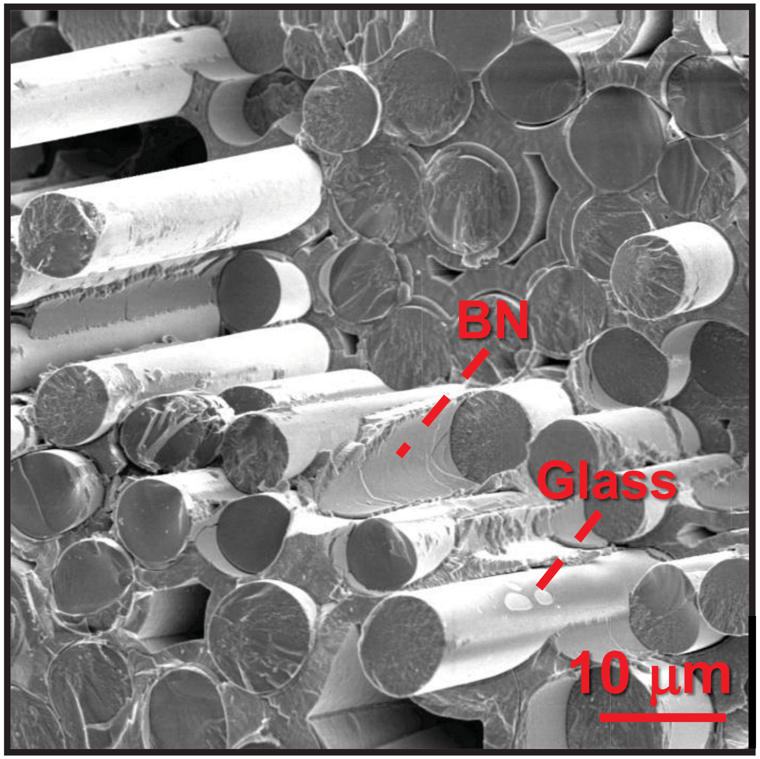
- Matrix fills space and provides a thermally conductive path.
- Fracture toughness due to crack bridging and interface debonding.
- Relatively low matrix cracking strength - $\sigma_{design} < \sigma_{proportional\ limit}$

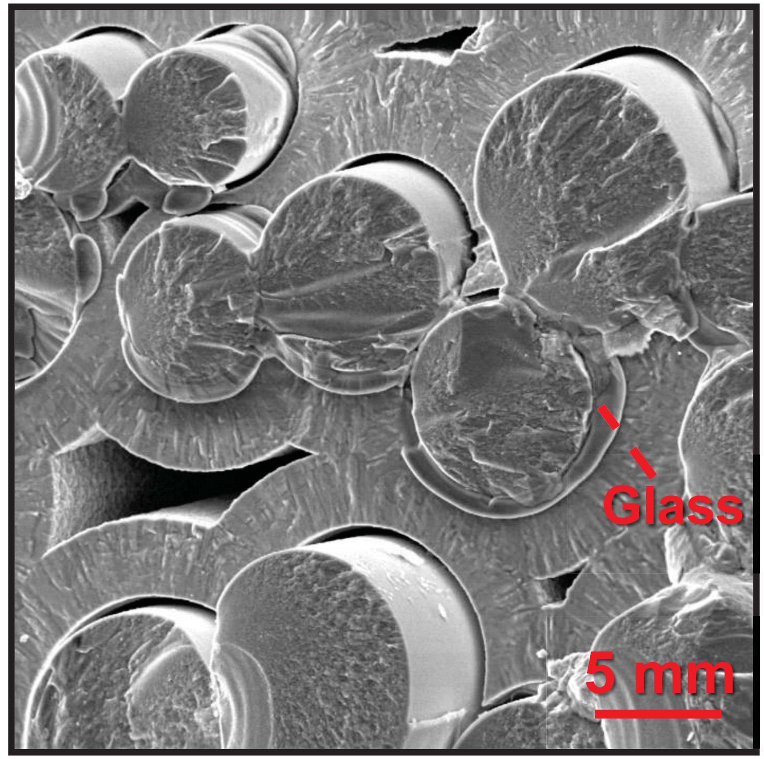
- Brittle at all temperatures.
- No crack tip blunting – fast crack propagation.
- No self-healing.
- Oxygen ingress to fibers shortens fiber life.
- Free Si in the matrix limits temperature usage (melting point of Si: 1687 K; 1414 ºC; 2577 ºF).

Recession of BN and Formation of Glassy Phase in BN-Coated Hi-Nicalon MI SiC Composites

(Courtesy M. Singh)

T = 973 K; σ = 250 MPa;1000 h in air





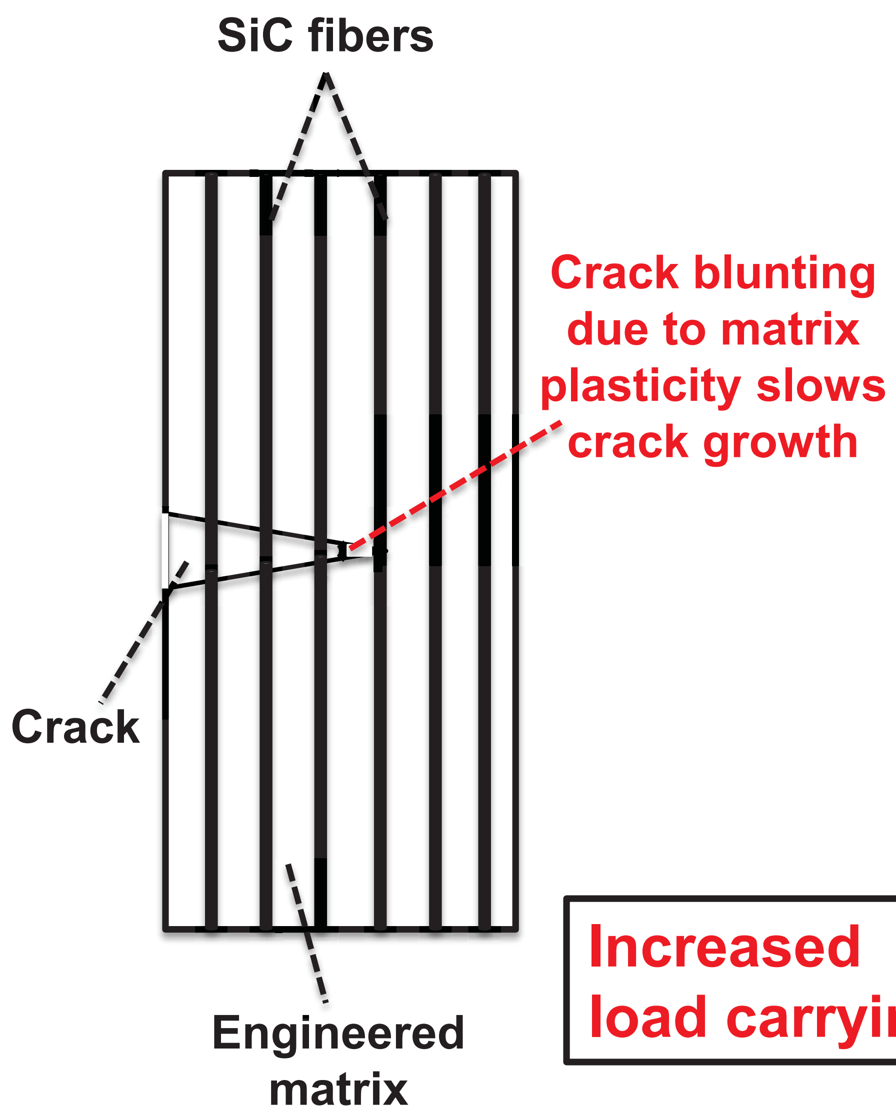
$$2BN\ (s) + 3/2\ O_2\ (g) = B_2O_3\ (l) + N_2\ (g)$$

B_2O_3 - SiO_2: Low eutectic temperature of 372 °C

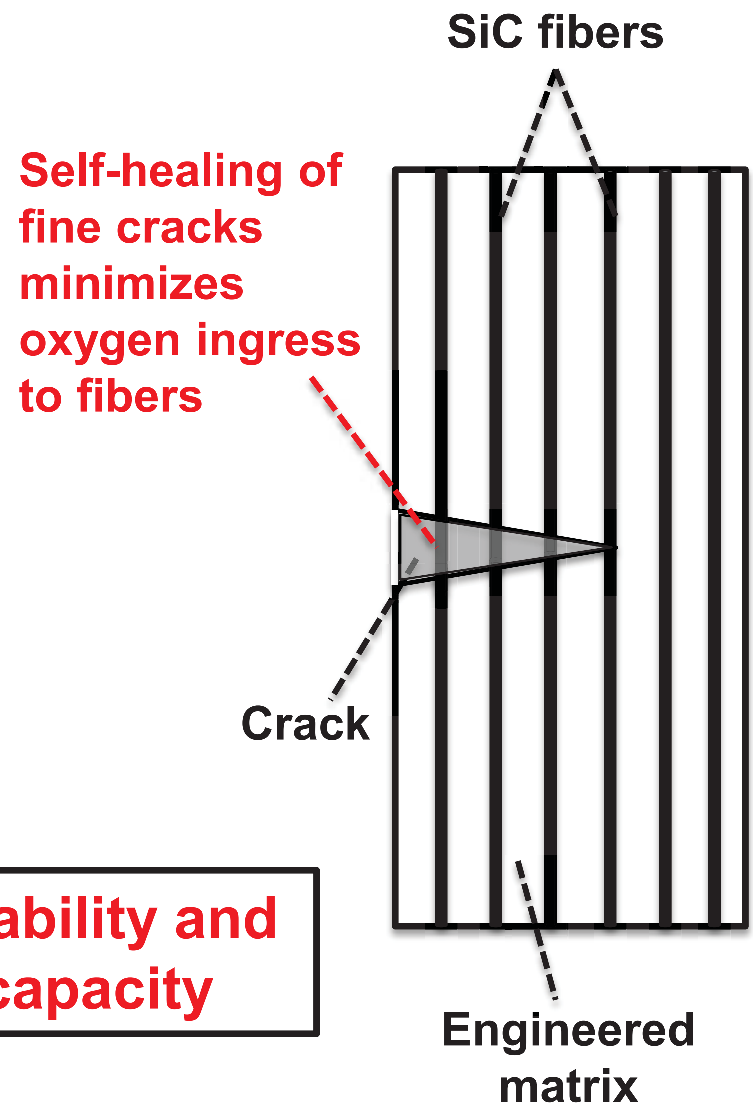
Important Question

Can the matrix constituents be suitably engineered to develop a new generation of Engineered Matrix (Ceramic) Composites (EMCs) with improved properties and tailored for a specific component?

Crack Tip Blunting and Self-Healing



Increased reliability and load carrying capacity



Innovation and Expected Impact

- **High temperature matrix -** greater than 1589 K (1315 ºC/2400 ºF)
- **Matrix plasticity -** increased reliability, compliant matrix.
- **Chemical and thermal strain compatibility** with the coated SiC fibers.
- **Self-healing matrix -** prevents or minimizes oxygen ingress.
- **Low free Si -** reduces fiber attack, reduces incipient melting, increased high temperature capability.
- **Dense matrix -** high thermal conductivity.

Historical Perspective

Pre-1980s	Current	Concept
Monolithic ceramics	Ceramic matrix composites (CMCs)	Engineered matrix composites (EMCs)
Low toughness Low strength	Higher toughness Higher strength Free silicon	Crack blunting & self-healing Low free silicon Higher toughness Higher strength Higher temperature

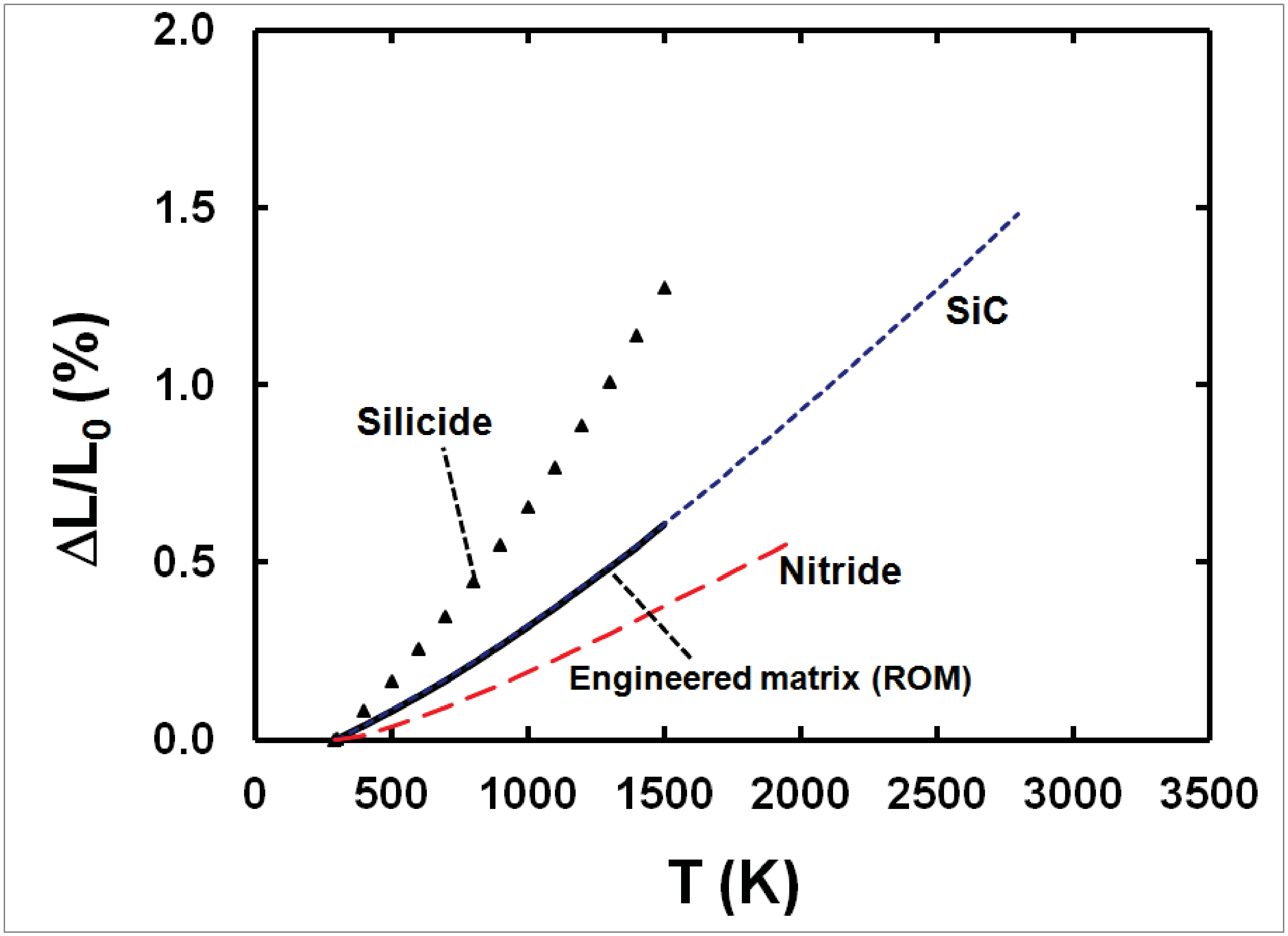
Technical Approach

- **Plasticity – Introduce a chemically stable metallic silicide.**
- **Temperature capability – Choose silicides with melting points higher than that of Si (m.p. 1687 K; 1414 ºC; 2577 ºF).**
- **Thermal expansion – Match thermal expansion of the engineered matrix (EM) with the SiC fibers.**
- **Self-healing capability – Add constituents to heal cracks with low viscosity oxides or silicates.**
- **Low Si – Melt infiltrate with silicide instead of Si.**
- **Dense EMCs – Slurry infiltration and melt infiltration.**

Silicide Additives

- $CrSi_2$
- $MoSi_2$
- $TiSi_2$
- WSi_2
- CrMoSi alloy

Matching Thermal Strains: Theoretical Concept



Matrix Design Concept

$$(\Delta L/L_0)_{fiber} = (\Delta L/L_0)_{EM} = V_{silicide}(\Delta L/L_0)_{silicide} + V_{SiC}(\Delta L/L_0)_{SiC} + V_{Si3N4}(\Delta L/L_0)_{Si3N4}$$

Concept	$V_{silicide}$ (%)	V_{SiC} (%)	V_{Si3N4} (%)
Traditional	0	100	0
Present investigation	x	(100-x-y)	y

Objectives

- Evaluate different engineered matrices based on theoretical concepts.
- Proof of concept: Demonstrate thermal strain compatibility with SiC.
- Evaluate bend and oxidation properties.
- Evaluate self-healing compositions.
- Fabricate and test engineered matrix composites.

