Invited Lecture at ISASC-2012, Seoul, Korea

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.

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

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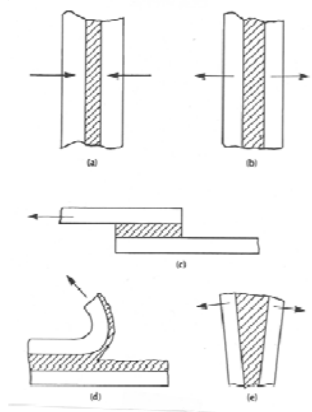
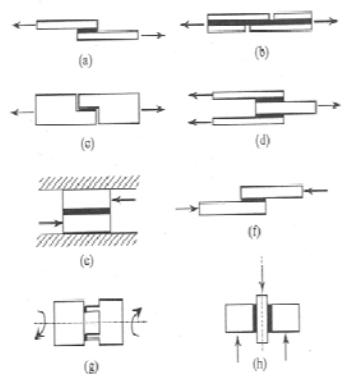
Challenges in Design and Testing of Integrated Structures



(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

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Wetting and Interfacial Phenomena in Ceramic-Metal System

<u>Key Challenges:</u>

- ***Poor Wettability of Ceramics and Composites:*** **(poor flow and spreading characteristics)**
- ***Surface Roughness and Porosity of Ceramic Substrates***
- ***Thermoelastic Incompatibility***

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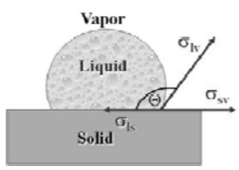
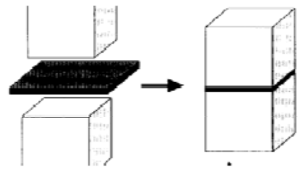
Wettability is Important Factor in Brazing

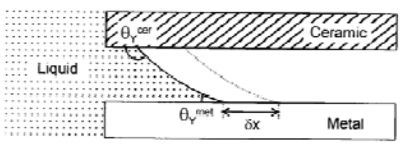
Young's equation
$\sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos\theta$



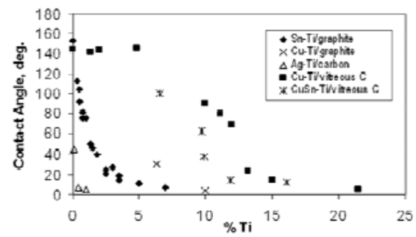
Contact angle of braze should be small



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

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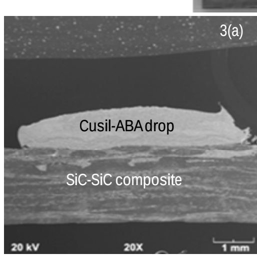
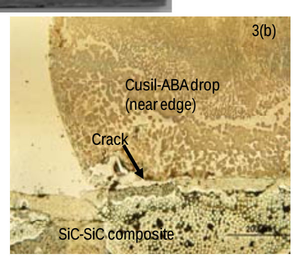
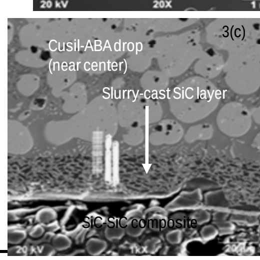
Wetting and Interfacial Microstructure of SiC-SiC/ Cusil-ABA (1088 K, 5 min.)

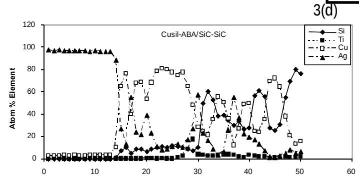




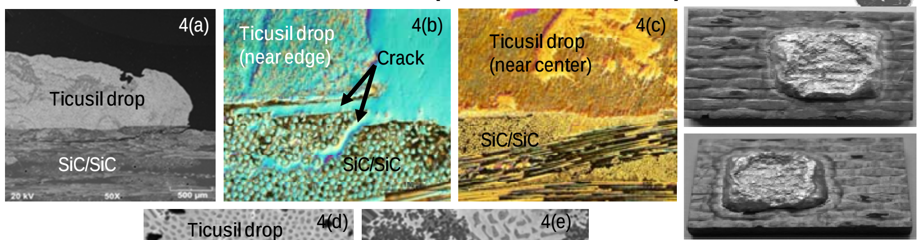
- **Partial droplet/ composite de-cohesion near perimeter**
- **No delamination within SiC-SiC**
- **Excess Ti at the interface**

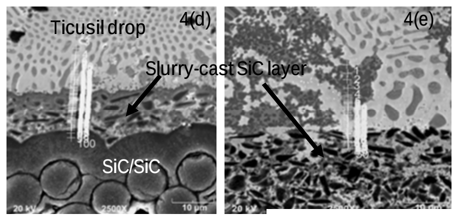


3(d)

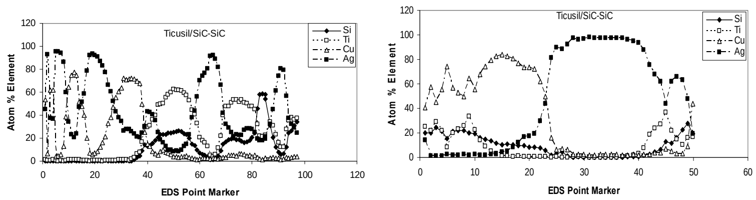


SiC-SiC/Ticusil (1181 K, 5 min.)

