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

40th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, Florida, January 24-29, 2016.

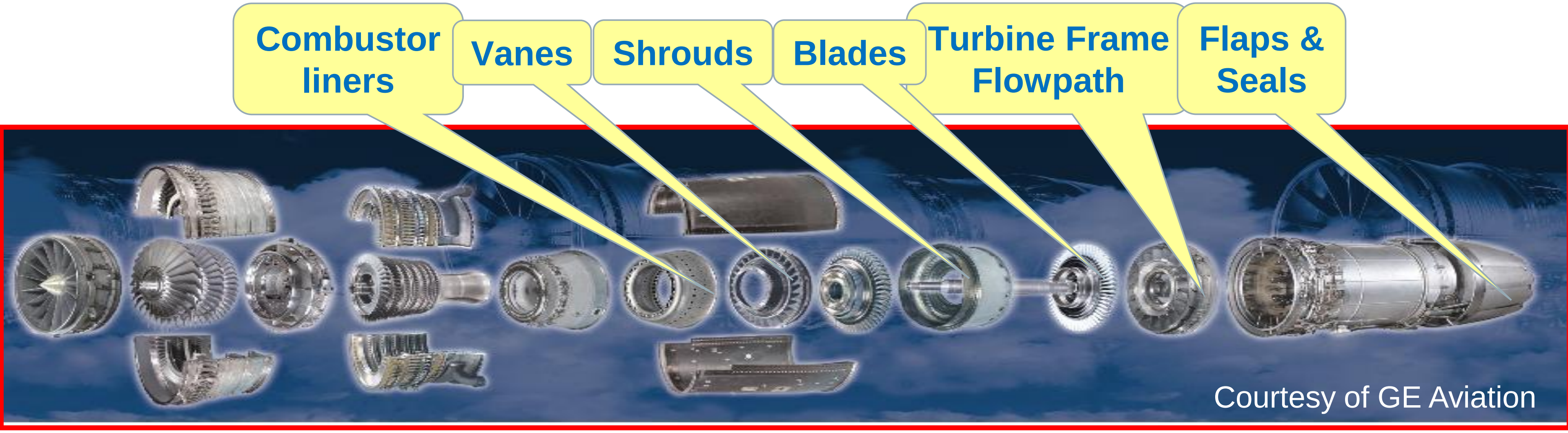
Outline

- 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

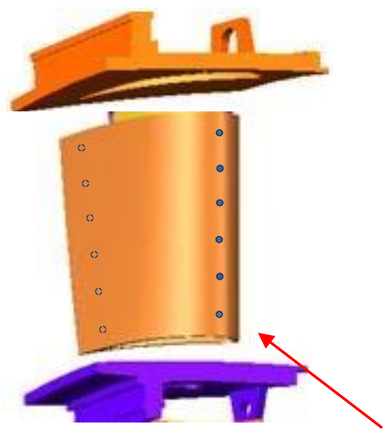
- **Deliver the benefits of ceramics in turbine engine applications**: higher temperature capability, and reduced cooling and weight, which contribute to increased fuel efficiency, performance, range, and payload, and lower emissions and lower operation costs for future engines.
- **Develop joining and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

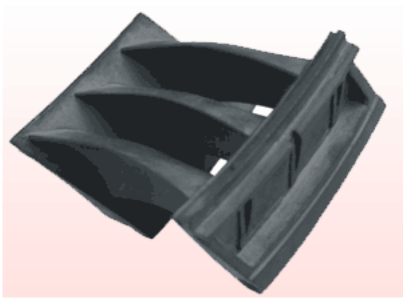
CMC Turbine Engine Components and Joining Needs



Courtesy of GE Aviation

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

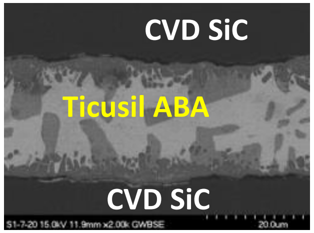
Joining and Integration of Ceramics and CMCs for Turbine Engine Components

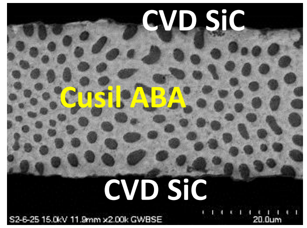
Development Approach

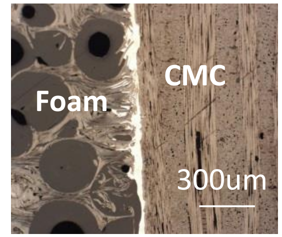
- Develop single, multiple, and hybrid interlayer approaches to aid in the joining of CMCs to CMCs and to metals.
- Optimize processing conditions so that joints and parts remain strong and crack free.
- Investigate inter-relations between processing, microstructure, and properties.
- Evaluate the thermal 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.

