Joining and Integration of Silicon Carbide-Based Materials for High Temperature Applications

Michael C. Halbig \(^1\) and Mrityunjay Singh \(^2\)

\(^1\) NASA Glenn Research Center, Cleveland, OH
\(^2\) Ohio Aerospace Institute, Cleveland, OH

40\(^{th}\) International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, Florida, January 24-29, 2016.
Outline

• Introduction
  - Objectives, Components and Benefits

• NASA GRC Joining Technologies: CMCs to CMCs
  ➢ Brazing
    - modify joint properties: particulate additions
  ➢ ARCJoinT - Affordable, Robust Ceramic Joining Technology
  ➢ Diffusion Bonding
    - Advanced microscopy (TEM)
  ➢ REABond - Refractory Eutectic Assisted Bonding
    - modify joint properties: nanotube additions
  ➢ SET Joining - Single-Step Elevated Temperature Joining
    - Mechanical testing of joints

• Summary/Conclusions
Objectives

- **Deliver the benefits of ceramics in turbine engine applications**: higher temperature capability, and reduced cooling and weight, which contribute to increased fuel efficiency, performance, range, and payload, and lower emissions and lower operation costs for future engines.

- **Develop joining and integration technologies** which enable the wider utilization of ceramic matrix composite (CMC) turbine engine components by allowing for the fabrication of complex shaped CMC components and their incorporation within surrounding metal based systems.
CMC Turbine Engine Components and Joining Needs

Combustor liners
Vaness
Shrouds
Blades
Turbine Frame Flowpath
Flaps & Seals

Joining of singlet vanes to form doublets and joining of vane airfoils to ring sections (for smaller engines) - Allows for a reduction in part count, seals, and leakage

Joining of airfoil and end caps - Easier fabrication compared to a continuous 3-D CMC vane
Joining and Integration of Ceramics and CMCs for Turbine Engine Components

Development Approach
- Develop single, multiple, and hybrid interlayer approaches to aid in the joining of CMCs to CMCs and to metals.
- Optimize processing conditions so that joints and parts remain strong and crack free.
- Investigate inter-relations between processing, microstructure, and properties.
- Evaluate the thermal and mechanical properties of the joint.
- Scale-up of processing to larger and more complex shaped sub-components.
- Evaluate joints in relevant conditions which are comparable to engine operating environments.
Ceramic to Ceramic (CMC to CMC) System:

- **Brazing** - liquid metal flows into a narrow gap between the mating surfaces and solidifies to form a permanent bond. *Also for ceramic to metal joining.*

- **High Temperature Reactive Joining** - two step reactive formation of high temperature capable joints using carbon paste and Si infiltration (*ARCJoinT*).

- **Diffusion Bonding** - mating surfaces are pressed together and heated to cause bonding by interdiffusion of the components.

- **Refractory Eutectic Phase Bonding** - melting of a eutectic phase from a solid to a single phase liquid (*REABond*).

Uniform, dense, crack-free joints from all approaches.
Design and Understanding of Interfaces is Key to Successful Integration
Potential Applications for Ceramic to Metal Integration

Lean Direct Fuel Injector
Enabling for internal fuel circuit, sensor and actuator integration, and incorporation into metallic fuel system

NASA/Boeing Variable Geometry Chevron

“Chevrons” could deploy on take-off to reduce jet noise, retract in cruise to reduce drag.
Concept courtesy of Eric Eckstein, University of Bristol, U.K.

Key Technologies:
• Bonding of SiC to SiC
• Brazing of SiC Laminates to Metallic (Kovar) Fuel Tubes
Thermally-Actuated, High Temp. Morphing Composites

Isotropic Bimorph-Omnidirectional Moments

High expansion layer
Low expansion layer

Composite Construction Allows General Planforms

Metal, high CTE
UD composite, low CTE along fibers

Courtesy of Eric Eckstein, University of Bristol, U.K.
Brazing of CVD SiC to CVD SiC

Joining CVD SiC to CVD SiC with –
Ticusil (Ag-26.7Cu-4.5Ti) paste

Location 1 (EDS Analysis)

Location 1 (CVD SiC)

Location 2 (CVD SiC)

Location 3 (CVD SiC)

(a) Location 1

Uniform and crack-free joints are observed.
Relatively low temperature capability and extra challenges in brazing to metals.