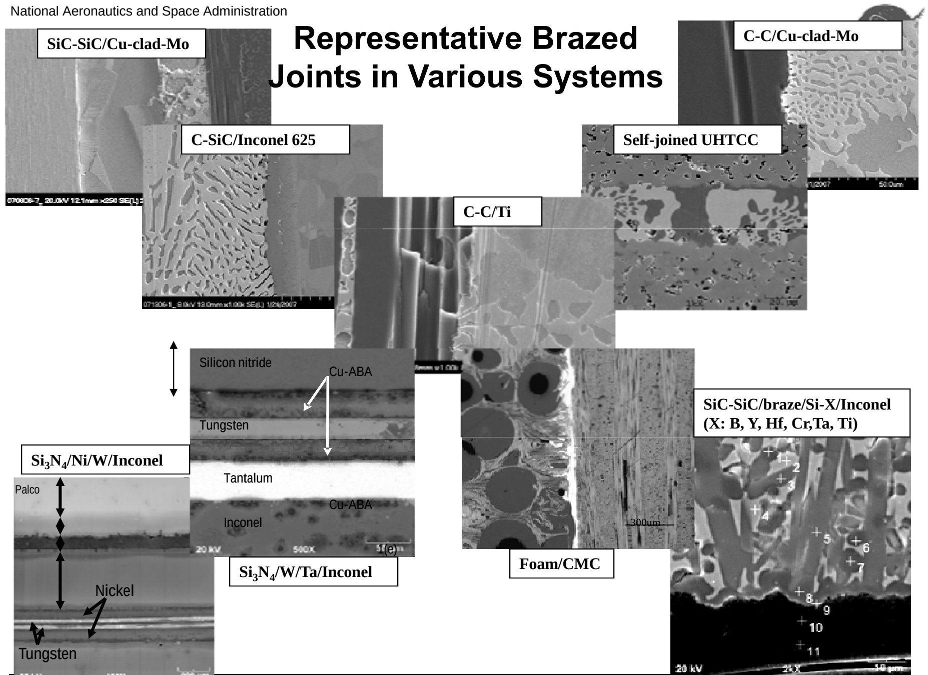




- De-cohesion and de-lamination within CMC near perimeter.
- Intimate contact near center.
- Excess Ti at interface.



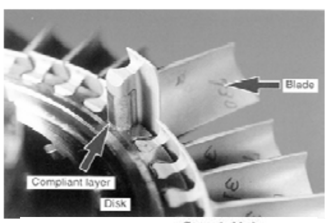
Representative Brazed Joints in Various Systems

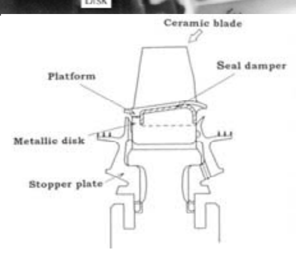


Integration Technologies for Improved Efficiency and Low Emissions

- **Gas Turbine Components**

Advanced Silicon Nitride Based Components for Aerospace and Energy Systems





Hybrid Gas Turbine Blade (Ceramic Blade and Metallic Disk) in NEDO's Ceramic Gas Turbine R&D Program, Japan (1988-1999)

Hybrid Vane for HPT

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**

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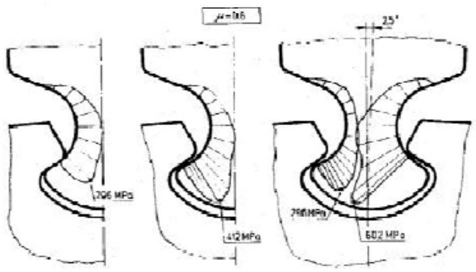
Integration Technologies for Silicon Nitride Ceramics to Metallic Components

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.

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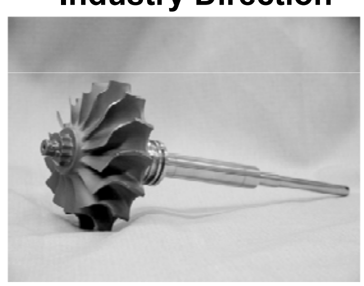
Integration Technologies for Silicon Nitride Ceramics to Metallic Components

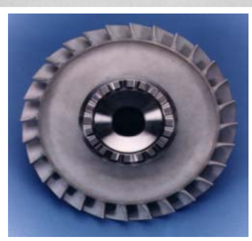
INTEGRAL ROTORS

- 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

Industry Direction



Mark van Roode, Solar Turbines



IR Silicon Nitride Rotor, DOE Microturbine Program (top)
H-T. Lin, ORNL

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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.