Integration and Joining Technology Development

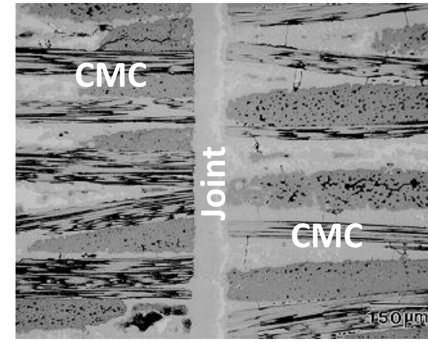
Ceramic to Ceramic (CMC to CMC) System:





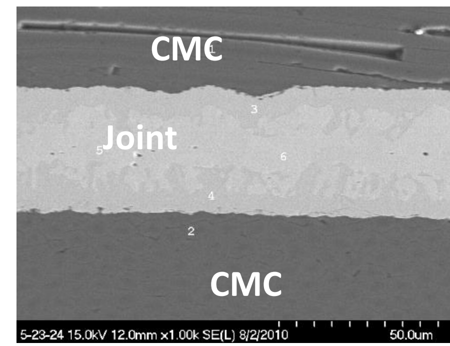


Brazing Examples

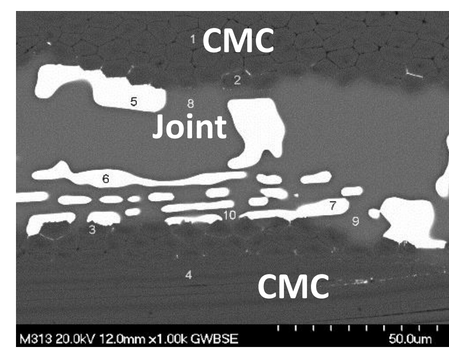


ARCJoinT

- **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).**



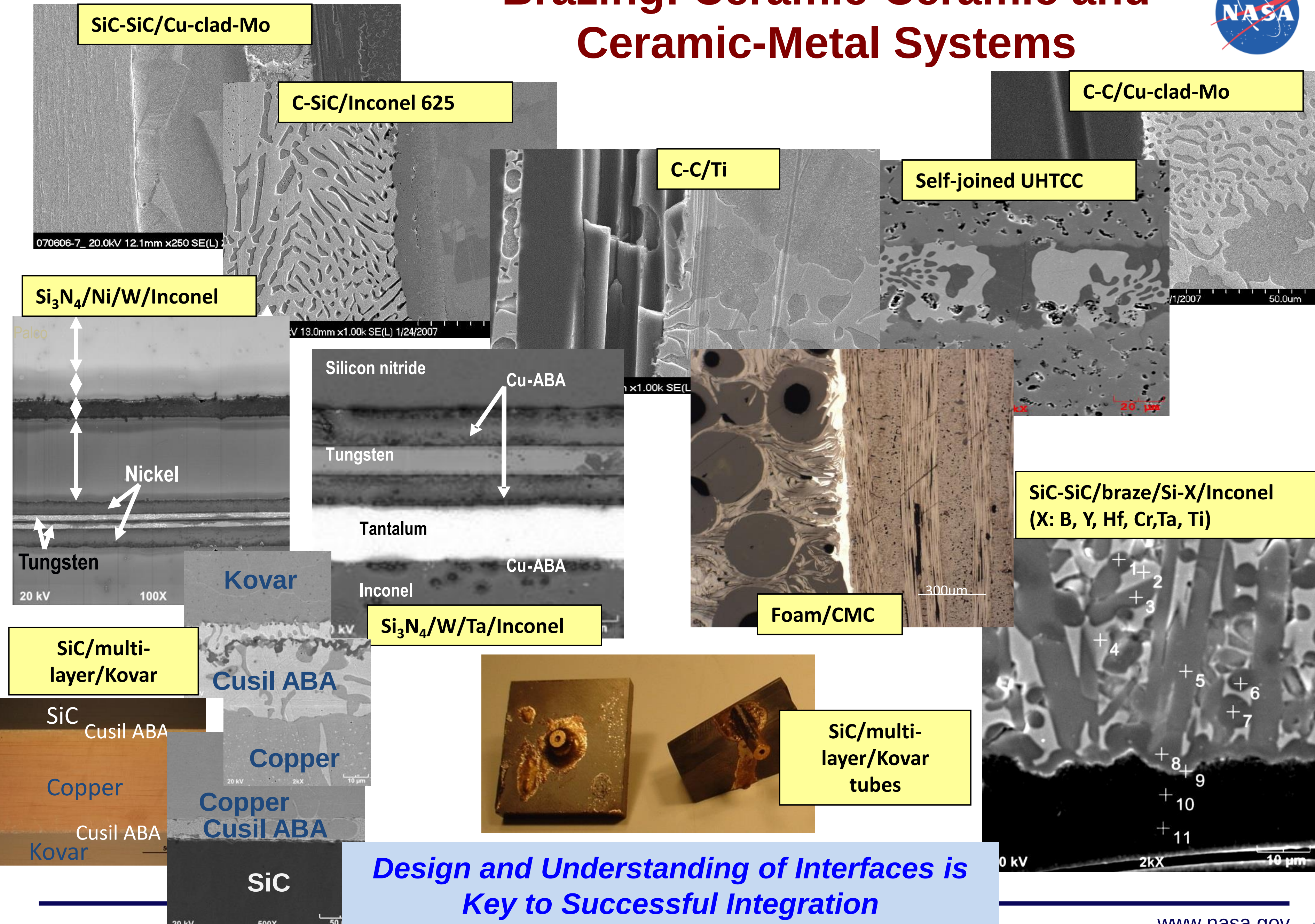
Diffusion Bonding



Eutectic Phase Bonding

Uniform, dense, crack-free joints from all approaches.

