Development of Engineered Ceramic Matrix Composites

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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 °F) (cooled).
  ➢ Medium term 1755 K (2700 °F) (cooled).
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

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

- Matrix fills space and provides a thermally conductive path.
- Fracture toughness due to crack bridging and interface debonding.
- Relatively low matrix cracking strength - \( \sigma_{\text{design}} < \sigma_{\text{proportional limit}} \)
Recession of BN and Formation of Glassy Phase in BN-Coated Hi-Nicalon MI SiC Composites

(Courtesy M. Singh)

\[ T = 973 \text{ K}; \ \sigma = 250 \text{ MPa}; 1000 \text{ h in air} \]

\[ 2\text{BN (s)} + \frac{3}{2} \text{O}_2 (g) = \text{B}_2\text{O}_3 (l) + \text{N}_2 (g) \]

\( \text{B}_2\text{O}_3 - \text{SiO}_2: \text{Low eutectic temperature of 372 } ^\circ\text{C} \)
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

Crack blunting due to matrix plasticity slows crack growth.

Self-healing of fine cracks minimizes oxygen ingress to fibers.

Increased reliability and load carrying capacity.
Innovation and Expected Impact

- High temperature matrix - greater than 1589 K (1315 °C/2400 °F)
- 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

Monolithic ceramics

Low toughness
Low strength

Current

Ceramic matrix composites (CMCs)

Higher toughness
Higher strength
Free silicon

Concept

Engineered matrix composites (EMCs)

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 °C; 2577 °F).

• **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

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

<table>
<thead>
<tr>
<th>Concept</th>
<th>(V_{\text{silicide}}(%))</th>
<th>(V_{\text{SiC}}(%))</th>
<th>(V_{\text{Si3N4}}(%))</th>
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</thead>
<tbody>
<tr>
<td>Traditional</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Present investigation</td>
<td>(x)</td>
<td>(100-(x)-(y))</td>
<td>(y)</td>
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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

- **Powder Weighing**
  - SiC
  - Si₃N₄
  - silicide

- Wet ball grinding → Drying → Hand grinding

- Data Analysis
  - Testing
  - Machining
  - Hot pressing
Hot-Pressed Plate and Optical Micrograph

CrMoSi/SiC/Si$_3$N$_4$ (CrMoSi-EM)

50 x 50 x 4 mm

Optical micrograph
Back Scattered Image and Energy Dispersion Spectra: CrMoSi/SiC/Si$_3$N$_4$ (CrMoSi-EM)
Proof-of-Concept: Thermal Strains

Disilicides / (Cr,Mo)₃Si

ΔL/L₀ (%) vs. T (K)

- CrSi₂
- (Cr,Mo)₃Si
- Si₃N₄
- SiC
- TiSi₂
- WSi₂
- CrSi₂/SiC/Si₃N₄
- (Cr,Mo)₃Si/SiC/Si₃N₄
- TiSi₂/SiC/Si₃N₄
- WSi₂/SiC/Si₃N₄

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Macrograph of the Surface of a Thermally Cycled CTE MoSi$_2$/SiC/Si$_3$N$_4$ Specimen

- MoSi$_2$/SiC/Si$_3$N$_4$ engineered matrix dropped from the program.
Isothermal Oxidation Behavior of Engineered Matrices

TiSi$_2$/SiC/Si$_3$N$_4$ and WSi$_2$/SiC/Si$_3$N$_4$ engineered matrices dropped from the program.
Crack blunting due to crack tip plasticity increases bend strength.
Four-Point Bend Stress-Strain Curves for a CrMoSi Engineered Matrix

![Four-Point Bend Stress-Strain Curves](image)

- **Stress (MPa)**
- **Strain (%)**

**Air tested**
- 1473 K
- 1643 K
- 1698 K
- 1573 K

**CrMoSi-SiC-Si₃N₄**
- 620-2-RT
- 620-5-RT
- 620-8-1200
- 620-9-1200
- 638-13-1300
- 620-1-1370
- 620-6-1370
- 620-3-1425
- 620-10-1425
- 638-19-1425
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

Composite Fabrication

- Powder Weighing
- Wet attrition milling
- Slurry preparation
- Testing & data analysis
- Melt Infiltration
- Pyrolysis
- SiC/SiC Preform infiltration
Microstructures of TiSi$_2$-EM-Infiltrated SiC Fiber Preform

Coated Preform

Fibers and tows

Particulates

Voids

5 mm

1 mm

1 mm
CT Scans of TiSi₂/SiC/Si₃N₄ Particulate Epoxy and Si-Melt Infiltrated Preform

As-received Preform
Area fraction of porosity ~ 21-23%

Particulate Infiltrated
Area fraction of porosity ~ 0.9%

Pyrolized
Area fraction of porosity ~ 6.6%

Si Melt Infiltrated
Area fraction of porosity ~ 1.8%

The red regions are voids
TiSi$_2$/SiC/Si$_3$N$_4$ epoxy infiltrated preforms
CrMoSi/SiC/Si$_3$N$_4$ Epoxy Infiltrated Preforms

Fibers

200 μm

0.5 mm

100 μm

Epoxy – Particulate mixture.

Fibers
Particulate and Silicon Melt Infiltrated SiC/SiC Preforms
Room Temperature Bend Stress-Strain Curves for CrMoSi EMCs

4-Point Bend Test
T = 300 K

σ (MPa)

ε (%)
Heat treated in air at 1600 K for 50 h
Assessment of the Self-Healing Characteristics of Different Additives to CrMoSi-SiC at 1600 K

- CrB$_2$ addition shows the best ability to heal scratches

Pre-drilled hole ~ 1 mm dia.

Before Oxidation

After Oxidation for 24 h

• 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
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.
  ➢ CrSi₂/SiC/Si₃N₄ and CrMoSi/SiC/Si₃N₄ engineered matrices have been identified for 1589 K (2400 °F) and 1755 K (2700 °F).

• 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 silicide alloys.
Distribution and Dissemination

  
  **Title:** Engineered Matrix Self-Healing Composites
  
  S/N: 13/905,333; Filed: 5/30/13
  
  **Inventors:** Sai Raj, Mrityunjay Singh, Ramakrishna Bhatt


- 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.

• Final ARMD report.