Material	CTE ×10^6/K	Yield Strength, MPa
Silicon nitride	3.3	-
Inconel 625	13.1	-
Ta	6.5	170
Mo	4.8	500
Ni	13.4	14-35
Nb	7.1	105
Kovar	5.5-6.2	270
W	4.5	550

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

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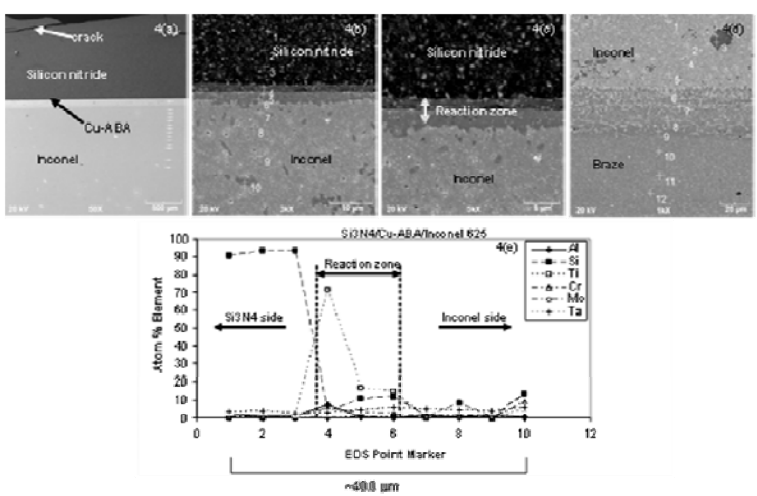
Si_3N_4 (NT 154) bonded to Inconel 625 at 1317 K for 30 min

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

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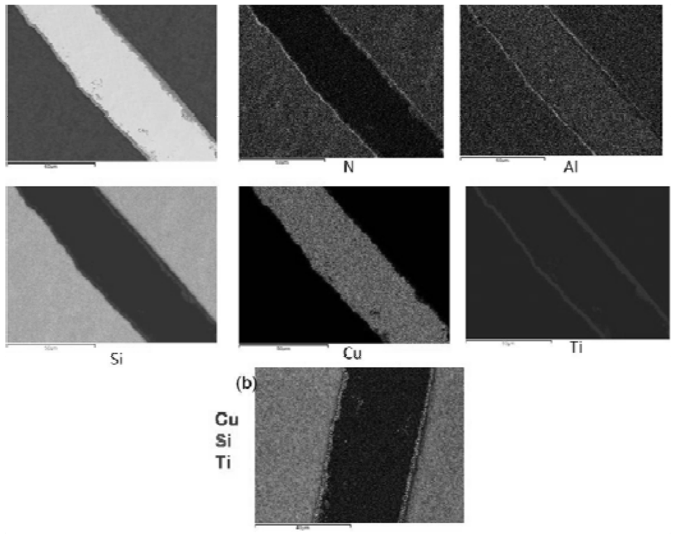
EDS Compositional Maps of Silicon Nitride/Silicon Nitride Joints Using Cu-ABA Interlayers



Titanium Segregation at the Interface

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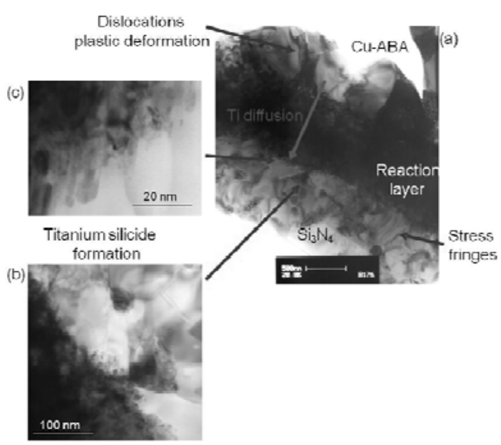
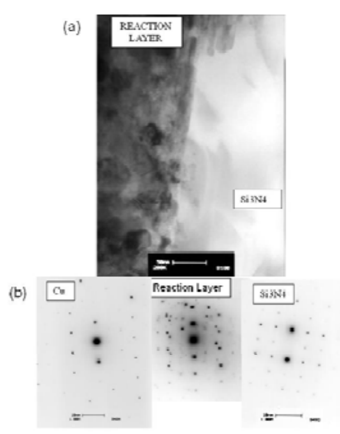
TEM Analysis Silicon Nitride/Silicon Nitride Joints Using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers



(a) Reaction layer at the Si_3N/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 Si_3N_4, reaction layer and joint interior (Cu-ABA).