Joining CVD SiC to CVD SiC with –
Cusil-ABA (Ag-35.3Cu-1.75Ti) paste

Avg. composition: Si
12 Ti 21 C 52 (Cu,Ag)

Joint Property Modifications: SiC Particulate Additions to Ticusil Brazing Paste - CVD SiC to CVD SiC Joining

CVD SiC/Ticusil (10vol% SiCp)/CVD SiC

CVD SiC/Ticusil (15vol% SiCp)/CVD SiC

Mean (μ) & Standard Deviation (σ) HK of Ticusil Joints

<table>
<thead>
<tr>
<th>Ticusil Paste</th>
<th>0 wt% SiCp</th>
<th>5 wt% SiCp</th>
<th>10 wt% SiCp</th>
<th>15 wt% SiCp</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ ± σ</td>
<td>μ ± σ</td>
<td>μ ± σ</td>
<td>μ ± σ</td>
<td>μ ± σ</td>
</tr>
<tr>
<td>CVD SiC</td>
<td>3442 ± 71</td>
<td>3304 ± 86</td>
<td>3134 ± 117</td>
<td>3305 ± 119</td>
</tr>
<tr>
<td>Braze</td>
<td>252 ± 58</td>
<td>86 ± 5</td>
<td>117 ± 52</td>
<td>106 ± 31</td>
</tr>
<tr>
<td>CVD SiC</td>
<td>3286 ± 71</td>
<td>3287 ± 95</td>
<td>3241 ± 51</td>
<td>3239 ± 111</td>
</tr>
</tbody>
</table>

Particulate additions were shown to decrease the hardness of the braze layer and were predicted to lower the volumetric CTE by 40-60% with 40 vol% SiCp.

SiC v/f, %

Predicted effect of SiC reinforcement on the volumetric CTE of Ticusil (or Cusil-ABA) braze.

[1] - Kerner's Equation
[2] - Turner's Equation

Volumetric CTE, ppm/K

SiC v/f, %
ARCJoinT: Joining of Ceramic Components Using 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 (M. Singh)

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: Typical Microstructure of Joined SiC-Based Ceramic Matrix Composites

Novoltex® C/SiC Composite with as-processed porosity

MI C/SiC Composite with as-processed microcracks

Joined Novoltex® Composite

Joined MI C/SiC Composite

Joint-Composite Interface

Good quality joints and the ability to fix CMC material processing flaws such as porosity and microcracking.

Very good quality, high strength bonds are obtained. However, the joining method requires a two-step process and is limited to temperatures <2400°F (1316°C).
Diffusion Bonding and REABond Joining Processes

Ceramic substrates were ultrasonically cleaned in Acetone for 10 minutes. Substrates were sandwiched around braze and foil layers. Mounted in epoxy, polished, and joints characterized using optical microscopy and scanning electron microscopy with energy dispersion spectroscopy analysis.

**Diffusion Bonding**
- Atmosphere: Vacuum
- Temperature: Ti 1200ºC, B-Mo 1400ºC
- Pressure: 30MPa
- Duration: Ti 4 hr B-Mo 4 hr
- Cool down: 2 ºC/min

**Materials (dimensions 0.5” x 1”)**
- Substrates: CVD SiC, SA-Tyrannohex (parallel), and SA-Tyrannohex (perpendicular).
- Interlayers: Ti foil (10, 20 micron) and B-Mo alloy foil (25 micron).

**REABond**
- Atmosphere: Vacuum
- Temperature: 1340ºC (10ºC above the braze liquidus temperature)
- Load: 100 g/sample
- Duration: 10 minutes
- Cool down: 2 ºC/min

**Materials (dimensions 0.5” x 0.5”)**
- CMC materials: C/C, MI SiC/SiC, CVI SiC/SiC, prepreg MI SiC/SiC, and SA-Tyrannohex.
- Interlayer: Si-Hf Eutectic tapes of 1, 2, and 3 layers.

**Materials**
- CVD SiC => chemically vapor deposited SiC
- SA-Tyrannohex => Woven SA-Tyranno fiber hot pressed composite like material
Diffusion Bonding with 10 µm Ti Foil and 25 µm B-Mo Alloy Foil

Very good quality bonds are obtained that are uniform and crack free. However, the joining process requires high applied loads and flat sub-elements for joining.
### Advanced Analysis - Transmission Electron Microscopy (TEM)

**Calculated Volume Fraction of Phases Formed During Diffusion Bonding (%)**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>CVD-SiC</th>
<th>SA-THX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
<td>PVD-Ti</td>
<td>Ti foil</td>
</tr>
<tr>
<td>thickness (μm)</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>fiber direction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti&lt;sub&gt;3&lt;/sub&gt;SiC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>91.4</td>
<td>75.9</td>
</tr>
<tr>
<td>Ti&lt;sub&gt;5&lt;/sub&gt;Si&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;x&lt;/sub&gt;</td>
<td>2.9</td>
<td>13.8</td>
</tr>
<tr>
<td>TiSi&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.7</td>
<td>10.3</td>
</tr>
<tr>
<td>TiC</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>unknown</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**In collaboration with H. Tsuda, Osaka Prefecture University, Japan**

Phases determined by selected area diffraction spot analysis.
(a) Ti<sub>3</sub>SiC<sub>2</sub> (B=[11-20])
(b) Ti<sub>5</sub>Si<sub>3</sub>C<sub>x</sub> (B=[411]=[72-53])
(c) TiSi<sub>2</sub> (B=[102])
Volume fraction of formed phases and crack existence

Substrates: CVD-SiC and SA-THX
Interlayer: PVD-Ti, Ti foil

Phase and trend identification leads to optimized processing and avoidance of crack formation.