Matrix Processing Steps

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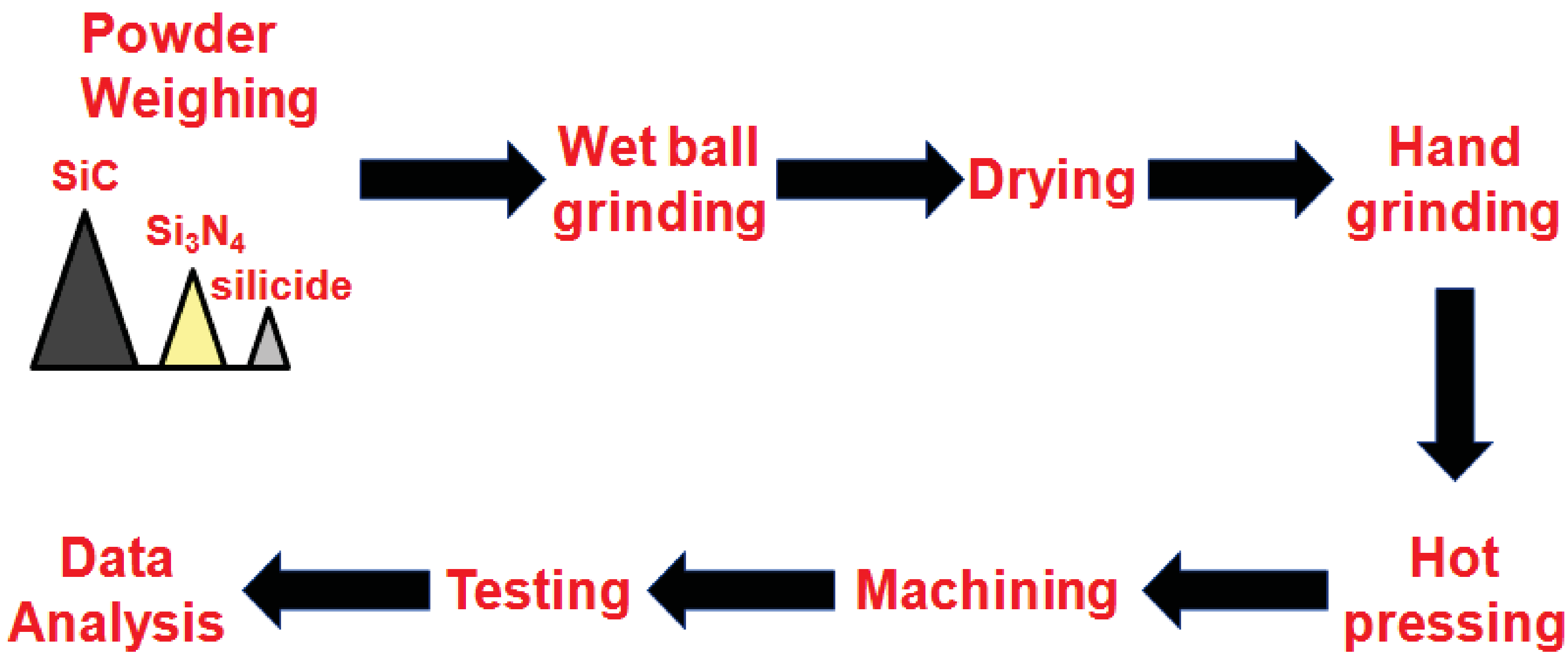
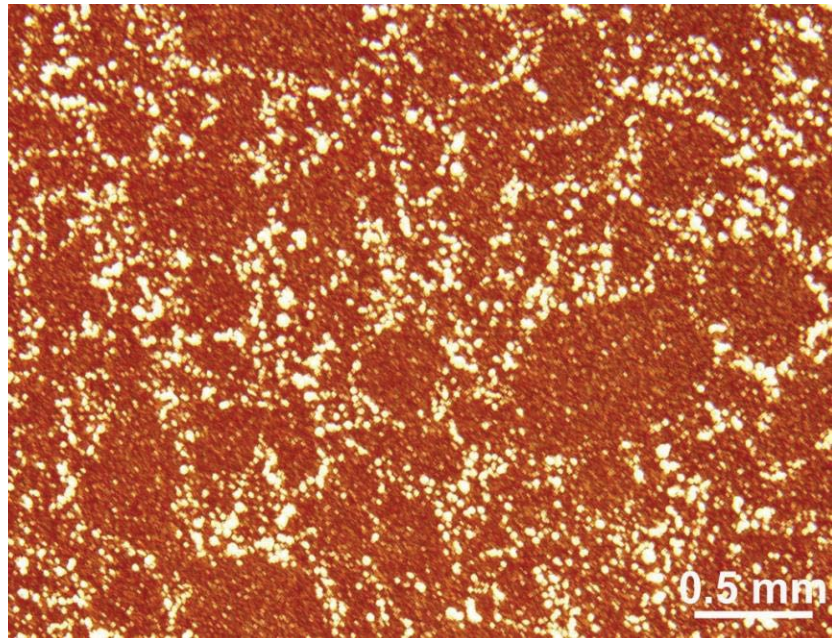


Hot-Pressed Plate and Optical Micrograph

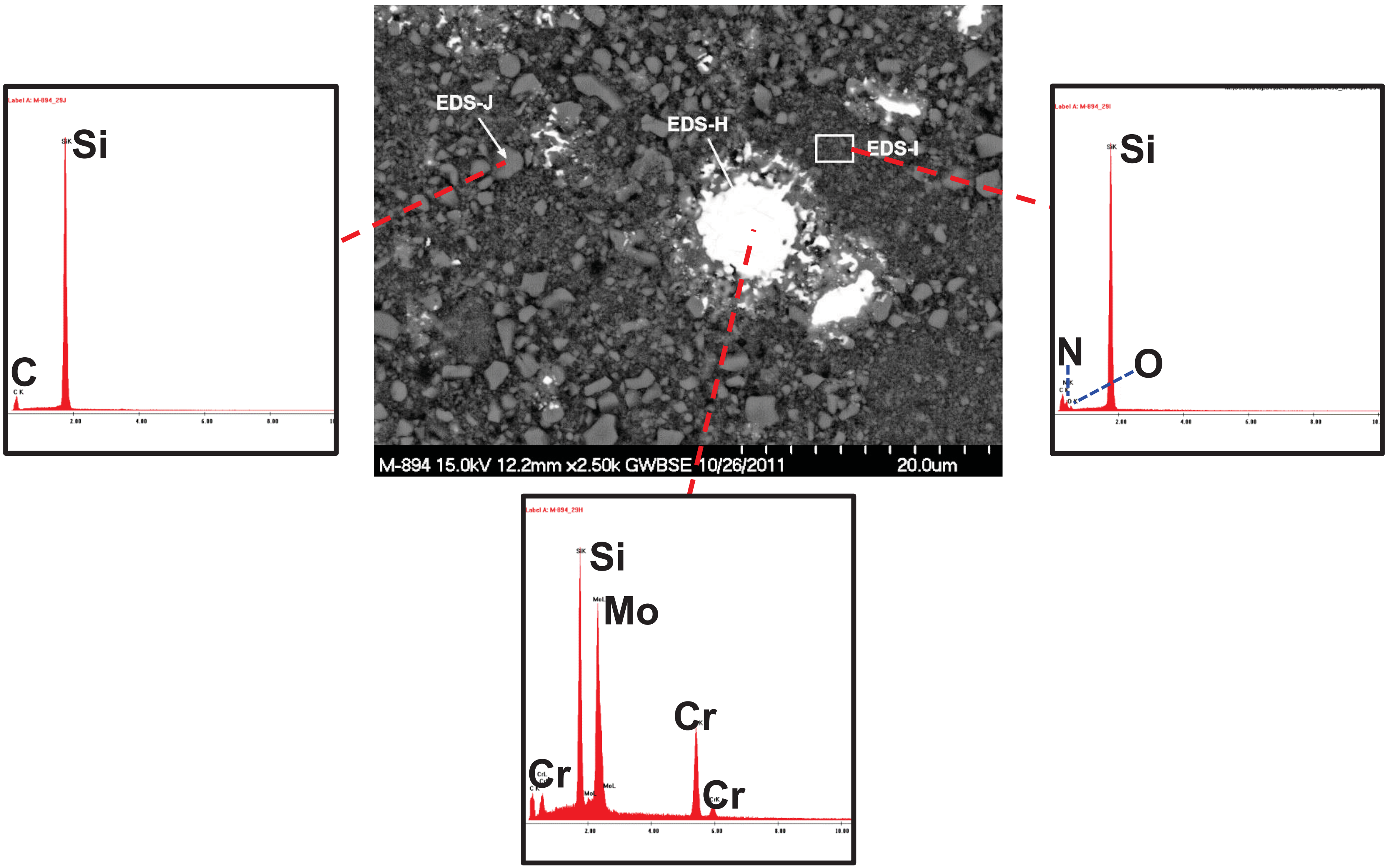
CrMoSi/SiC/Si_3N_4 (CrMoSi-EM)

50 x 50 x 4 mm

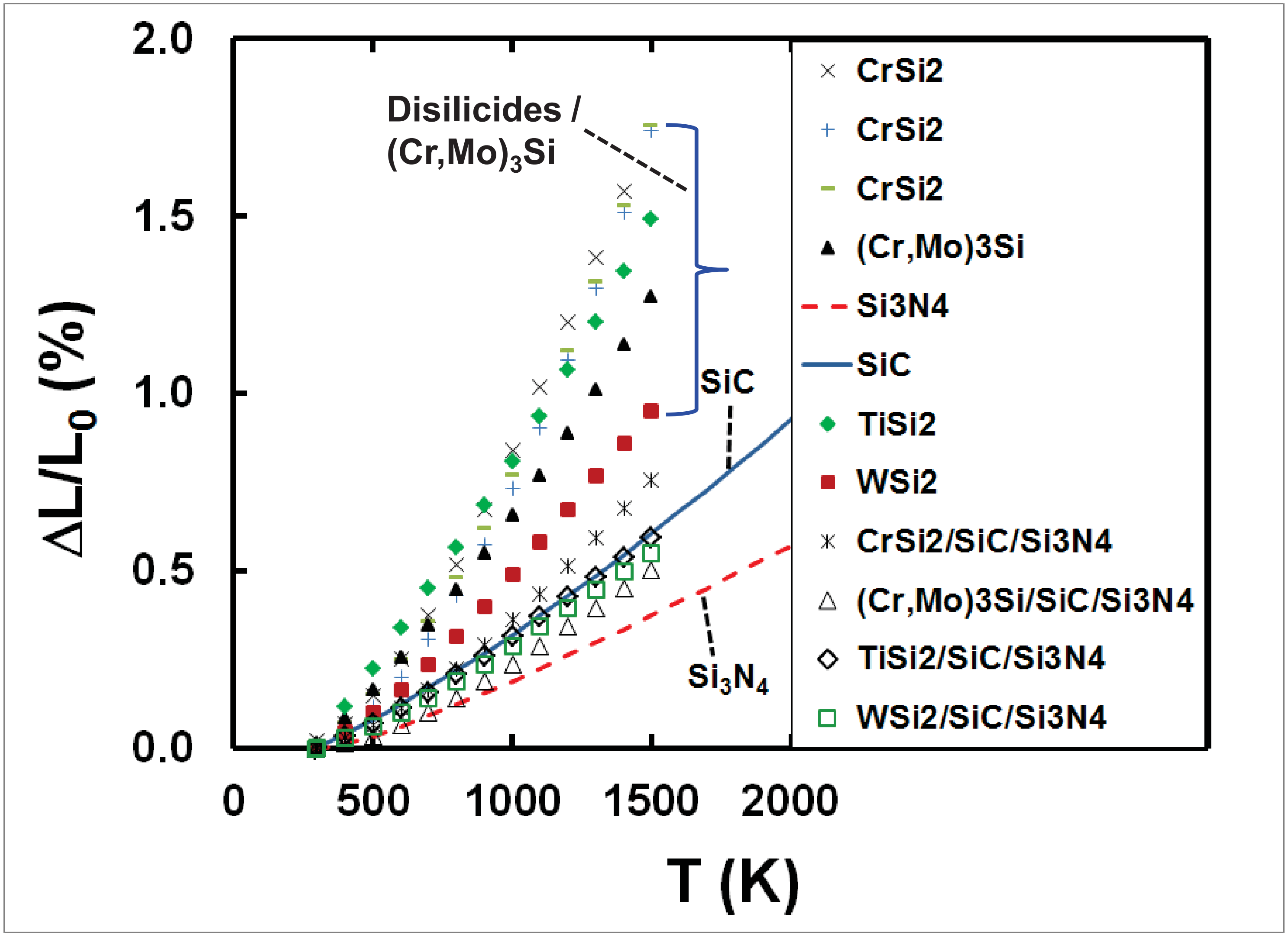
Optical micrograph



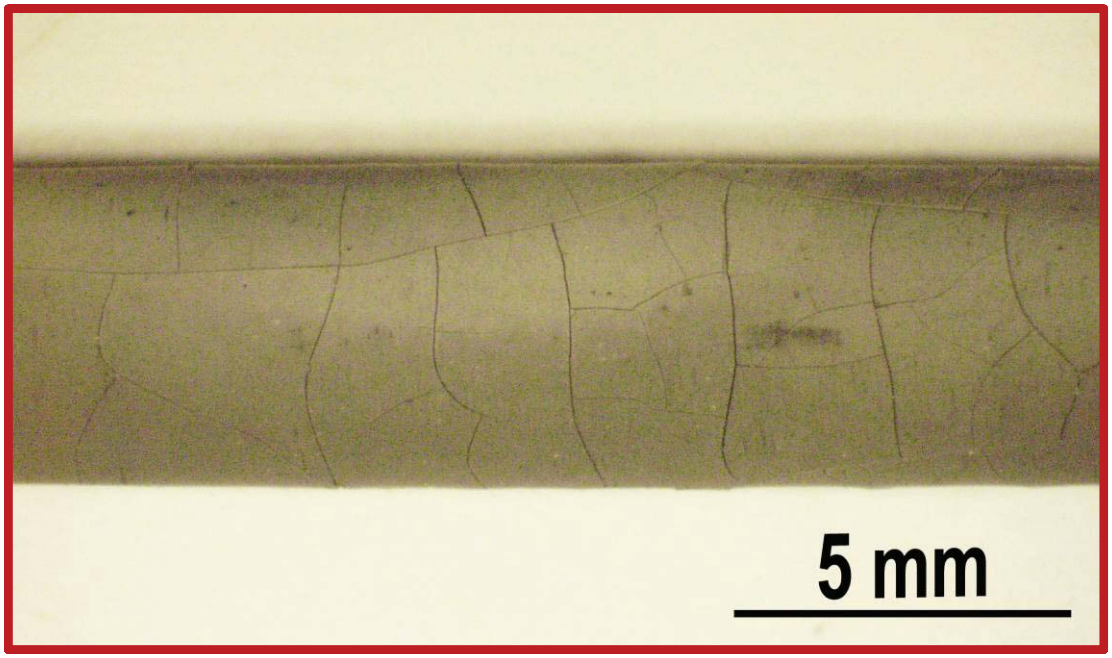
Back Scattered Image and Energy Dispersion Spectra: CrMoSi/SiC/Si_3N_4 (CrMoSi-EM)