M. Singh, R. Asthana, F.M. Varela, J.M. Fernandez, J. Eur. Ceram. Soc. . 31 (2011) 1309-16

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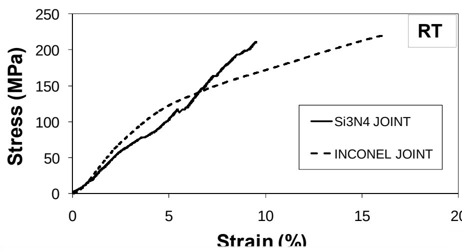
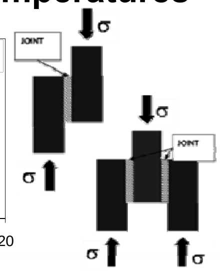
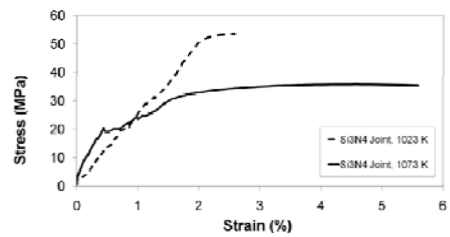
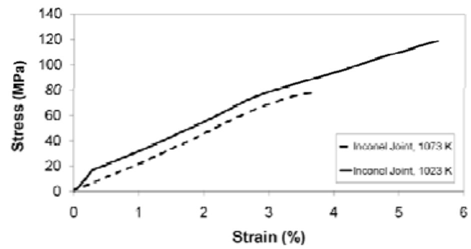
Typical Shear Behavior of Joints at Different Temperatures









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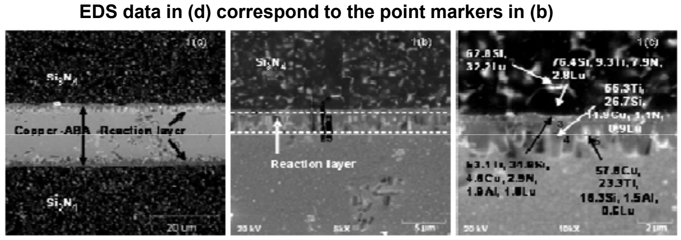
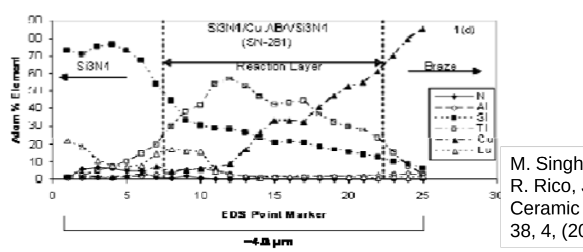
Kyocera SN-281 Si_3N_4 bonded at 1317 K for 5 min using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers

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





M. Singh, R. Asthana, J. R. Rico, J.M. Fernandez, Ceramic International, 38, 4, (2012) 2793-2802

- **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 Si_3N_4 .**

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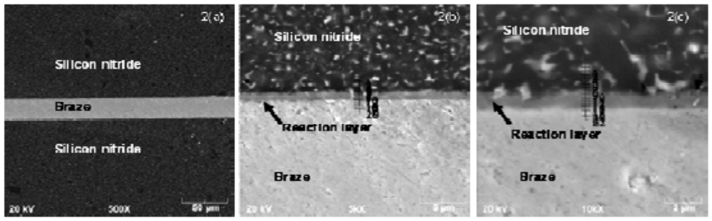
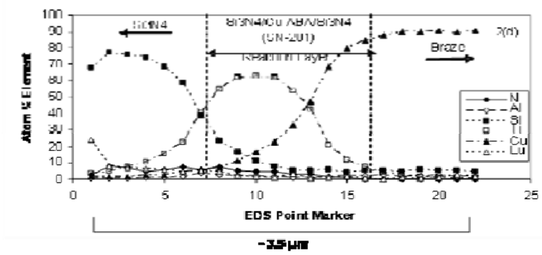
Kyocera SN-281 Si_3N_4 bonded at 1317 K for 30 min

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





M. Singh, R. Asthana, J. R. Rico, J.M. Fernandez, Ceramic International, 38, 4, (2012) 2793-2802

- **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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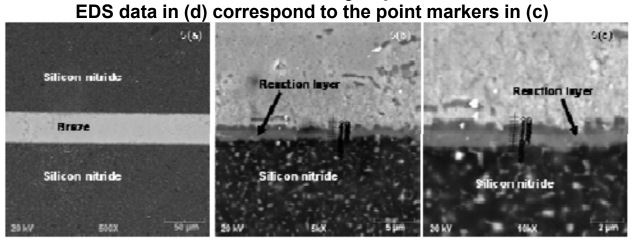
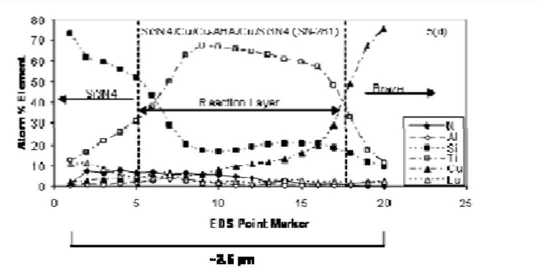
Kyocera SN-281 bonded at 1317K for 30 min. (5 µm thick Cu foil inserts: Si_3N_4/Cu/Cu-ABA/Cu/Si_3N_4)