Microcracks were observed. Ti₅Si₃CX (Ti₅Si₃) is highly anisotropic in its thermal expansion where CTE(c)/CTE(a) = 2.72 (Schneibel et al). Naka et al suggest that this is an intermediate phase.
More Detail on the Diffusion Bonding Approach and Characterization Can be Found in a Previous Publication

REABond: Joined with Two Si-8.5Hf Eutectic Tapes [210 microns each]

REABond provides simple processing with very good results for joining various CMCs even with uneven surfaces. Relatively high temp. capability, but limited to below the use temperature of the free silicon.
Joint Modification: SiC Nanotube Interlayer Integration for “Composite-Like” Joint Properties

FE SEM of Green REABOND Tape with 5 wt.% SiC Nanotube Additions - through thickness edge view

Cross-sections of as processed joint: REABOND (left) and REABOND w/5vol.% nano (right).

X-Ray Diffraction of “SiC” Nanotubes

Nonotubes contained residual carbon which may affect their reactivity with the Si-Hf REABond joining interlayer.
Limitations of Current Joining Approaches

Non-SiC-Based Approach
- Chemical and thermal incompatibility of interlayer and substrate
- Residual thermal stresses => lower strength, microcracking, and debonding
- Lower temperature capability than parent material capability
- Formation of intermediate or non-favorable phases

Other SiC-Based Approaches
- Two-step, two-phase processes
- Residual carbon is prone to oxidation leading to porosity
- Residual silicon lowers temp. capability to <2400°F (1316°C)

A new high temperature SiC-based joining approach is needed.
Overview of Pre-ceramic Paste Composition for High Temperature Joints
- Single-step Elevated Temperature Joining (SET)

J5A, J5A Nano 1, J5A Nano 2 - in descending order of SiC particle size
Furnace Weight Loss Studies

Materials:
J5A, J5A Nano 1, and J5A Nano 2 + 10, 20, 30 wt% Silicon

Procedure:

Cure
90°C overnight

Binder burnout
1000°C in Argon

Pyrolysis
1200°C, 1350°C, or 1450°C

Binder Burnout
1000°C in Argon

1200°C - 1450°C in low vacuum (10^-2 Torr)

1450°C in high vacuum (10^-6 – 10^-9 Torr)
Weight Retention of Pre-Ceramic Pastes

Weight retention values are promising for all samples → secondary infiltration steps may not be necessary.

Weight loss trends from furnace weight loss studies similar to TGA data.
• **All compositions after pyrolysis show a high yield of SiC.**
• **Vaporization of Si occurs in vacuum due to its high vapor pressure.**
Single-Step Elevated Temperature Joining: Higher Temperature Capable C, Si, and SiC-Based Pastes

**Approach:** 30 mil thick green tapes of SiC, Si, and carbon powders of varying particle sizes as well as several other additives.

**Benefits:** high temp. capability and one-step SiC formation.

X-Ray Diffraction analysis of three slurry compositions heat treated at 1450°C for 30 min.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiC</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>J5A+Si</td>
<td>99</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>J5A+N1+Si</td>
<td>91</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>J5A+N2+Si</td>
<td>92</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

High conversion to SiC suggests the compositions will provide one-step SiC formation.

Good initial results with J5A+N1+Si and J5A+N2+Si. Repeat and optimize with J5A+Si for less shrinkage.
Joining of SiC-Based Composites Using Pastes - Perpendicular SA-Tyrannohex with N1+J5A+Si

Perpendicular SA-Tyrannohex with N1+J5A+Si (x1 tape)
## Comparison of CMC Joining Approaches