Proof-of-Concept: Thermal Strains

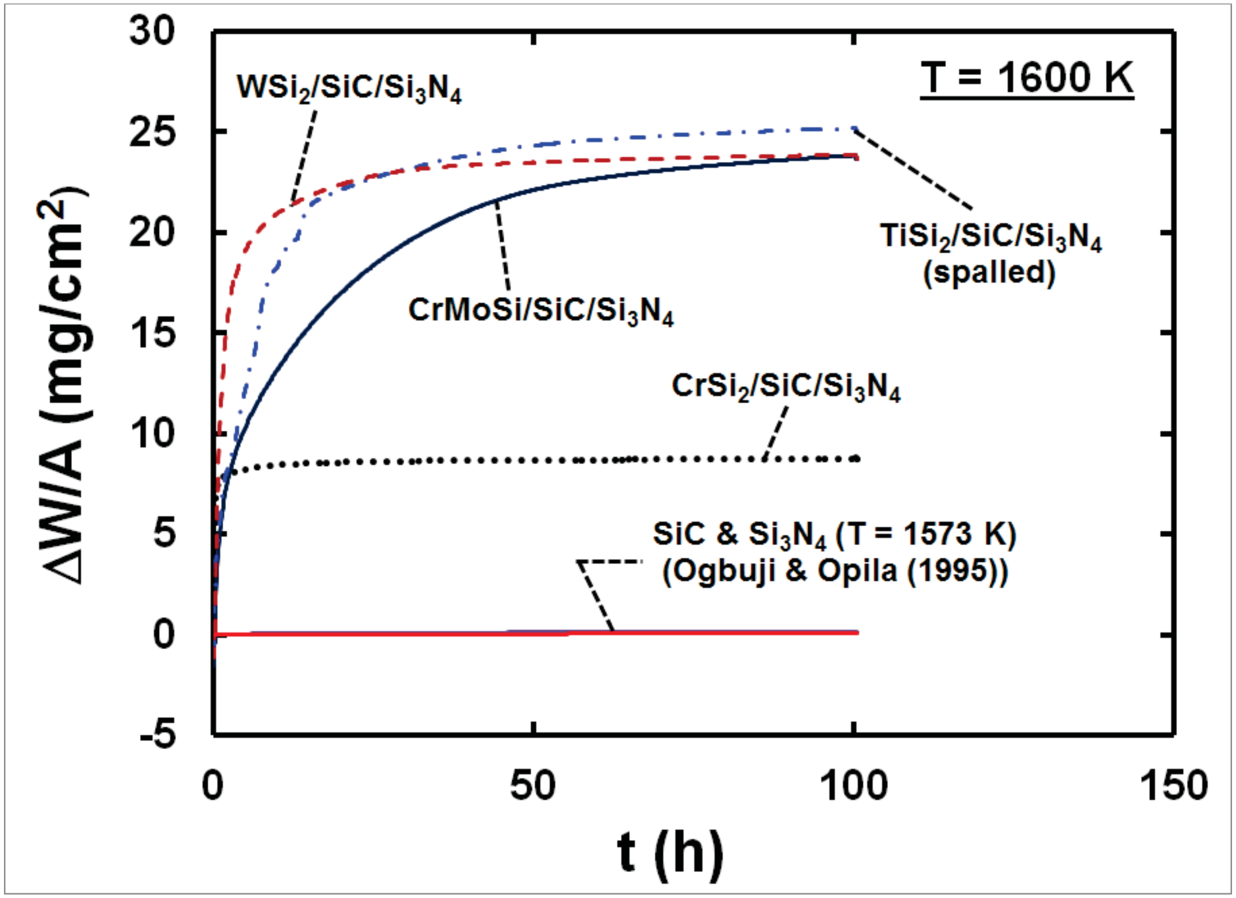


Macrograph of the Surface of a Thermally Cycled CTE $MoSi_2/SiC/Si_3N_4$ Specimen



- $MoSi_2/SiC/Si_3N_4$ engineered matrix dropped from the program.

Isothermal Oxidation Behavior of Engineered Matrices



$TiSi_2/SiC/Si_3N_4$ and $WSi_2/SiC/Si_3N_4$ engineered matrices dropped from the program

Four-Point Bend Stress-Strain Curves for a $CrSi_2$ Engineered Matrix

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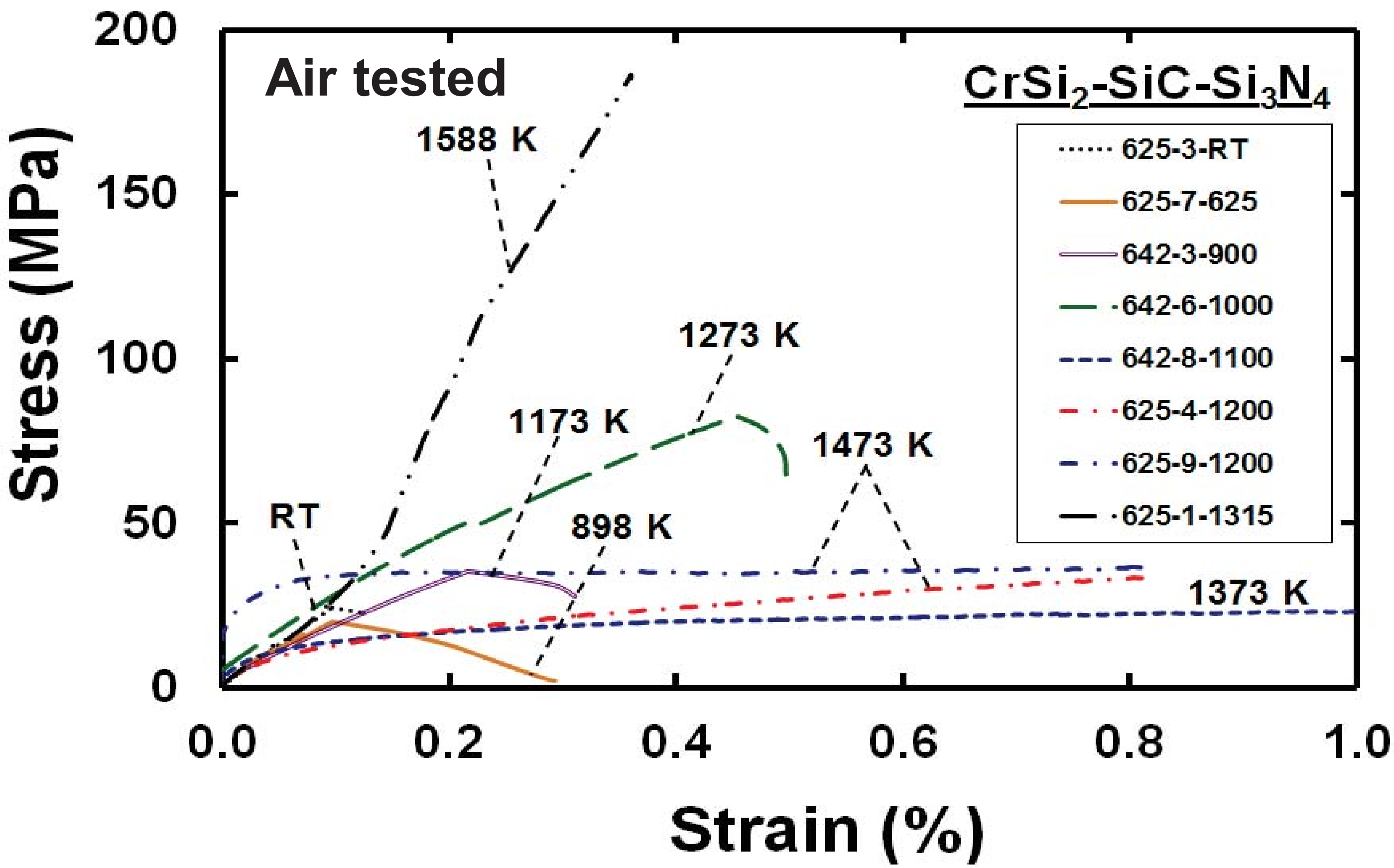

- Crack blunting due to crack tip plasticity increases bend strength

Four-Point Bend Stress-Strain Curves for a CrMoSi Engineered Matrix

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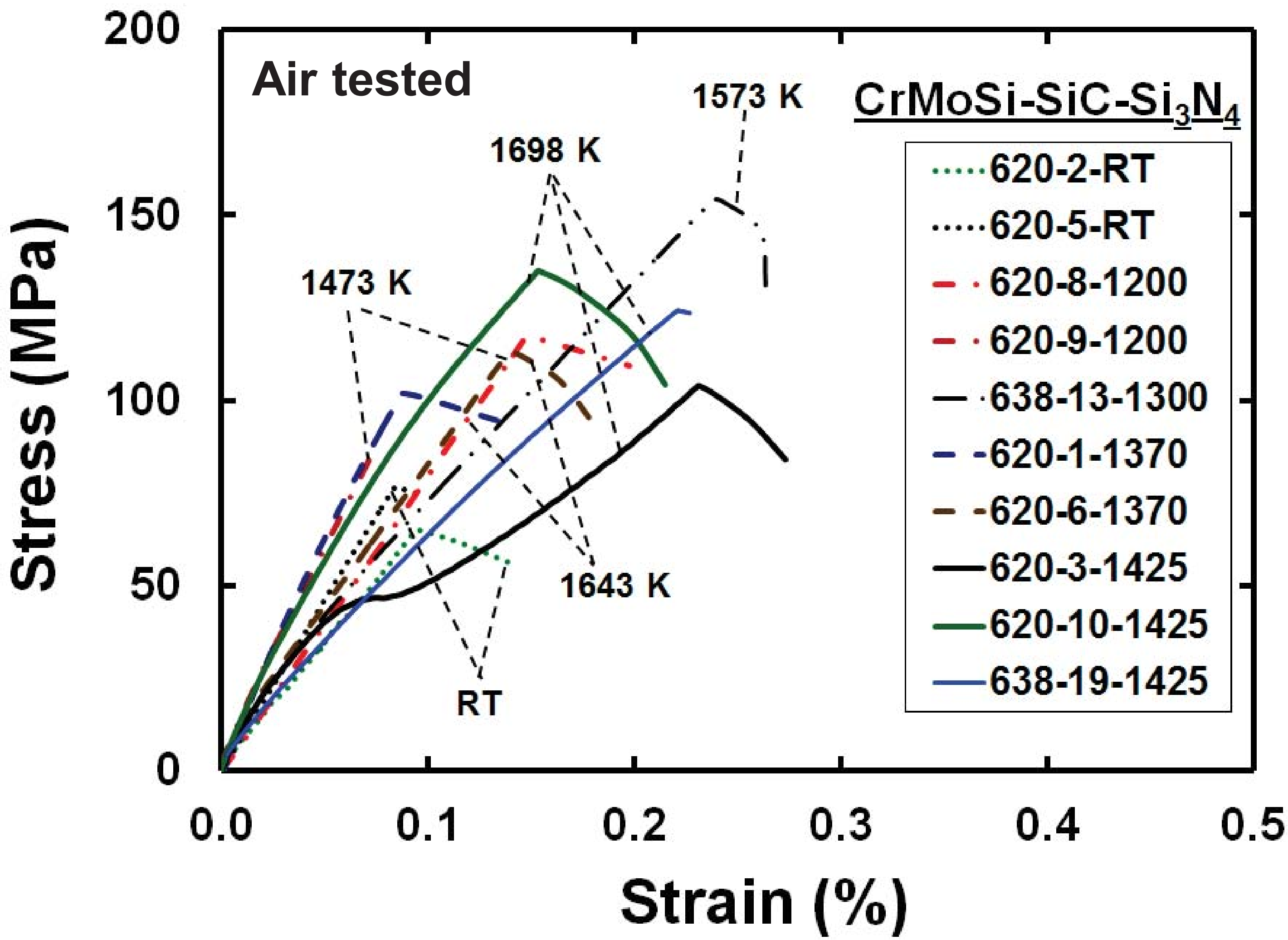
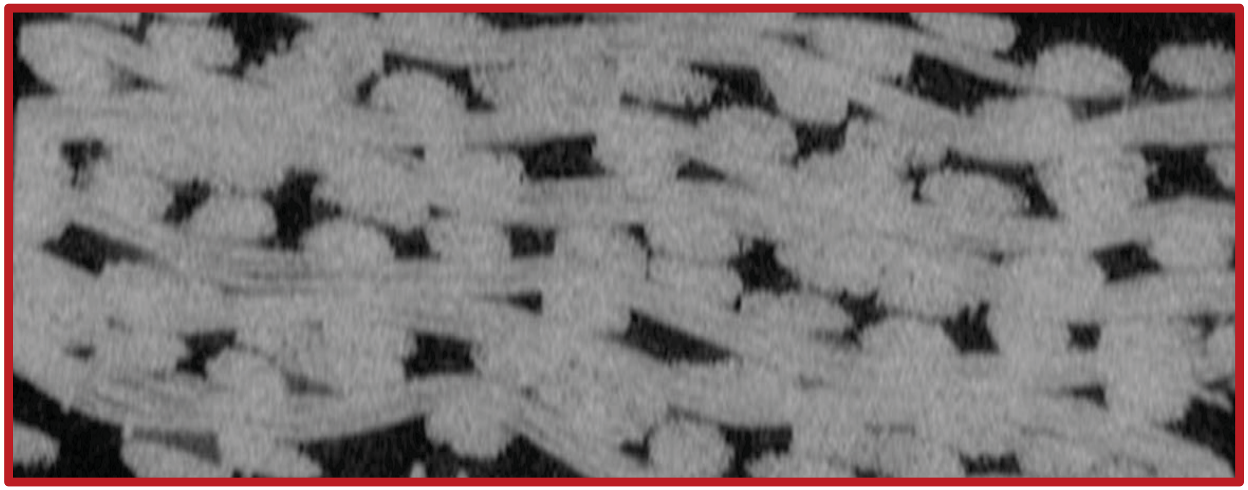


