Integration Science and Technology of Silicon-Based Ceramics and Composites: Technical Challenges and Opportunities

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Abstract
Ceramic integration technologies enable hierarchical design and manufacturing of intricate ceramic and composite parts starting with geometrically simpler units that are subsequently joined to themselves and/or to metals to create components with progressively higher levels of complexity and functionality. However, for the development of robust and reliable integrated systems with optimum performance for high temperature applications, detailed understanding of various thermochemical and thermomechanical factors is critical. Different technical approaches are required for the integration of ceramic to ceramic and ceramic to metal systems. Active metal brazing, in particular, is a simple and cost-effective method to integrate ceramic to metallic components. Active braze alloys usually contain a reactive filler metal (e.g., Ti, Cr, V, Hf etc) that promotes wettability and spreading by inducing chemical reactions with the ceramics and composites. In this presentation, various examples of brazing of silicon nitride to themselves and to metallic systems are presented. Other examples of joining of ceramic composites (C/SiC and SiC/SiC) using ceramic interlayers and the resulting microstructures are also presented. Thermomechanical characterization of joints is presented for both types of systems. In addition, various challenges and opportunities in design, fabrication, and testing of integrated similar (ceramic-ceramic) and dissimilar (ceramic-metal) material systems will be discussed. Potential opportunities and need for the development of innovative design philosophies, approaches, and integrated system testing under simulated application conditions will also be presented.
Integration Science and Technology of Silicon-Based Ceramics and Composites

Technical Challenges and Opportunities

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Outline

- Introduction and Background
- Technical Challenges in Integration
  - Similar vs Dissimilar Systems
    - Role of Interfaces
    - Thermal Expansion Mismatch and Residual Stresses
    - Design and Testing
- Ceramic Integration Technologies
  - Wetting and Interfacial Effects
  - Ceramic-Metal Systems
  - Ceramic-Ceramic Systems
  - Testing and Characterization
- Concluding Remarks
Overview of Key Ceramic Integration Technologies

Joining Technologies
- Ceramic-Ceramic
- Ceramic-Metal

Component & System Level Integration

Repair/Refurbishment
- In-Situ Repair
- Ex-Situ Repair

Mechanical Fastening
- Ceramic-Ceramic
- Ceramic-Metal
- Rivets/Bolts

Robust Manufacturing
- Large Components
- Complex Shapes
- Multifunctional

Technical Challenges in Integration of Ceramic-Metal vs Ceramic-Ceramic Systems

Ceramic-Metal System
- Flow and wettability
- Roughness
- Residual stress (ΔCTE)
- Multi-axial stress state
- Joint design
- Joint stability in service
- Metal – forgiving
- Elastic-plastic system
- Lower use temperatures
- Less aggressive environment

Ceramic-Ceramic System
- Reaction and diffusion
- Roughness
- Residual stress (ΔCTE)
- Multi-axial stress state
- Joint design
- Joint stability in service
- Ceramic – unforgiving
- Elastic-elastic system
- Higher use temperatures
- More aggressive environment

Common Issues
Challenges in Design and Testing of Integrated Structures

(a) Compression; (b) Tension; (c) Shear; (d) Peel; (e) Cleavage

Different Types of Shear Tests

Typical Integrated Systems will have Combination of Stresses Under Operating Conditions

Wetting and Interfacial Phenomena in Ceramic-Metal System

Key Challenges:
- Poor Wettability of Ceramics and Composites: (poor flow and spreading characteristics)
- Surface Roughness and Porosity of Ceramic Substrates
- Thermoelastic Incompatibility
Wettability is Important Factor in Brazing

Young's equation

\[ \sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos \theta \]

Contact angle of braze should be small

Braze layer melts and spreads between the substrates to form the joint

Ordinary braze alloys wet the metal but not the ceramic systems

Must use ‘active’ brazes that wet and bond with both metal and ceramics

Wetting and Interfacial Microstructure of SiC-SiC/Cusil-ABA (1088 K, 5 min.)

- Partial droplet/composite de-cohesion near perimeter
- No delamination within SiC-SiC
- Excess Ti at the interface
**SiC-SiC/Ticusil (1181 K, 5 min.)**

- Ticusil drop
- Cracks
- De-cohesion and delamination within CMC near perimeter.
- Intimate contact near center.
- Excess Ti at interface.