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).**

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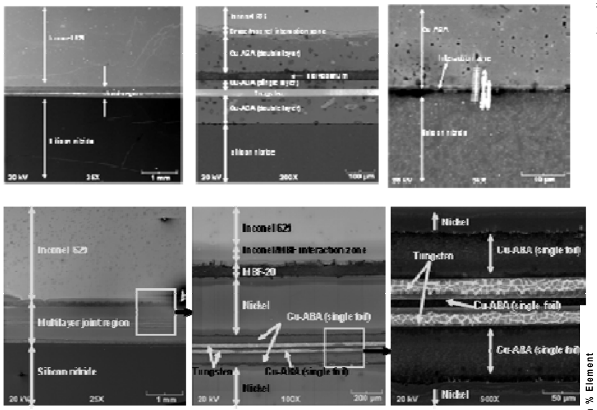
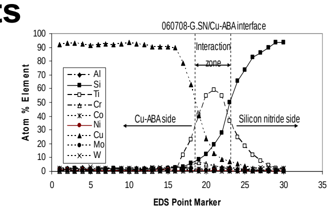
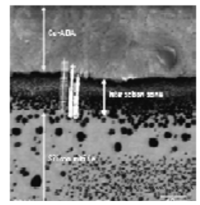
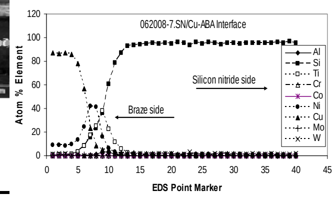
Microstructure of Silicon Nitride/Inconel 625 Multilayer Joints

Si_3N_4/W/Mo/Inconel 625 (Cu-ABA, brazed at 1044C, 30 min.).









Si_3N_4/Ni/W/Ni/Inconel 625
(with Cu-ABA on SN side and MBF on Inconel side)
(brazed at 1044C, 30 min.).

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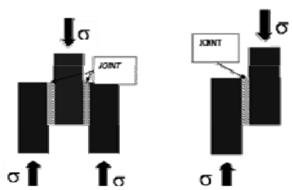
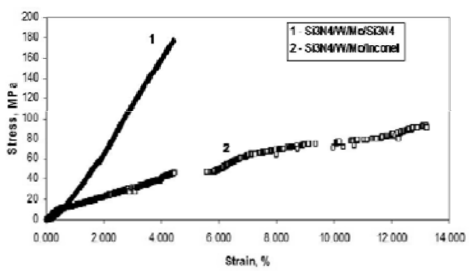
Typical Shear Behavior of Multilayer Joints at Different Temperatures





- Si_3N_4/W/Mo/Si_3N_4 joint strength (142 MPa) is comparable to Si_3N_4/Si_3N_4 strength (141 MPa)
- Si_3N_4/W/Mo/Inconel joint strength (54 MPa) is greater than strength (15 MPa) of Si_3N_4/Inconel

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Integration Technologies for Improved Efficiency and Low Emissions

- **MEMS-LDI Fuel Injector**

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Integration Technologies for 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

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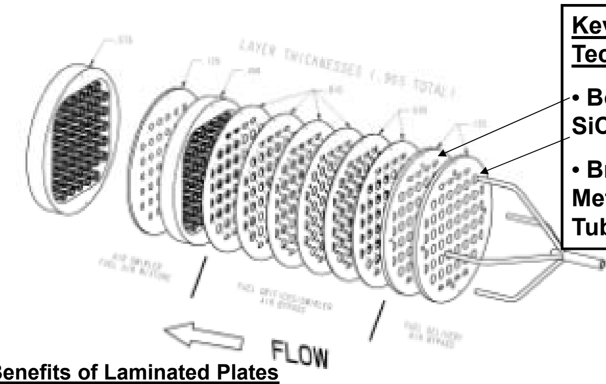
Lean Direct Injector Fabricated by Bonding of SiC Laminates