CT Scan and a Schematic of the BN-Coated SiC/SiC Preform



CT Scan

Schematic of void distribution

Void volume fraction ~ 25%

Steps in Engineered Matrix Composite Fabrication

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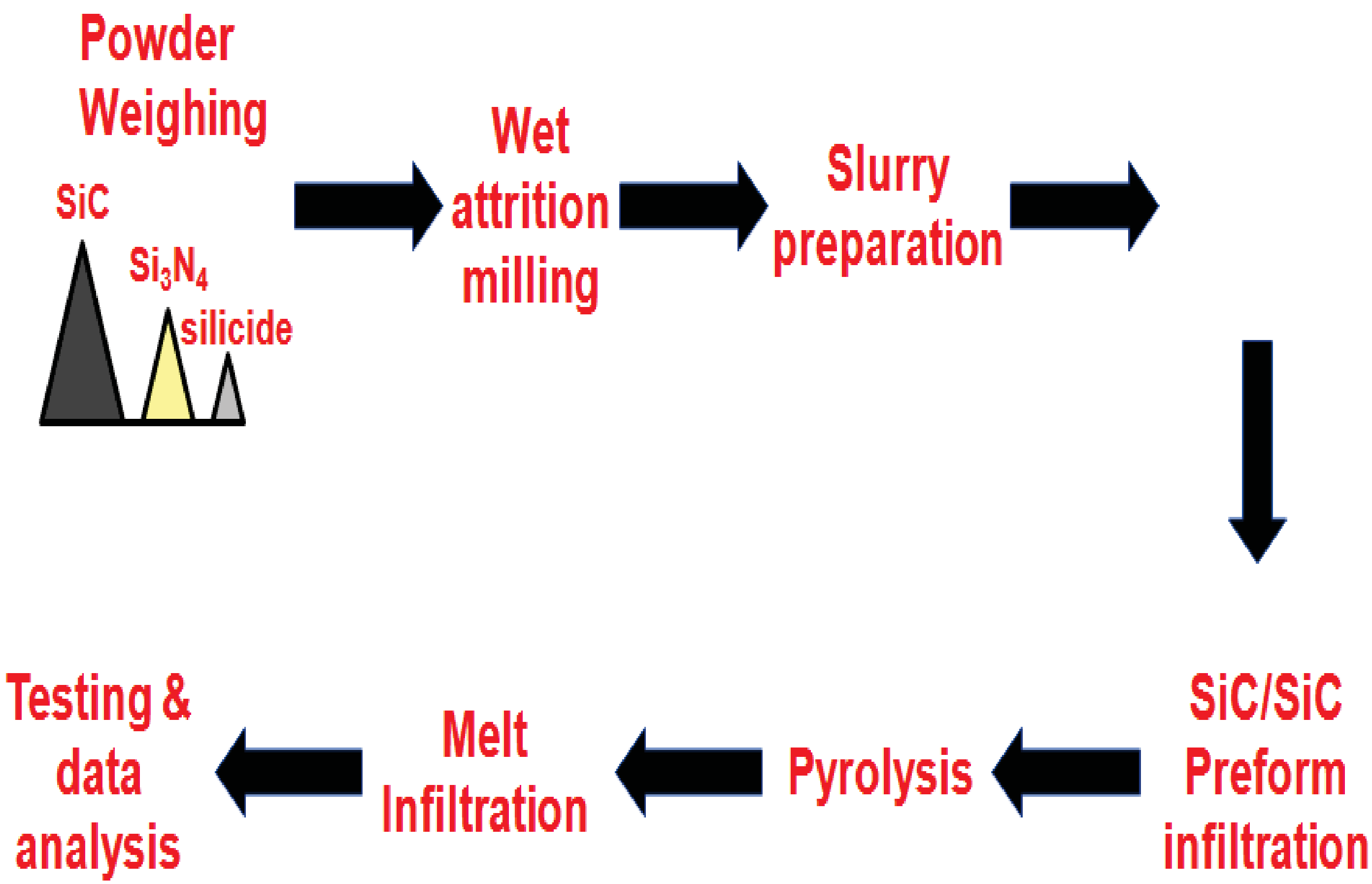
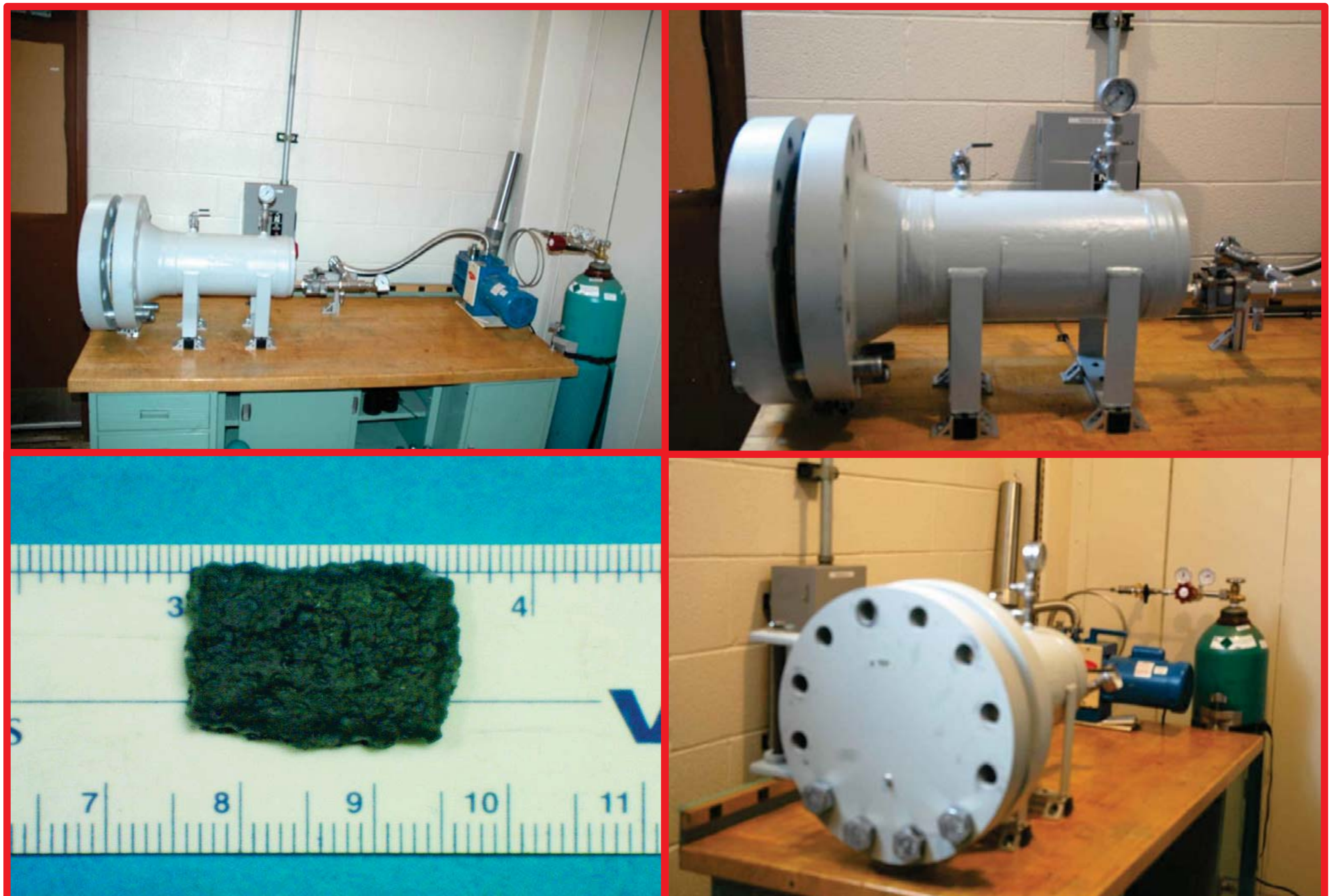
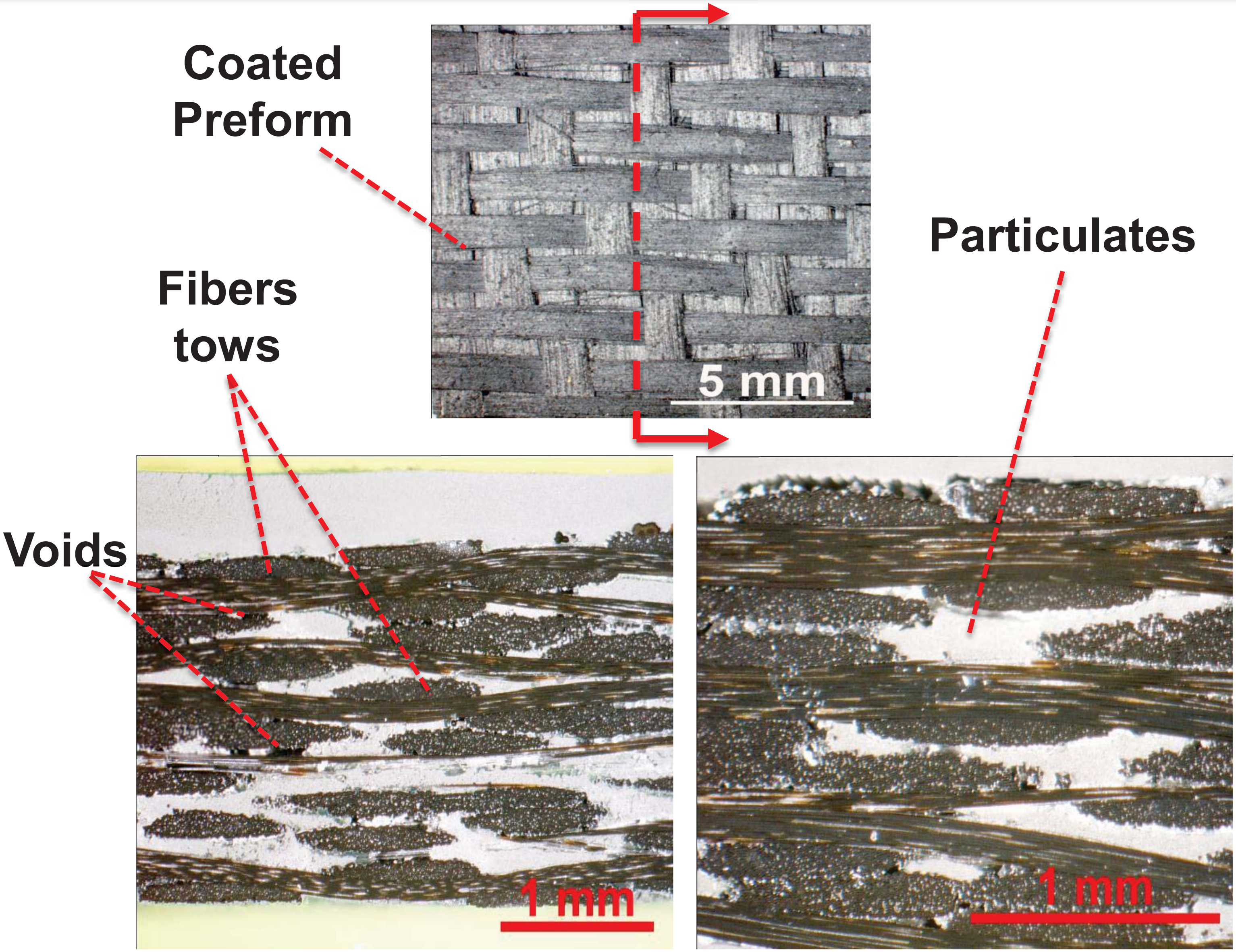
Composite Fabrication



Epoxy pressure infiltration unit



Microstructures of $TiSi_2$-EM-Infiltrated SiC Fiber Preform



CT Scans of $TiSi_2/SiC/Si_3N_4$ Particulate Epoxy and Si- Melt Infiltrated Preform

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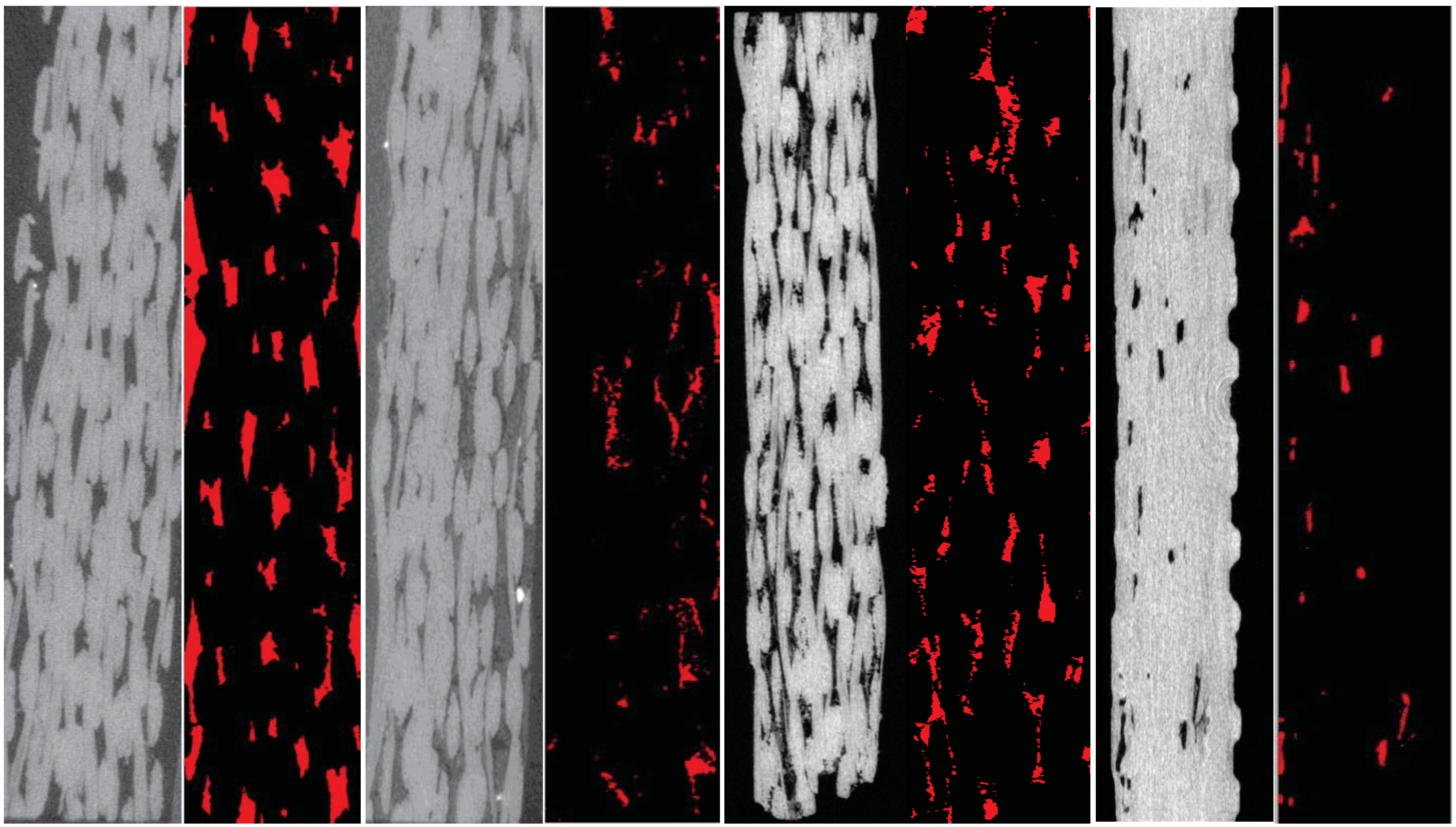
As-received Preform	Particulate Infiltrated	Pyrolized	Si Melt Infiltrated