**Representative Brazed Joints in Various Systems**

- SiC-SiC/Cu-clad-Mo
- C-SiC/Inconel 625
- C-C/Ti
- Self-joined UHTCC
- SiC-SiC/braze/Si-X/Inconel (X: B, Y, Hf, Cr, Ta, Ti)
- Si3N4/W/Ta/Inconel
- Foam/CMC
Integration Technologies for Improved Efficiency and Low Emissions

• Gas Turbine Components

Advanced Silicon Nitride Based Components for Aerospace and Energy Systems

Robust joining and integration technologies are required for a hybrid vane:
- Joining the airfoil to the end cap
- Ceramic to metal integration technologies
- Joining of singlet vanes to from doublets
Integration Technologies for Silicon Nitride Ceramics to Metallic Components

Issues with Ceramic Inserted Blades

There are contact stresses at the metal-ceramic interface. Compliant layers (i.e. Ni-alloy+Pt) are used to mitigate the stress and damage. Failures can occur in the compliant layer.

Mark van Roode, “Advances in the Development of Silicon Nitride and Other Materials”, Environmental Barrier Coatings Workshop, November 6, 2002, Nashville, TN.

Industry Direction

INTEGRAL ROTORS
• No Compliant Layer with Disk
• Attachment of Ceramic Rotor to Metal Shaft
• Primarily Small Parts
• Ability to Fabricate Larger Parts Has Improved
• Integral Rotors are Replacing Metal Disks with Inserted Blades

Mark van Roode, Solar Turbines

IR Silicon Nitride Rotor, DOE Microturbine Program (top)
H-T. Lin, ORNL
Integration of Silicon Nitride to Metallic Systems

**Approach:** Use multilayers to reduce the strain energy more effectively than single layers.

**Challenge:** Multiple interlayers increase the number of interfaces, thus increasing the probability of interfacial defects.

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE ×10^{-6}/K</th>
<th>Yield Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon nitride</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td>Ta</td>
<td>6.5</td>
<td>170</td>
</tr>
<tr>
<td>Mo</td>
<td>4.8</td>
<td>500</td>
</tr>
<tr>
<td>Ni</td>
<td>13.4</td>
<td>14-35</td>
</tr>
<tr>
<td>Nb</td>
<td>7.1</td>
<td>105</td>
</tr>
<tr>
<td>Kovar</td>
<td>5.5-6.2</td>
<td>270</td>
</tr>
<tr>
<td>W</td>
<td>4.5</td>
<td>550</td>
</tr>
</tbody>
</table>

Various combinations of Ta, Mo, Ni, Nb, W and Kovar to integrate Silicon nitride to Nickel-Base Superalloys

Si$_3$N$_4$ (NT 154) bonded to Inconel 625 at 1317 K for 30 min

EDS data in (e) correspond to the point markers in (b)

The reaction zone (point 4) is rich in Ti and Al, but also contains Cu, Ni, Si, and Cr. No discontinuity, cracking or microvoids are noted in the reaction zone.
**EDS Compositional Maps of Silicon Nitride/Silicon Nitride Joints Using Cu-ABA Interlayers**

Titanium Segregation at the Interface

**TEM Analysis Silicon Nitride/Silicon Nitride Joints Using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers**

(a) Reaction layer at the Si₃N₄/braze interface and dislocations in braze, (b) titanium silicide formation, and (c) a higher magnification image of region shown in (b).

Details of joint microstructure (fine grains < 50 nm) form the reaction layer. (b) Electron diffraction patterns of the Si₃N₄ reaction layer and joint interior (Cu-ABA).

Typical Shear Behavior of Joints at Different Temperatures

Kyocera SN-281 Si₃N₄ bonded at 1317 K for 5 min using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers

EDS data in (d) correspond to the point markers in (b)

- An inhomogeneous reaction layer (2-2.5 µm) comprising of a dark-gray Ti-Si phase, possibly titanium silicide, and a lighter Cu (Si, Ti) phase has developed.
- The product phase crystals are oriented perpendicular to the interface (growth direction).
- No interfacial excess of Lu; exists in minute quantities in reaction layer and increases toward Si₃N₄.

Kyocera SN-281 Si$_3$N$_4$ bonded at 1317 K for 30 min

EDS data in (d) correspond to the point markers in (c)

- No increase in reaction layer thickness for 30 min. (faster kinetics in the early stages of reaction).
- Morphologically a more homogeneous, compact, and featureless reaction layer (possible coalescence of coarsened silicide crystals).