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

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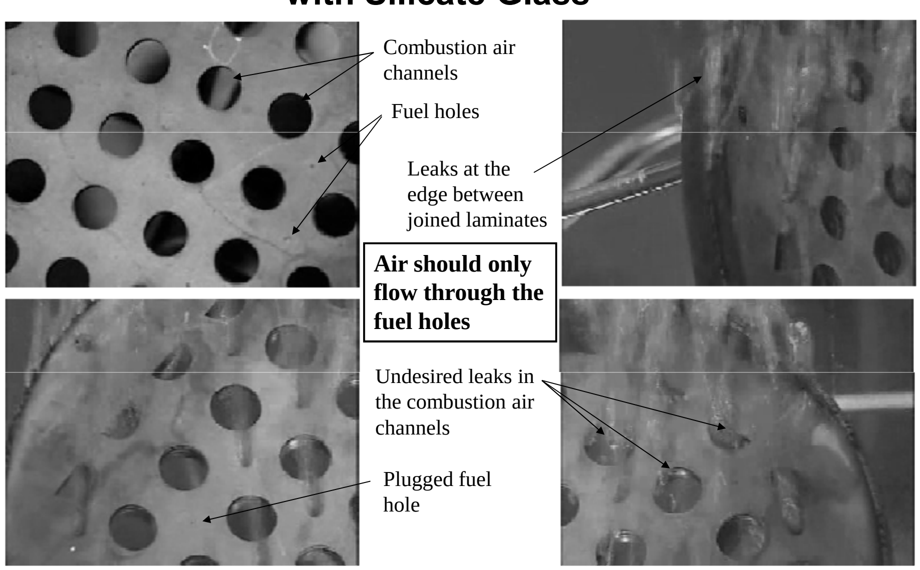
Leak Test of SiC Laminates Joined with Silicate Glass



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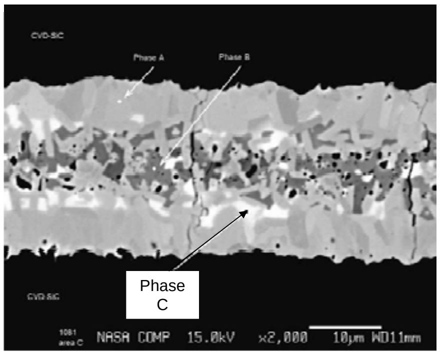
Diffusion Bonding of CVD-SiC Using PVD Ti Interlayer

20 Micron Ti Interlayer

Microcracking is still present due to the presence of $Ti_5Si_3C_X$.

Naka et al suggest that this is an intermediate phase.



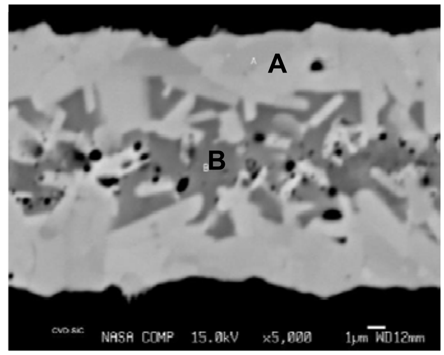
Phases in bond with the 20 µ Ti Interlayer – Atomic Ratios

Phase	Ti	Si	C
Phase A	56.426	17.792	25.757
Phase B	35.794	62.621	1.570
Phase C	58.767	33.891	7.140

10 Micron Ti Interlayer

No microcracking or phase of $Ti_5Si_3C_X$ is present.

Thin interlayers of pure Ti down-selected as the preferred interlayer.



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

Phase	Ti	Si	C
SiC	0.011	54.096	45.890
Phase A	56.621	18.690	24.686
Phase B	35.752	61.217	3.028

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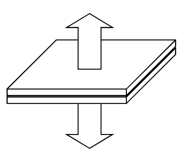
High Strength of Bonds Greatly Exceeds the Application Requirements

1" x 1" Bonded Substrates



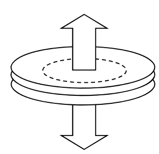
Pull test tensile strengths:

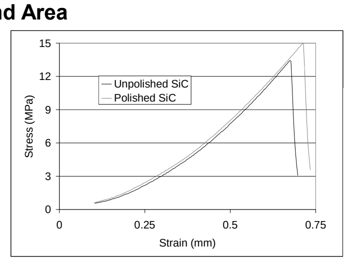
> 23.6 MPa (3.4 ksi)*

> 28.4 MPa (4.1 ksi)*

* failure in the adhesive to the test fixture

1" Diameter Discs with a 0.65" Diameter Bond Area





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).