Area fraction of porosity ~ 21-23%	Area fraction of porosity ~ 0.9%	Area fraction of porosity ~ 6.6%	Area fraction of porosity ~ 1.8%

The red regions are voids

$TiSi_2/SiC/Si_3N_4$ epoxy infiltrated preforms

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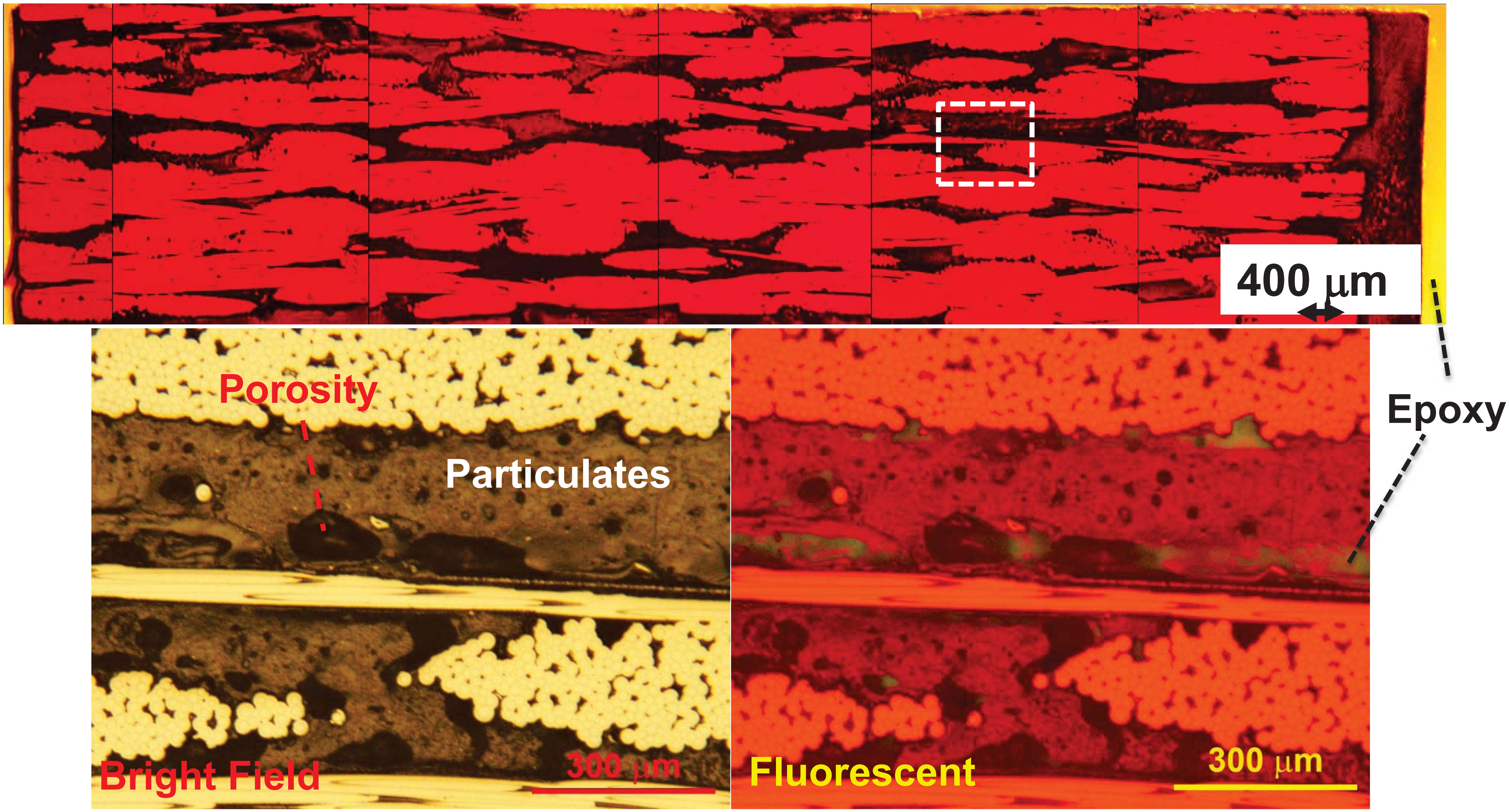
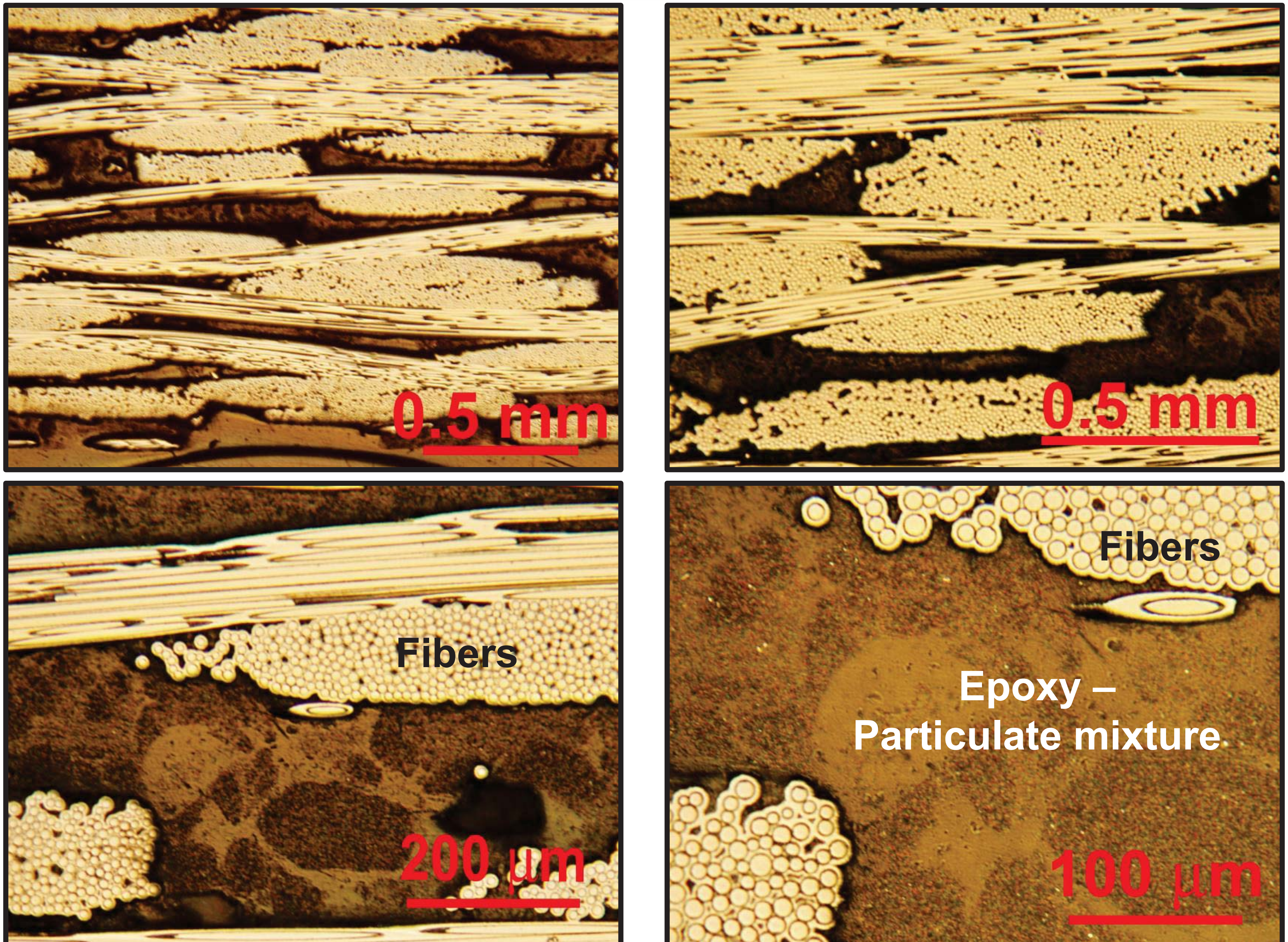
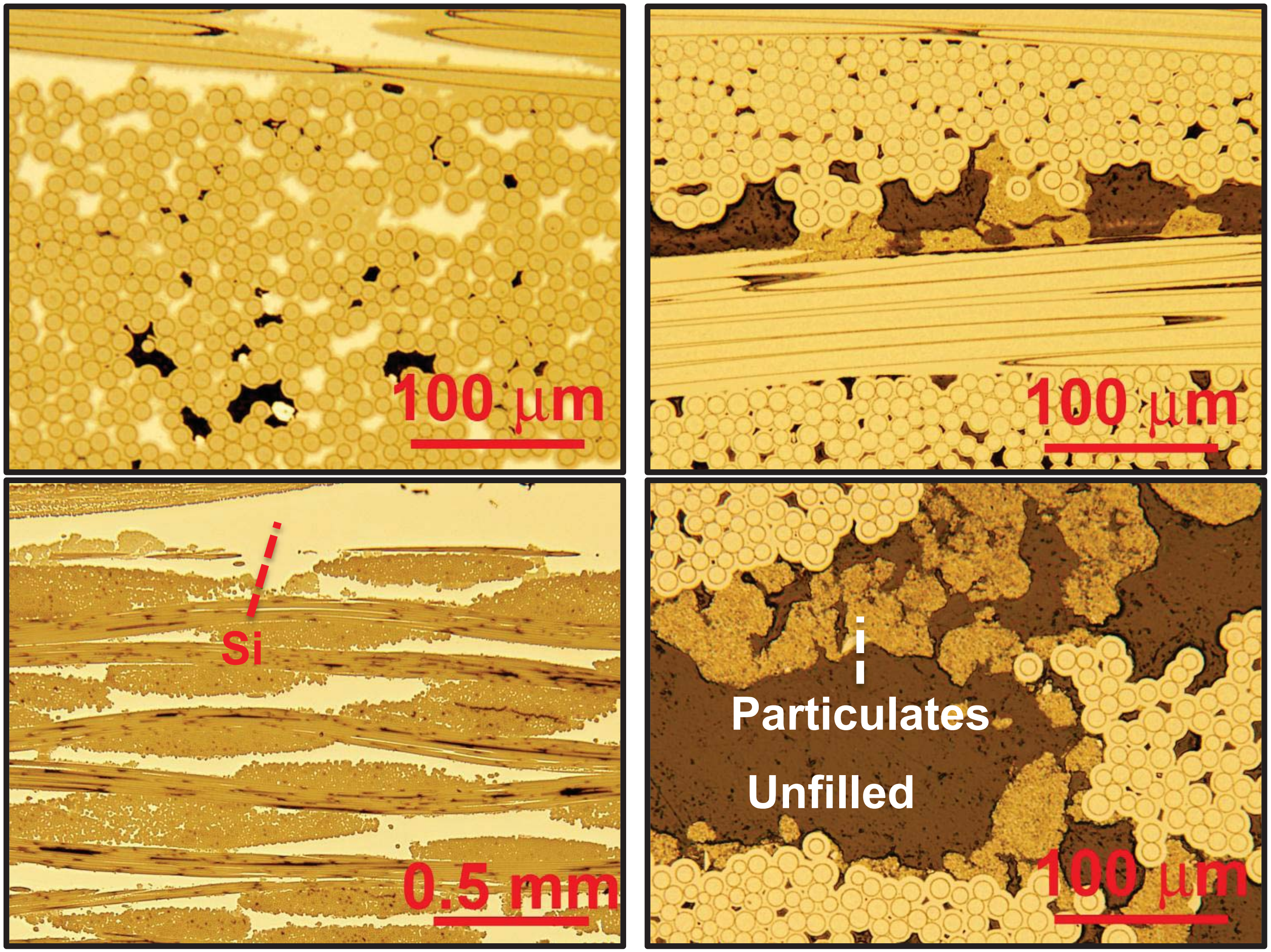


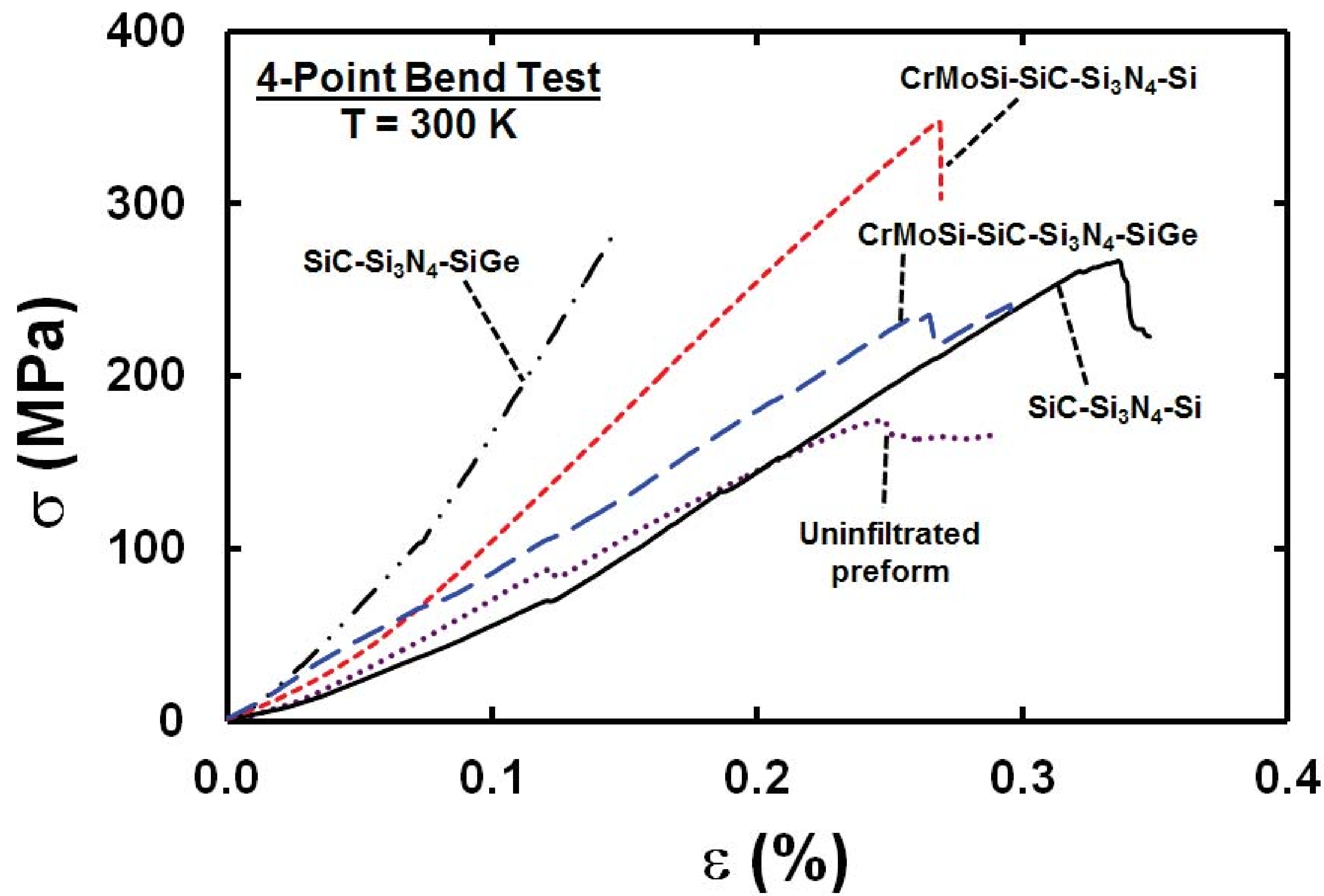
CrMoSi/SiC/Si_3N_4 Epoxy Infiltrated Preforms