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Kyocera SN-281 bonded at 1317K for 30 min.

(5 µm thick Cu foil inserts: Si$_3$N$_4$/Cu/Cu-ABA/Cu/Si$_3$N$_4$)

EDS data in (d) correspond to the point markers in (c)

- Sound joint with a compact and morphologically homogeneous reaction layer (~1-2 µm thick).
- Ti and Si enrichments at the interface (possible formation of a titanium silicide compound layer).

www.nasa.gov
**Microstructure of Silicon Nitride/Inconel 625 Multilayer Joints**

Si$_3$N$_4$/W/Mo/Inconel 625 (Cu-ABA, brazed at 1044°C, 30 min.).

**Typical Shear Behavior of Multilayer Joints at Different Temperatures**

- Si$_3$N$_4$/Mo/Si$_3$N$_4$ joint strength (142 MPa) is comparable to Si$_3$N$_4$/Si$_3$N$_4$ strength (141 MPa)
- Si$_3$N$_4$/W/Mo/Inconel joint strength (54 MPa) is greater than strength (15 MPa) of Si$_3$N$_4$/Inconel
Integration Technologies for Improved Efficiency and Low Emissions

- MEMS-LDI Fuel Injector

Objective: Develop Technology for a SiC Smart Integrated Multi-Point Lean Direct Injector (SiC SIMP-LDI)
- Operability at all engine operating conditions
- Reduce NOx emissions by 90% over 1996 ICAO standard
- Allow for integration of high frequency fuel actuators and sensors

Possible Injector Approaches

1. Lean Pre-Mixed Pre-Evaporated (LPP)
   
   **Advantages** - Produces the most uniform temperature distribution and lowest possible NOx emissions
   
   **Disadvantages** - Cannot be used in high pressure ratio aircraft due to auto-ignition and flashback

2. Lean Direct Injector (LDI)
   
   **Advantages** - Does not have the problems of LPP (auto-ignition and flashback)
   - Provides extremely rapid mixing of the fuel and air before combustion occurs
Lean Direct Injector Fabricated by Bonding of SiC Laminates
SiC laminates can be used to create intricate and interlaced passages to speed up fuel-air mixing to allow lean-burning, ultra-low emissions

Key Enabling Technologies:
- Bonding of SiC to SiC
- Brazing of SiC to Metallic (Kovar) Fuel Tubes

Benefits of Laminated Plates
- Passages of any shape can be created to allow for multiple fuel circuits
- Provides thermal protection of the fuel to prevent choking
- Low cost fabrication of modules with complicated internal geometries through chemical etching

Leak Test of SiC Laminates Joined with Silicate Glass
- Combustion air channels
- Fuel holes
- Leaks at the edge between joined laminates
- Air should only flow through the fuel holes
- Undetected leaks in the combustion air channels
- Plugged fuel hole
Diffusion Bonding of CVD-SiC Using PVD Ti Interlayer

20 Micron Ti Interlayer
Microcracking is still present due to the presence of Ti₅Si₃Cₓ.
Naka et al suggest that this is an intermediate phase.

10 Micron Ti Interlayer
No microcracking or phase of Ti₅Si₃Cₓ is present.
Thin interlayers of pure Ti down-selected as the preferred interlayer.

Phases in bond with the 20 µ Ti Interlayer – Atomic Ratios

<table>
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<tr>
<th>Phase</th>
<th>Ti</th>
<th>Si</th>
<th>C</th>
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<tr>
<td>SIIC</td>
<td>0.011</td>
<td>54.096</td>
<td>45.890</td>
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<tr>
<td>Phase A</td>
<td>56.621</td>
<td>18.690</td>
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<tr>
<td>Phase B</td>
<td>35.794</td>
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<tr>
<td>Phase C</td>
<td>58.767</td>
<td>33.891</td>
<td>7.140</td>
</tr>
</tbody>
</table>

Phases in bond with the 10 µ Ti Interlayer – Atomic Ratios

<table>
<thead>
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<th>Phase</th>
<th>Ti</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase A</td>
<td>56.621</td>
<td>18.690</td>
<td>24.686</td>
</tr>
<tr>
<td>Phase B</td>
<td>35.752</td>
<td>61.217</td>
<td>3.028</td>
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<tr>
<td>Phase C</td>
<td>58.767</td>
<td>33.891</td>
<td>7.140</td>
</tr>
</tbody>
</table>