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Brazing (Cu-Si-Ti based)</th>
<th>ARCJoinT</th>
<th>Diffusion Bonding (Ti)</th>
<th>REABond (Si-Hf)</th>
<th>SET Joining (C,Si,SiC based)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature limit</strong></td>
<td>&lt;1472°F (800°C)</td>
<td>&lt;2400°F (1316°C)</td>
<td>~2373°F (1300°C)</td>
<td>&lt;2400°F (1316°C)</td>
<td>&gt;2400°F (1316°C)</td>
</tr>
<tr>
<td><strong>Little or no processing pressure</strong></td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>Curved shape joining</strong></td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>Simple, one-step processing</strong></td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>Substrate surface condition</strong></td>
<td>smooth or rough</td>
<td>smooth or rough</td>
<td>smooth</td>
<td>smooth or rough</td>
<td>smooth or rough</td>
</tr>
<tr>
<td><strong>Ceramic or metal joining</strong></td>
<td>both</td>
<td>ceramic</td>
<td>ceramic</td>
<td>ceramic</td>
<td>ceramic</td>
</tr>
<tr>
<td><strong>Interlayer type</strong></td>
<td>foils, pastes</td>
<td>pastes</td>
<td>foils, surface coatings</td>
<td>pastes, tapes</td>
<td>pastes, tapes</td>
</tr>
<tr>
<td><strong>Cure CMC processing flaws (e.g. porosity and microcracks)</strong></td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td><strong>Issues</strong></td>
<td>possible formation of brittle ceramic phases</td>
<td>free silicon</td>
<td>geometry limitations and processing stress</td>
<td>silicon rich phase</td>
<td>early in development</td>
</tr>
<tr>
<td><strong>Bond quality</strong></td>
<td>uniform, dense, and crack-free joints</td>
<td>uniform, dense, and crack-free joints</td>
<td>uniform, dense, and crack-free joints</td>
<td>uniform, dense, and crack-free joints</td>
<td>uniform, dense, and crack-free joints</td>
</tr>
</tbody>
</table>

Processing and microscopy conducted to obtain uniform, dense, and crack-free joints.

Second phase of development: advanced processing, analysis, and thermo-mechanical testing.
Mechanical Testing: Single Lap Offset - REABond Joined SA-Tyrannohex

As-processed joint for SA-THX in perpendicular orientation

Strengths of Perpendicular THX Joints

- Perpendicular Tyrannohex with 1 layer Si-Hf
- Perpendicular Tyrannohex with 2 layers Si-Hf

Residual Strength Test
- 350 hr run out at 1200°C and 25 MPa
- tested at 1200°C
- highest strength seen in a SLO test, 135 MPa

Excellent joint stability and strength retention

Single lap offset shear test to be used for in-house screening.
Mechanical Testing: In-House Capability for Testing According to ISO 13124

Schematic diagram of cross bonded sample and fixture for **measuring tensile bond strength**

Schematic diagram of cross bonded sample and fixture for **measuring shear bond strength**

Results and Analysis for Testing to ISO 13124 (with REABond Joining)

Testing in Tension

Results show the need for additional analysis and improved test methods.
Joining Technology Demonstration
- Sub-element testing in a relevant environment

Goal: Apply joining to sub-elements and sub-components and test to higher TRL in under relevant conditions.

Steps:
- Join coupons to form profiles of vane/blade sub-elements.
- Conduct thermal exposures and evaluate residual strength and damage (microscopy and NDE). Also conduct strength tests on non-exposed sub-element(s).
- Introduce mechanical stress for thermo-mechanical conditions, i.e. 2400°F laser induced thermal gradient exposure. Laser focused at airfoil or joint region.

1.25" (32mm) SiC Foam SiC/SiC Composite Axial Cooling Holes

NASA environmental barrier coating applied
Summary and Conclusions

• Good quality joints are obtained from all five CMC to CMC joining methods: Brazing, ARCJoinT, Diffusion Bonding, REABond, and SET.

• REABond and SET approaches are the most versatile allowing for tailored interlayers for pressureless joining of complex shapes with smooth or rough surfaces in one-step processing.

• SET joining approach offers: low residual C or Si, high weight retention and SiC conversion, and use temperatures >2400°F.

• Particulate additions to the braze were shown to modify the hardness and thermal expansion of the joint.

• Mechanical tests to include ISO 13124 and single-lap offset shear are being used but additional analysis and improved test methods are needed.

• Higher TRL joining to be demonstrated on vane sub-elements in relevant thermo-mechanical engine conditions.
Acknowledgements

- This work was supported by various NASA projects to include:
  - the NASA Transformational Tools and Technologies (TTT) Project of the Transformative Aeronautics Concepts Program
  - the NASA Aeronautical Sciences Project of the Aeronautics Research Mission Directorate (ARMD).
- Thanks to John Setlock for preparing REABond tapes, Craig Smith for single-lap off-set testing, Ron Phillips and Jerry Lang for ISO 13124 testing and analysis, respectively.
- Special thanks to Dr. H. Tsuda, Osaka Prefecture University, Osaka, Japan for TEM analysis.