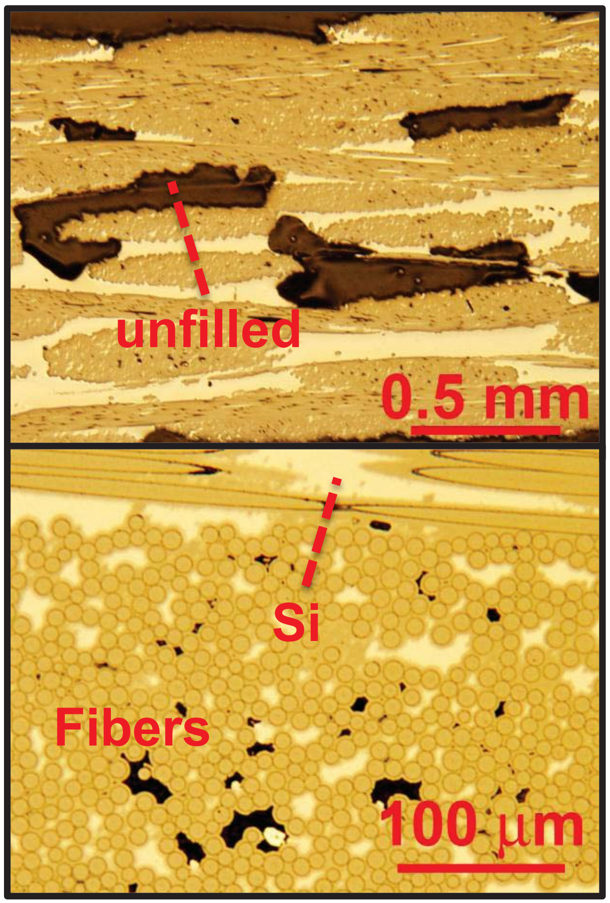
Particulate and Silicon Melt Infiltrated SiC/SiC Preforms



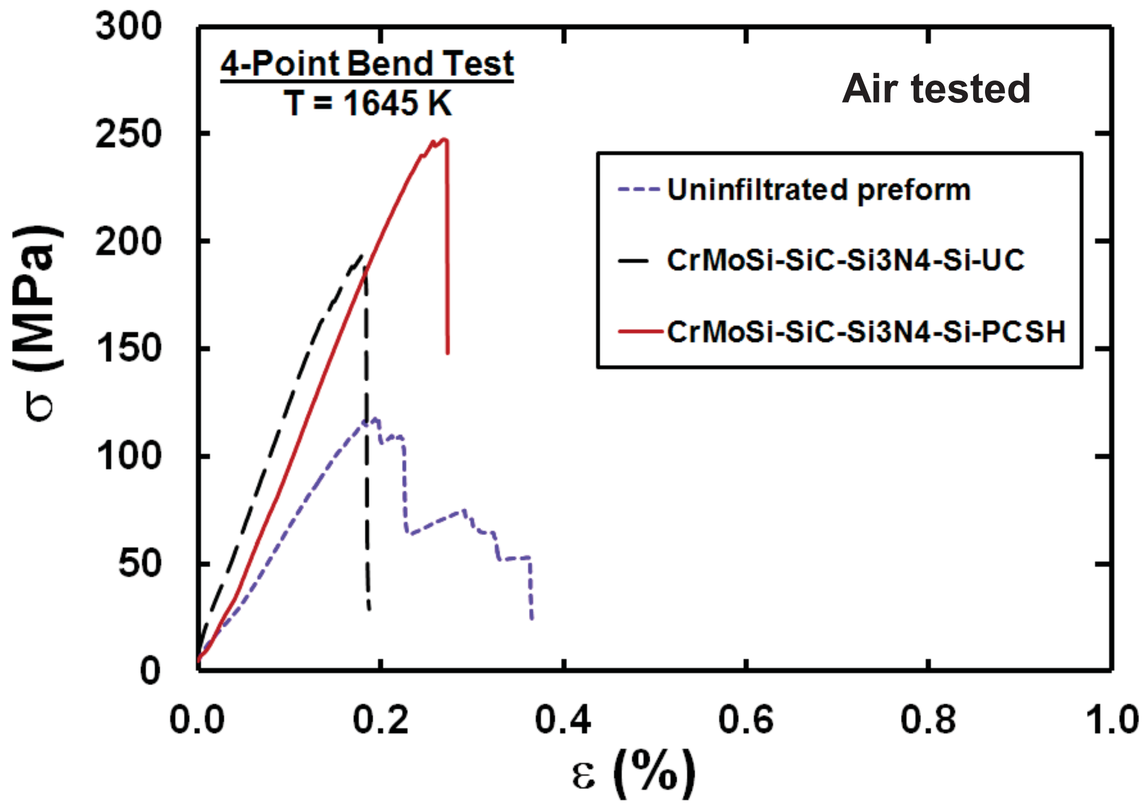
Room Temperature Bend Stress-Strain Curves for CrMoSi EMCs



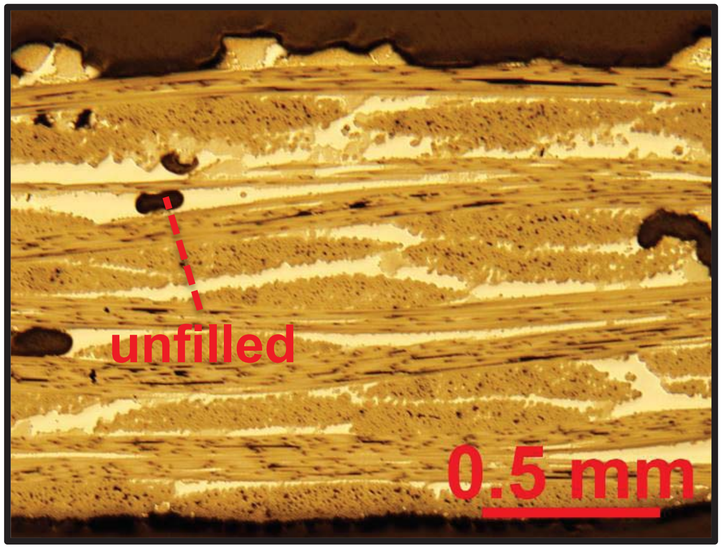
Preliminary Studies: Bend Strengths of CrMoSi-SiC-Si_3N_4-Si EMCs

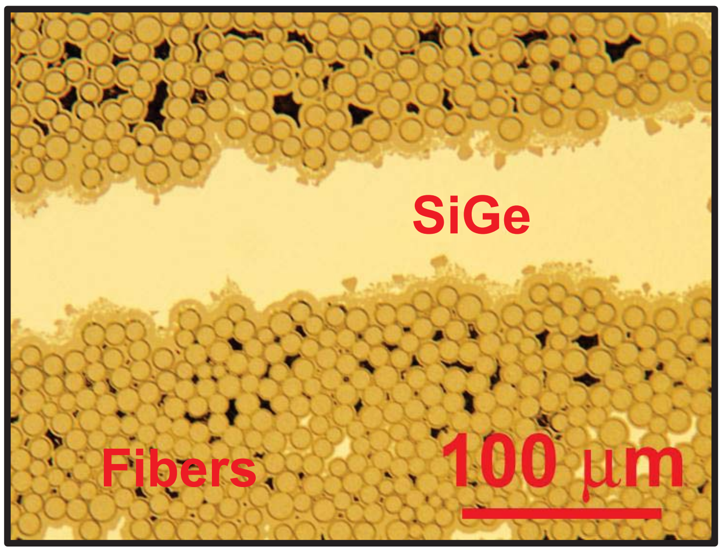


Heat treated in air at 1600 K for 50 h



Preliminary Studies: Bend Strengths of CrMoSi-SiC-Si_3N_4-SiGe EMCs





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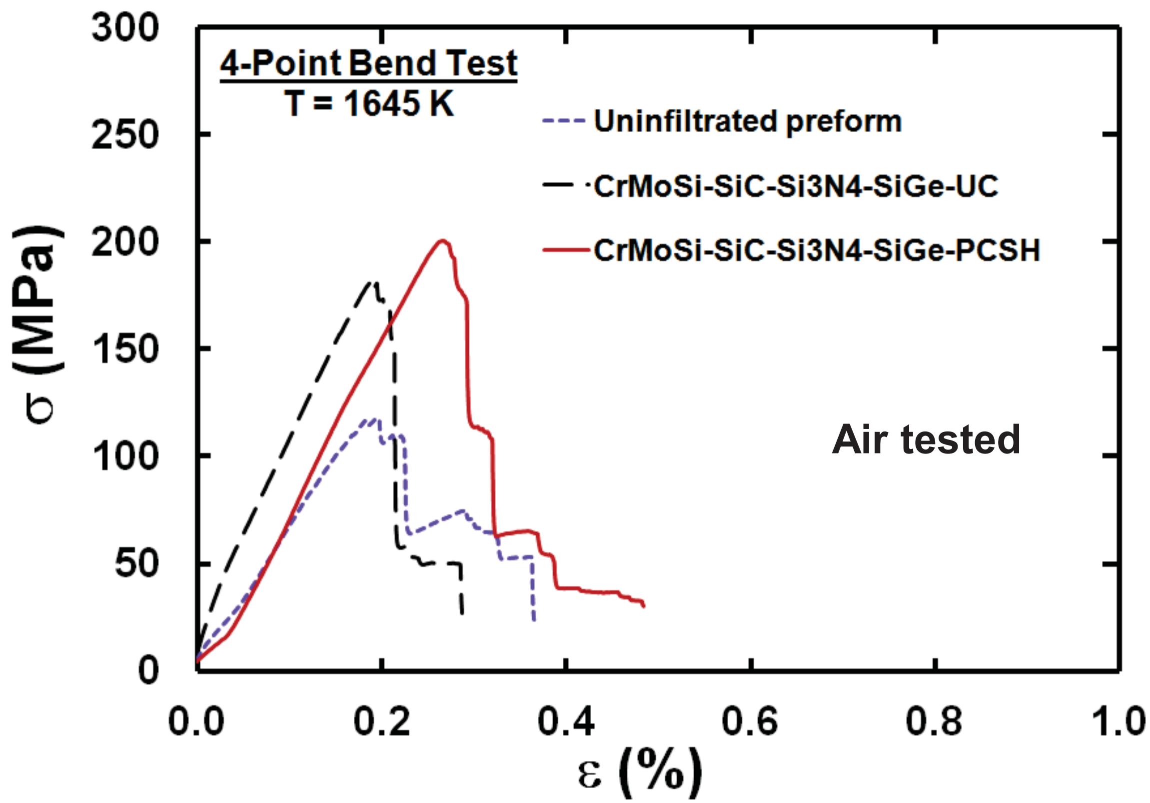
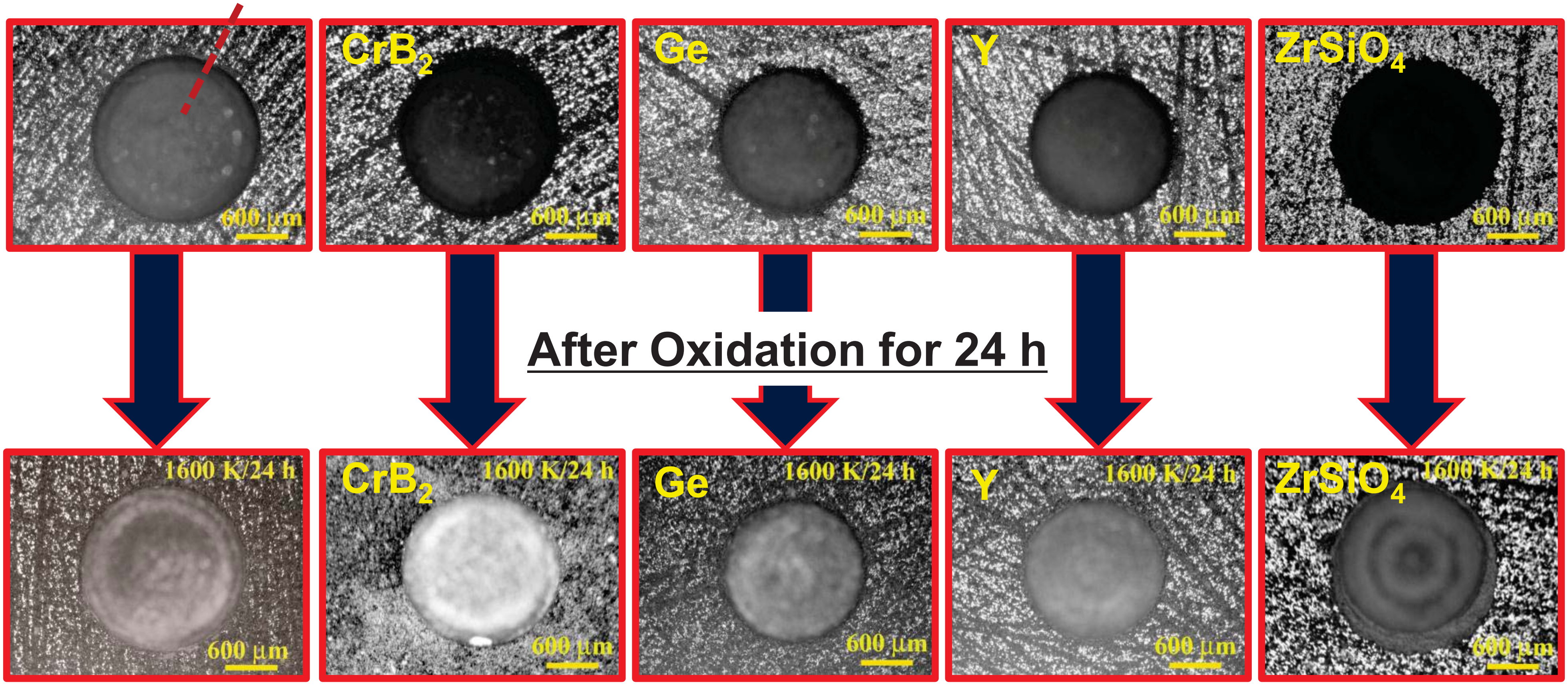


Assessment of the Self-Healing Characteristics of Different Additives to CrMoSi-SiC at 1600 K

Pre-drilled hole
~ 1 mm dia.