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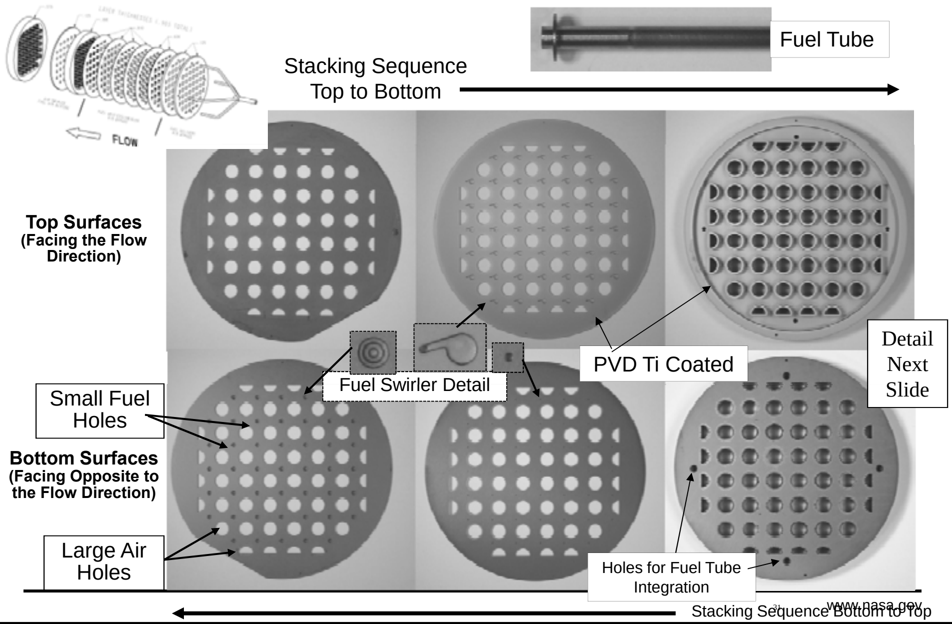
Details of Three Part 10 cm (4”) Diameter SiC Injector



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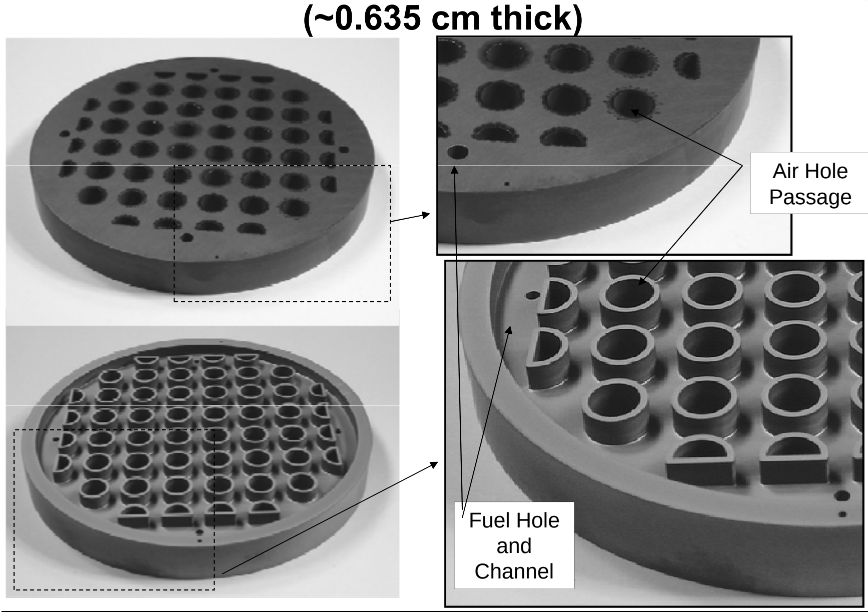
Detail of the Thickest Injector Substrate (~0.635 cm thick)



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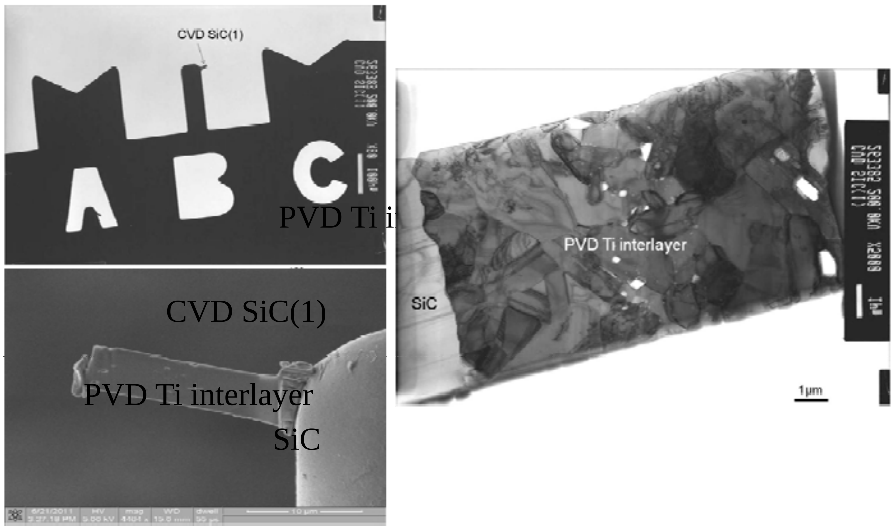
Transmission Electron Microscopy of Interfaces in SiC/Ti/SiC System (10 μm PVD-Ti, 1250 C, 2 hr)