High Strength of Bonds Greatly Exceeds the Application Requirements

1” x 1” Bonded Substrates
1” Diameter Discs with a 0.65” Diameter Bond Area

Pull test tensile strengths:
> 23.6 MPa (3.4 ksi)*
> 28.4 MPa (4.1 ksi)*

* failure in the adhesive to the test fixture

Pull test tensile strengths:
13.4 MPa (1.9 ksi)
15.0 MPa (2.2 ksi)

Slightly higher strength from the highly polished SiC suggests that a smoother surface contributes to stronger bonds or less flawed SiC.

Failures are primarily in the SiC substrate rather than in the bond area.

The injector application requires a strength of about 3.45-6.89 MPa (0.5 - 1.0 ksi).
Details of Three Part 10 cm (4”) Diameter SiC Injector

Stacking Sequence
Top to Bottom

Top Surfaces
(Facing the Flow Direction)

Small Fuel Holes

Fuel Swirler Detail

PVD Ti Coated

Detail
Next Slide

Bottom Surfaces
(Facing Opposite to the Flow Direction)

Large Air Holes

Holes for Fuel Tube Integration

Detail of the Thickest Injector Substrate
(~0.635 cm thick)

Air Hole Passage

Fuel Hole and Channel
Transmission Electron Microscopy of Interfaces in SiC/Ti/SiC System (10 µm PVD-Ti, 1250 C, 2 hr)

Transmission Electron Microscopy of Interfaces in SiC/Ti/SiC System (10 µm PVD-Ti, 1250 C, 2 hr)


Integration Technologies for Improved Efficiency and Low Emissions

• SiC/SiC Composites
**Affordable, Robust Ceramic Joining Technology (ARCJoinT)**

**Apply Carbonaceous Mixture to Joint Areas**
- Cure at 110-120°C for 10 to 20 minutes

**Apply Silicon or Silicon-Alloy (paste, tape, or slurry)**
- Heat at 1250-1425°C for 10 to 15 minutes

**Affordable and Robust Ceramic Joints with Tailorable Properties**

**Advantages**
- Joint interlayer properties are compatible with parent materials.
- Processing temperature around 1200-1450°C.
- No external pressure or high temperature tooling is required.
- Localized heating sources can be utilized.
- Adaptable to in-field installation, service, and repair.

ARCJoinT can be Used to Join a Wide Variety of Ceramic and Composite Materials

- **SiC-Based Ceramics**
  - Reaction Bonded SiC
  - Sintered SiC
  - CVD SiC, Porous SiC

- **SiC/SiC Composites**
  - Melt Infiltrated SiC/SiC
  - CVI SiC/SiC Composites
  - PIP SiC/SiC Composites

- **C/SiC Composites**
  - Melt Infiltrated C/SiC
  - CVI C/SiC Composites
  - PIP C/SiC Composites

- **C/C Composites**
  - CVI C/C Composites
  - Resin Derived C/C
  - C-C/SiC with MI

**Composites with Different Fiber Architectures and Shapes**
**Ceramics with Different Shapes and Sizes**
Material and Design Challenges in Joining of Ceramic Matrix Composites

- Optimization of in-plane tensile properties of CMCs by engineering the fiber/matrix interface are accomplished at the expense of interlaminar properties.
- Weak interfaces in composites complicate overall joint properties and performance
  - Composition and microstructure
  - Bonding and adhesion
  - Testing and data analysis
- High elastic modulus of ceramic joint materials provide significant challenges to joint design, fabrication, and characterization.
- Data analyses and utilization are based on strength, but it may be necessary to make extensive use of fracture mechanics principles.

Microstructure and Mechanical Properties of Joined MI Hi-Nicalon/BN/SiC Composites

![Joint-Composite Interface](image1)

![MI SiC/SiC Composite](image2)

Flexural Strength of Joined SiC/SiC Composites

![Graph](image3)
National Aeronautics and Space Administration

Concluding Remarks

- Ceramic integration technologies are critically needed for the successful development and applications of ceramic components in a wide variety of high temperature applications.
- Significant efforts are needed in developing joint design methodologies, understanding the size effects, and thermomechanical performance of integrated systems in service environments.
- Global efforts on standardization of integrated ceramic testing are required. In addition, development of life prediction models for integrated components is also needed.

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