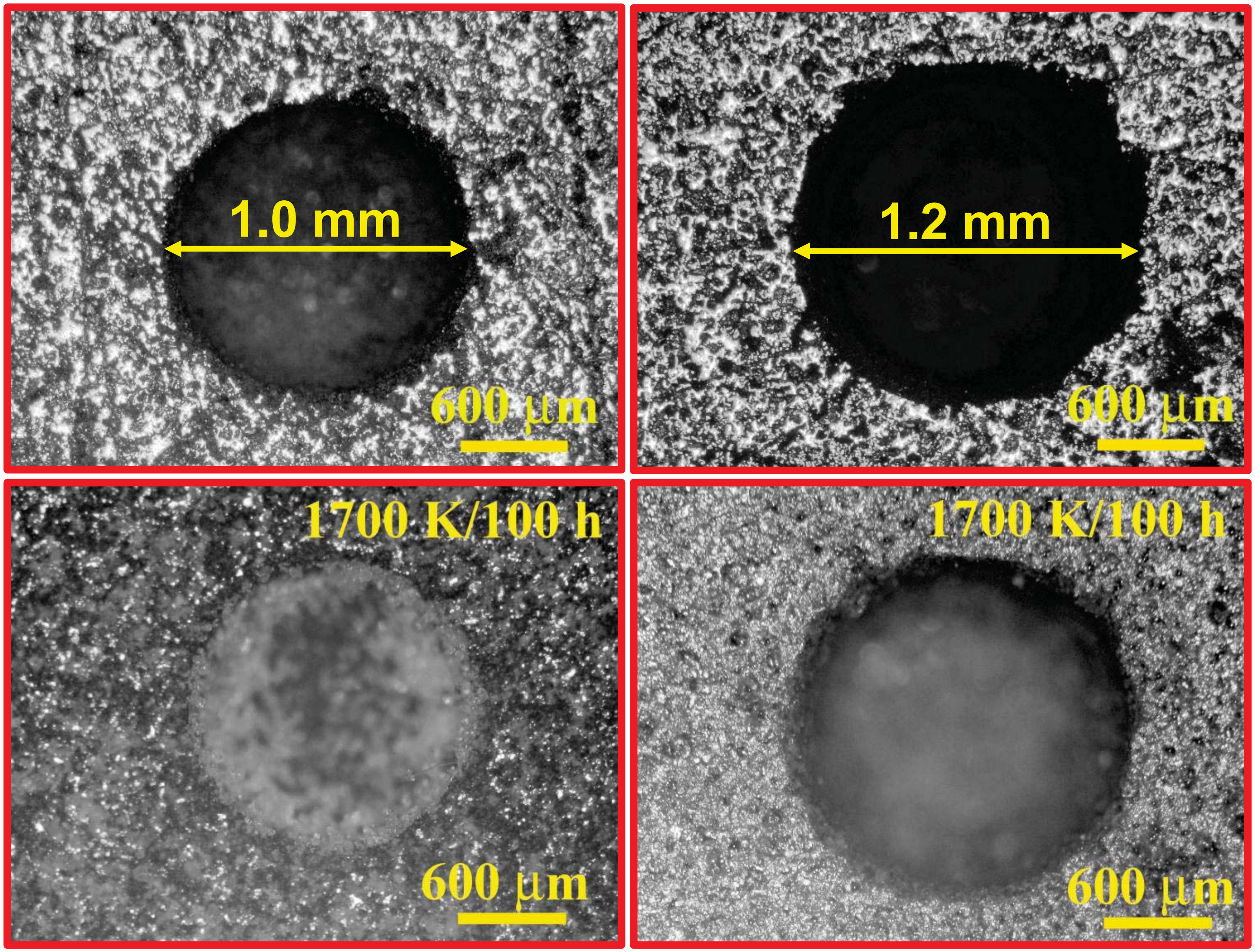
Before Oxidation



- CrB_2 addition shows the best ability to heal scratches

Self-Healing of CrMoSi-SiC with 5%CrB_2 at 1700 K after 100 h

Top Face **Rear Face**



Self-Healing Characteristics of CrMoSi-SiC-CrB_2 Oxidized at 1700 K for 100 h

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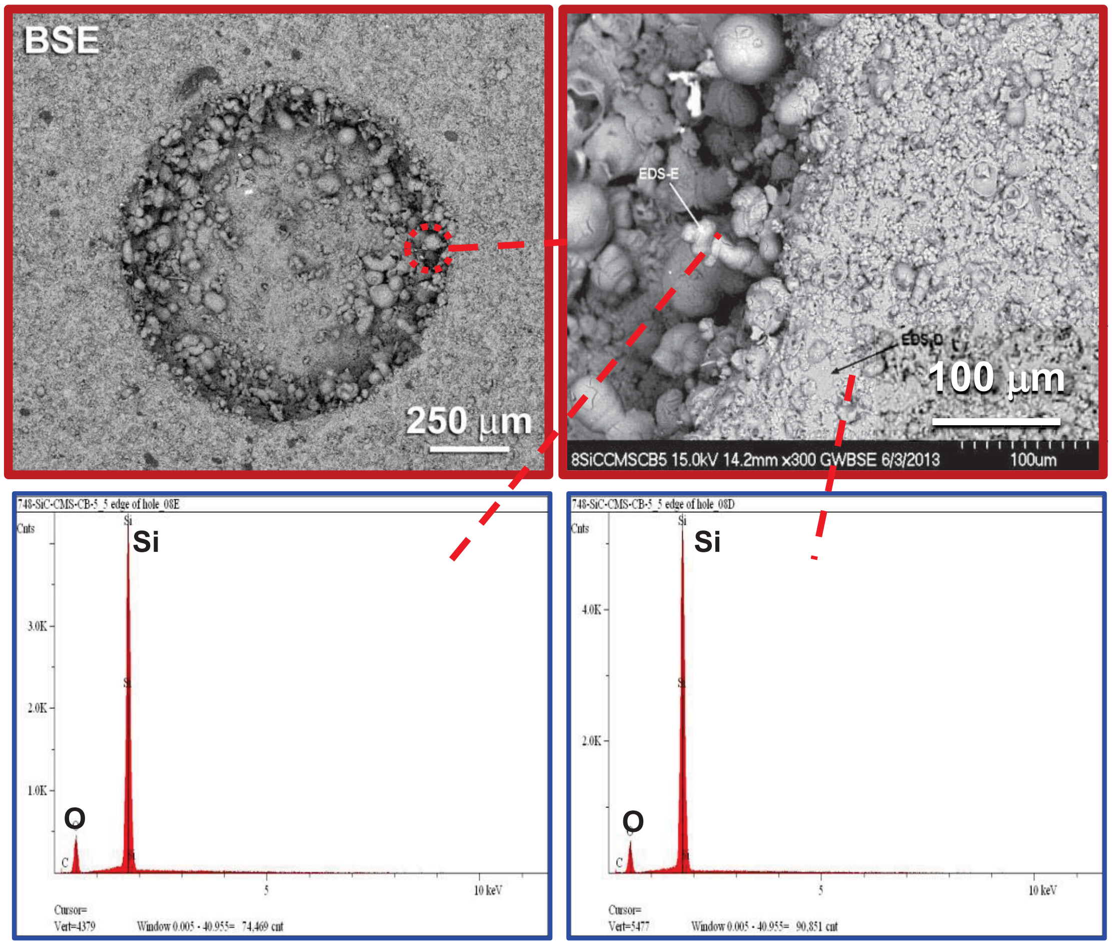
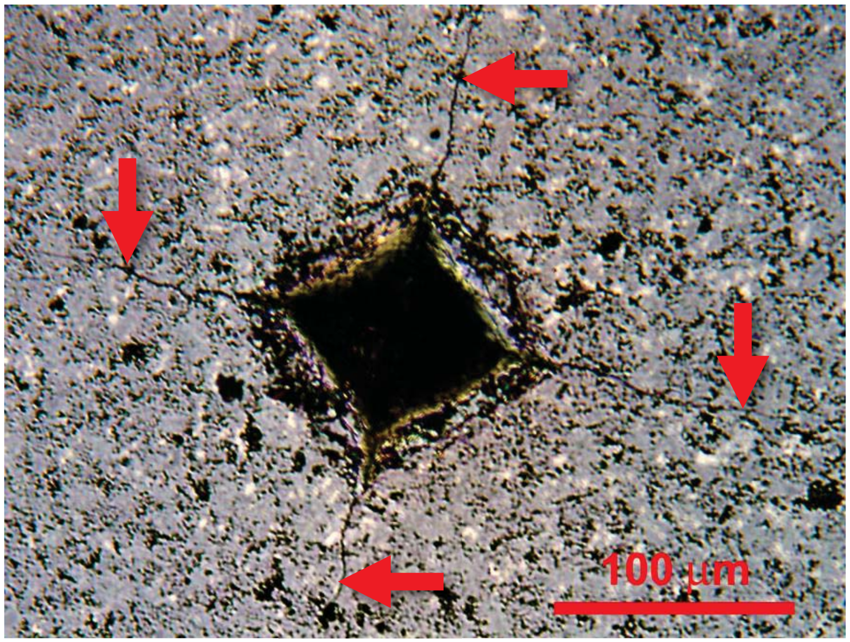


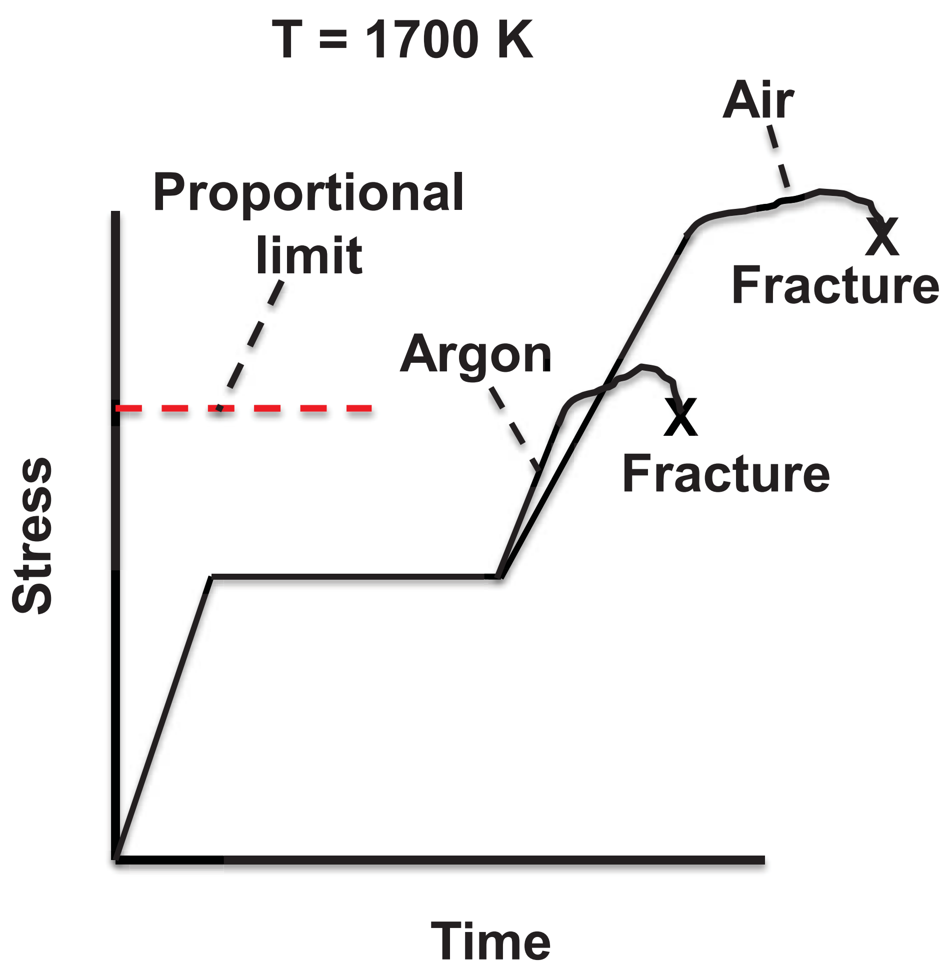
Self-Healing Studies (in progress)

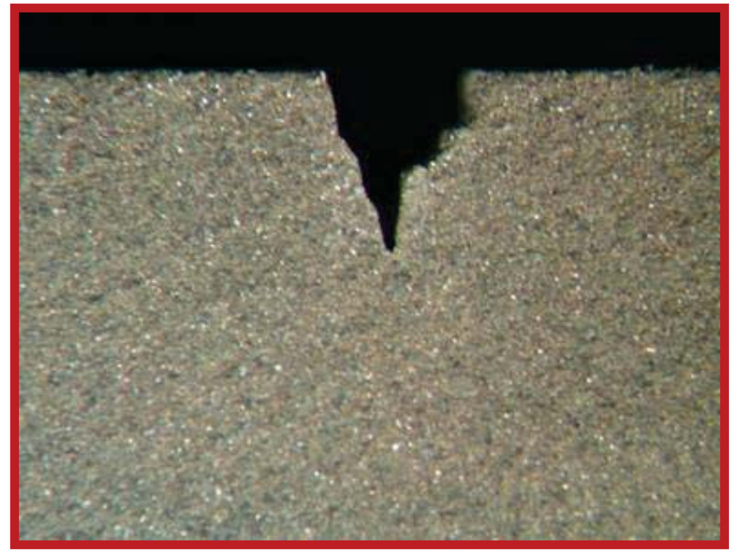
Cracks emanating from a Vickers indent



Perform qualitative healing studies on indented matrices to demonstrate crack healing.

Dynamic Loading Studies (in progress)





Notched specimens will be tested in air and inert gas to demonstrate that the air-tested specimens are stronger than those tested in inert gas due to self-healing of cracks.