H. Tsuda, M.C. Halbig, and M. Singh, Int. J. Appl. Ceram. Tech, (2012) in press.

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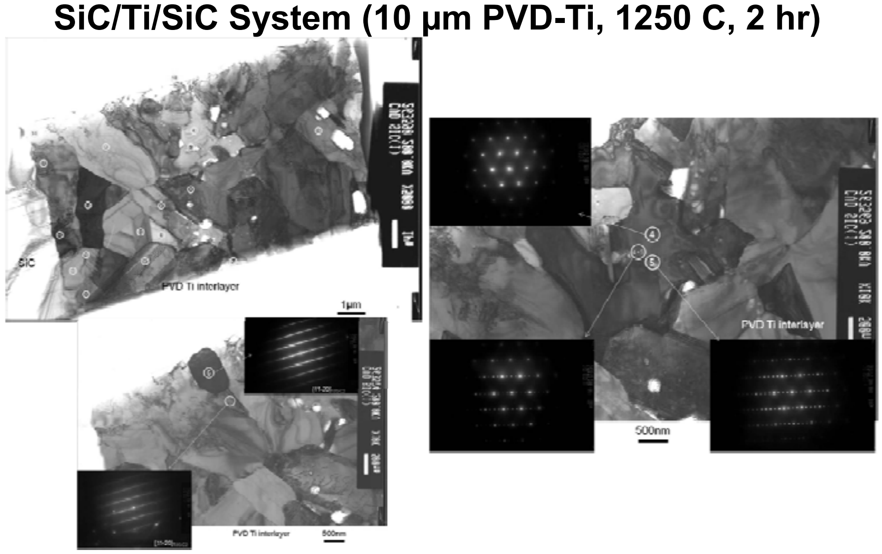
Transmission Electron Microscopy of Interfaces in SiC/Ti/SiC System (10 μm PVD-Ti, 1250 C, 2 hr)



H. Tsuda, M.C. Halbig, and M. Singh, Int. J. Appl. Ceram. Tech, (2012) in press.

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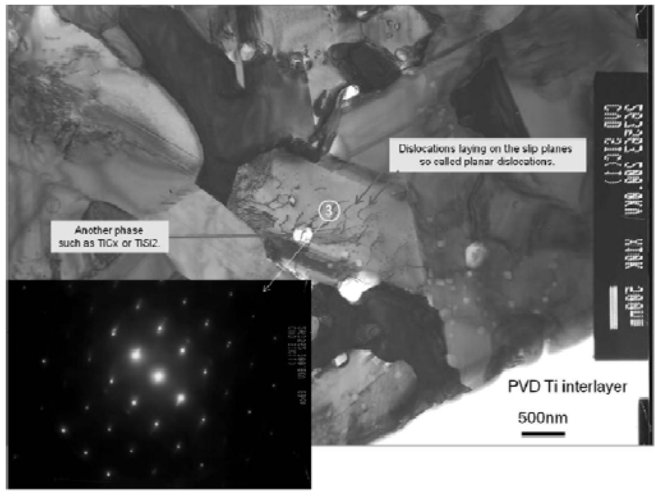
Transmission Electron Microscopy of Interfaces in SiC/Ti/SiC System (10 μm PVD-Ti, 1250 C, 2 hr)



H. Tsuda, M.C. Halbig, and M. Singh, Int. J. Appl. Ceram. Tech, (2012) in press.

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Integration Technologies for Improved Efficiency and Low Emissions

- **SiC/SiC Composites**

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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

1999 R&D 100 Award
2000 NorTech Innovation Award

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.

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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

ARCJoinT

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***

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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.

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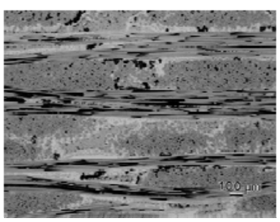
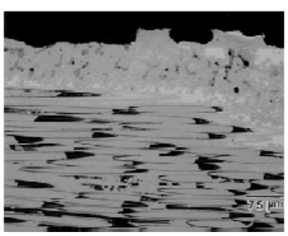
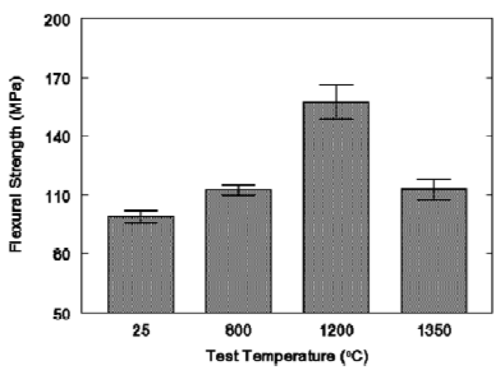
Microstructure and Mechanical Properties of Joined MI Hi-Nicalon/BN/SiC Composites



MI SiC/SiC Composite



Joint-Composite Interface



Flexural Strength of Joined SiC/SiC Composites

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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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