Optical Micrographs of Single Edge Pre-Cracked Beam (SEPB) Specimens Studies

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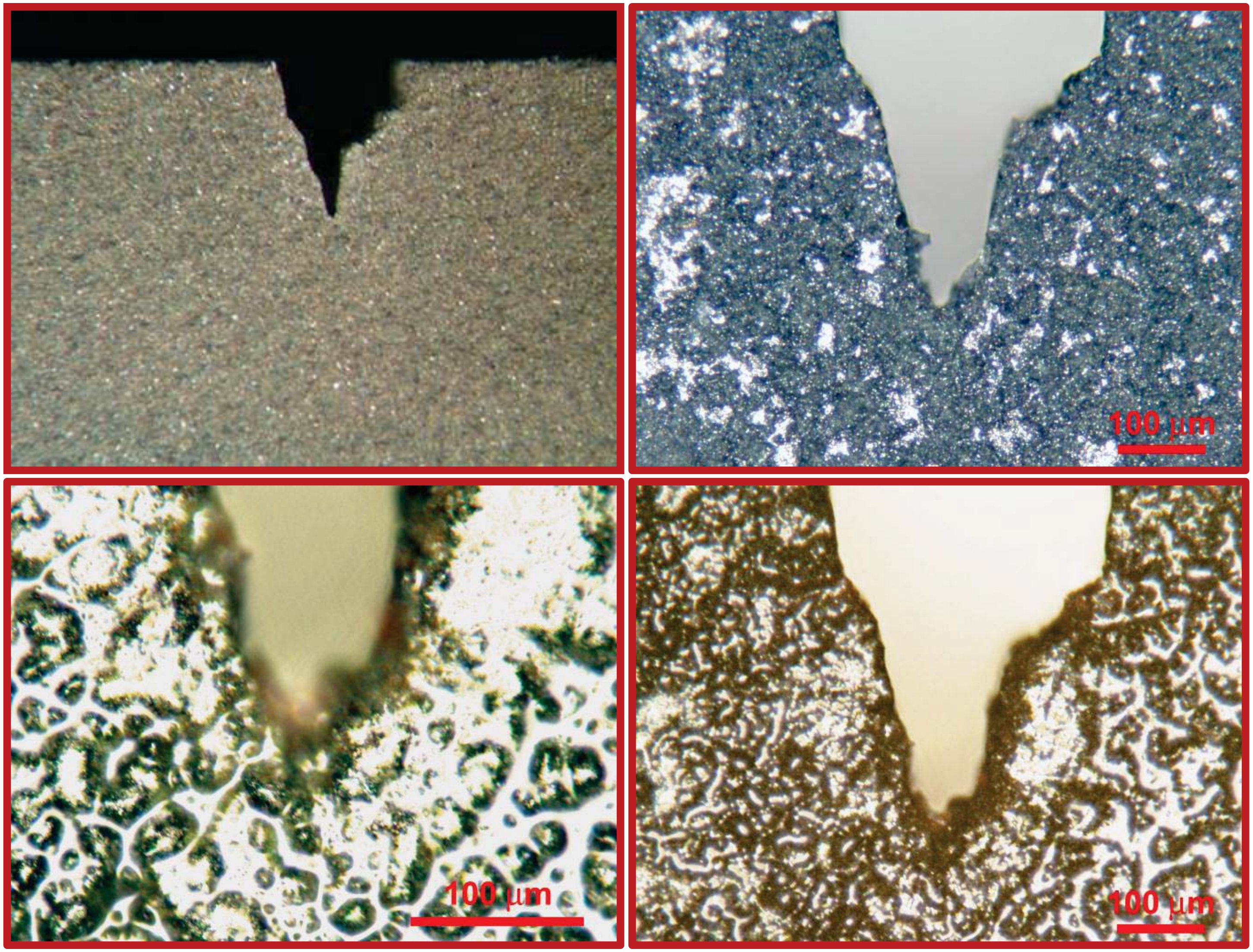
Unoxidized

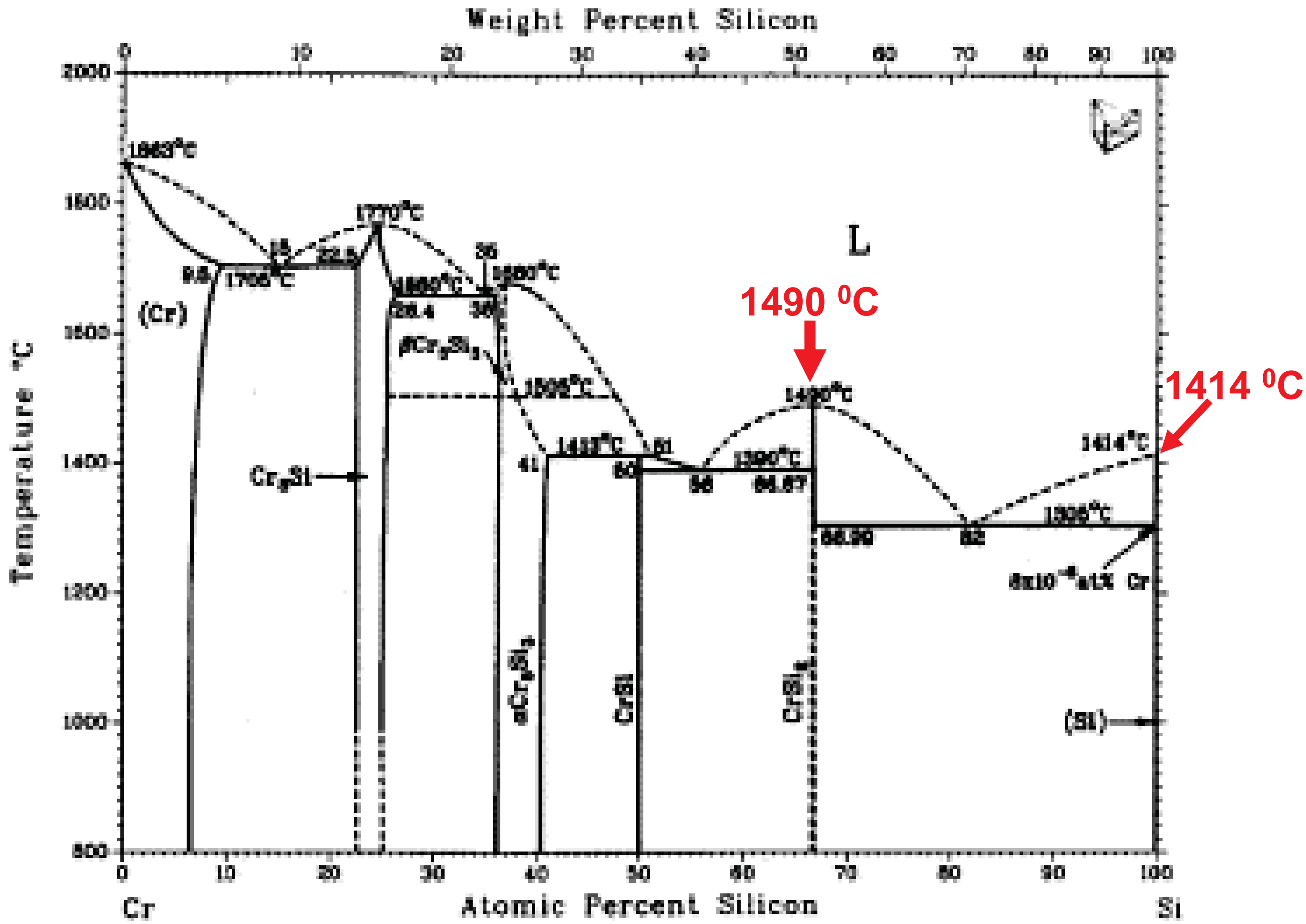
Unoxidized



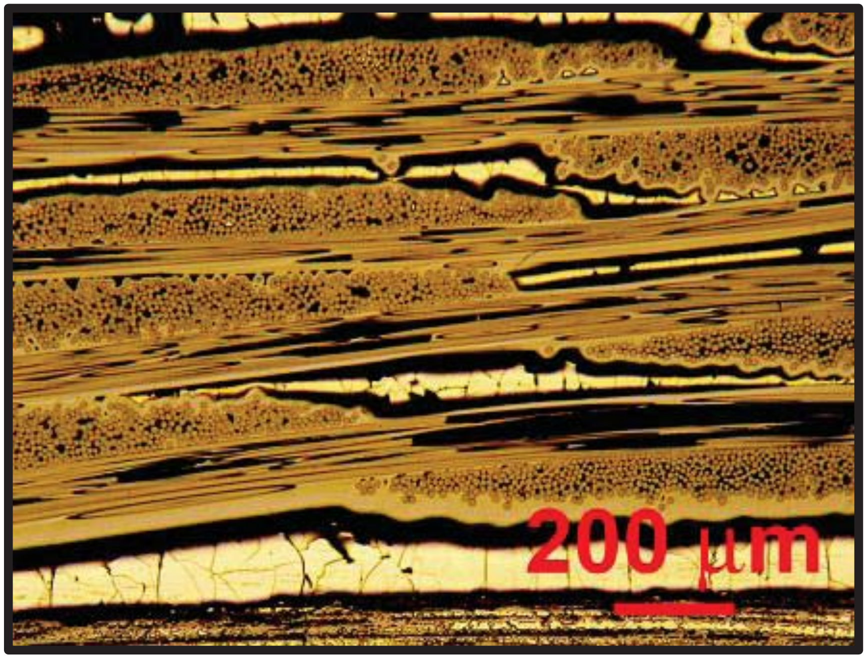
Oxidized **Top Surface**

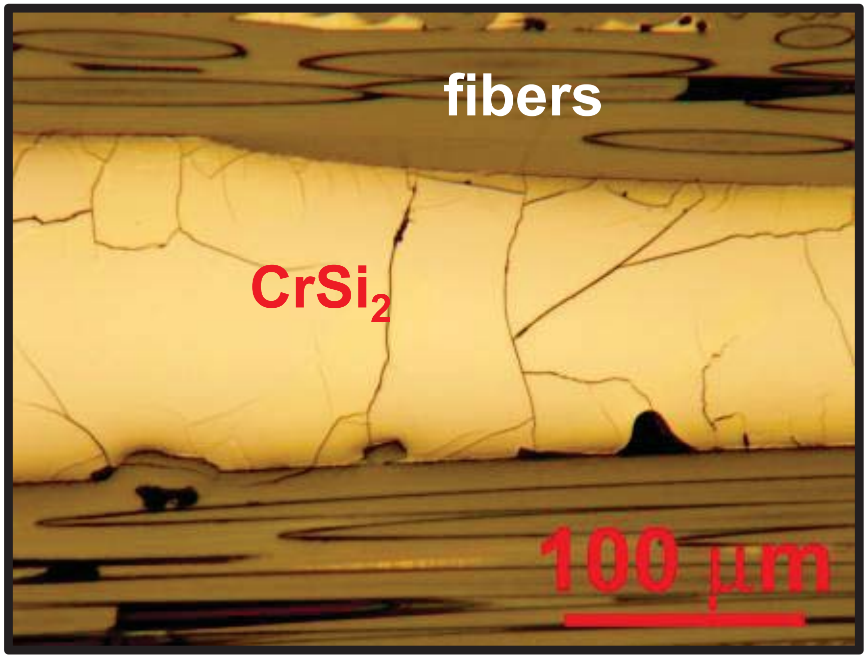
Oxidized **Bottom Surface**

Cr-Si Binary Phase Diagram

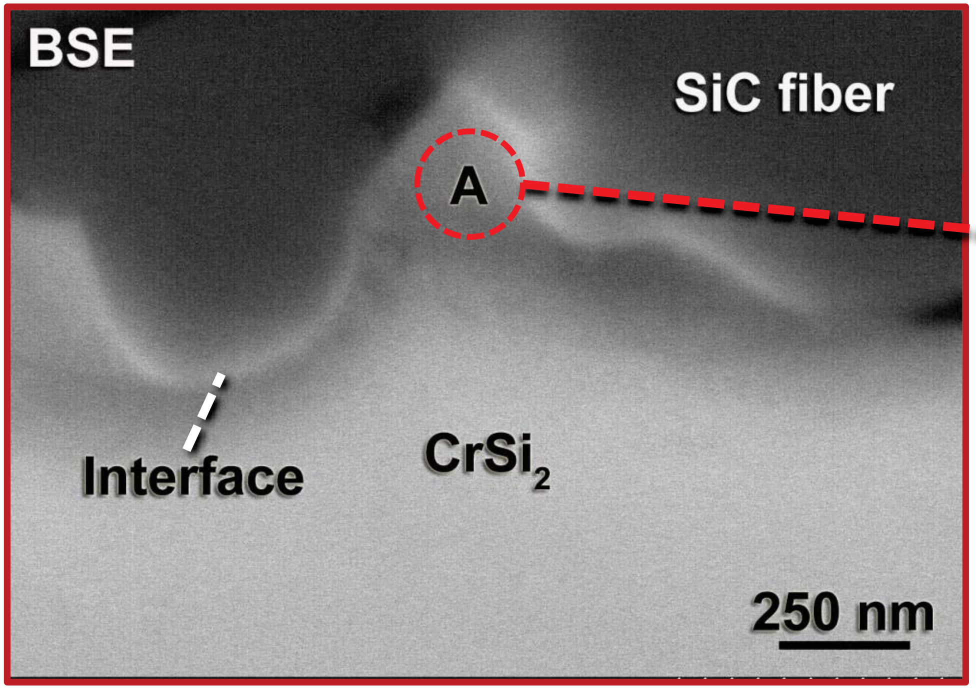


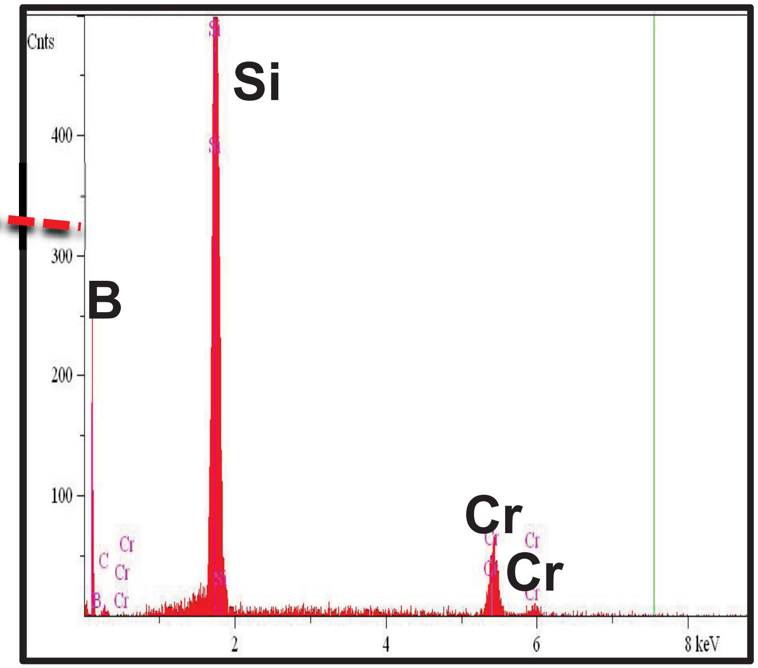
$CrSi_2$-Melt Infiltrated Tyranno SA Preforms





Composition Analysis of the $CrSi_2$-SiC Fiber Interface





No reaction of $CrSi_2$ with SiC – consistent with thermodynamic calculations

Summary and Conclusions

- A concept for developing a new class of high temperature engineered matrix composites (EMCs) with crack blunting, self-healing and low Si capabilities using intermetallic silicides is proposed.
- The following concepts have been demonstrated:
  - Thermal expansion of the engineered matrix can be matched with that of SiC.
  - Increased matrix ductility can lead to higher bend strengths due crack blunting.
  - Promising self-healing additives have been identified.
  - $CrSi_2/SiC/Si_3N_4$ and $CrMoSi/SiC/Si_3N_4$ engineered matrices have been identified for 1589 K (2400 ºF) and 1755 K (2700 ºF).
- Several new compositions have been formulated for further studies.
- Fabrication of dense EMCs has proved to be challenging due to insufficient particle infiltration in the coated SiC/SiC woven preforms and due to poor capillarity action of the Cr-Si alloys.

Distribution and Dissemination

- **Applied for US Patent (May 30, 2013) –NASA Docket No: LEW 18964-1**

  Title: Engineered Matrix Self-Healing Composites

  S/N: 13/905,333; Filed: 5/30/13

  Inventors: Sai Raj, Mrityunjay Singh, Ramakrishna Bhatt

- **S. V. Raj, M. Singh and R. Bhatt, "High-Temperature, Lightweight, Self-Healing Ceramic Composites for Aircraft Engine Applications", NASA Tech Briefs, vol. 37, No. 2, p. 40 February 2013; http://www.techbriefs.com/component/content/article/5-ntb/tech-briefs/materials/15663-lew-18964-1.**

- **S. V. Raj, M. Singh and R. Bhatt, "Preliminary Studies on the Development of Engineered Matrices for SiC Fiber-Reinforced Ceramic Composites", 38th Annual Conference on Composites, Materials and Structures, Cocoa Beach, FL Jan 26-30, 2014**

- **Journal paper submitted for DAA 1676 management approval.**

Next Steps

- The research has been transferred to ARMD's Aero Sciences Program (FY 14).
- Methods to increase particulate loading and silicide melt infiltration of the preforms are being studied.
- Dynamic fracture toughness tests are underway to quantify the self-healing capabilities of several engineered matrices.
- Bend and tensile creep tests of several engineered matrix specimens are planned.