Brazing: Ceramic-Ceramic and Ceramic-Metal Systems

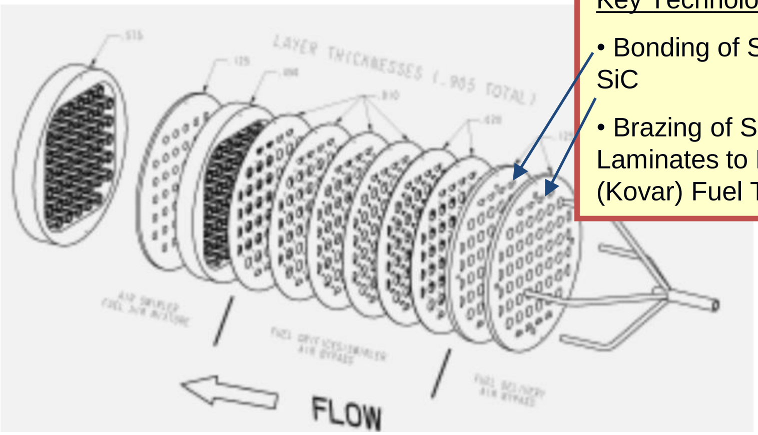


Design and Understanding of Interfaces is Key to Successful Integration

Potential Applications for Ceramic to Metal Integration

Lean Direct Fuel Injector

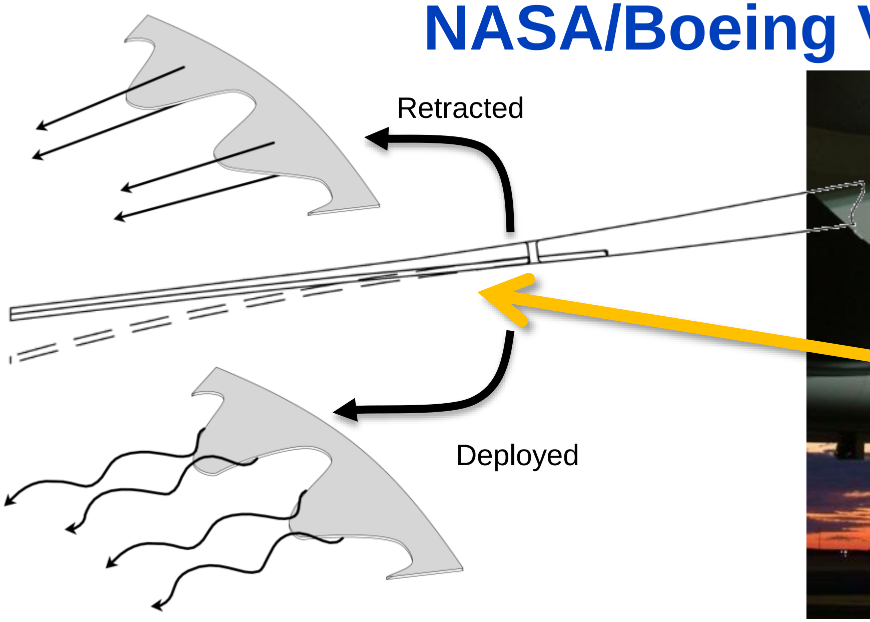
Enabling for internal fuel circuit, sensor and actuator integration, and incorporation into metallic fuel system



Key Technologies:

- Bonding of SiC to SiC
- Brazing of SiC Laminates to Metallic (Kovar) Fuel Tubes

NASA/Boeing Variable Geometry Chevron



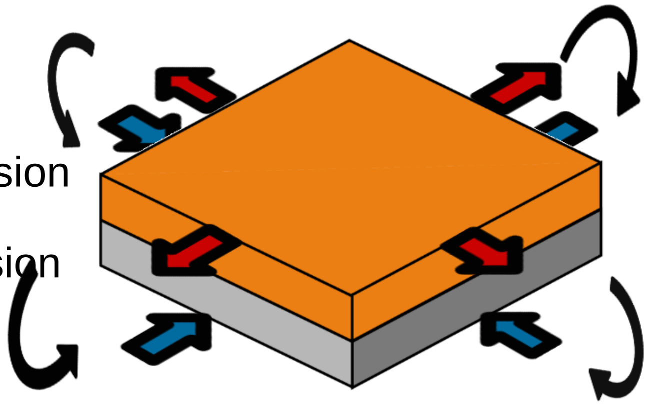
“Chevrons” could deploy on take-off to reduce jet noise, retract in cruise to reduce drag.

Concept courtesy of Eric Eckstein, University of Bristol, U.K.

Thermally-Actuated, High Temp. Morphing Composites

Isotropic Bimorph- Omnidirectional Moments

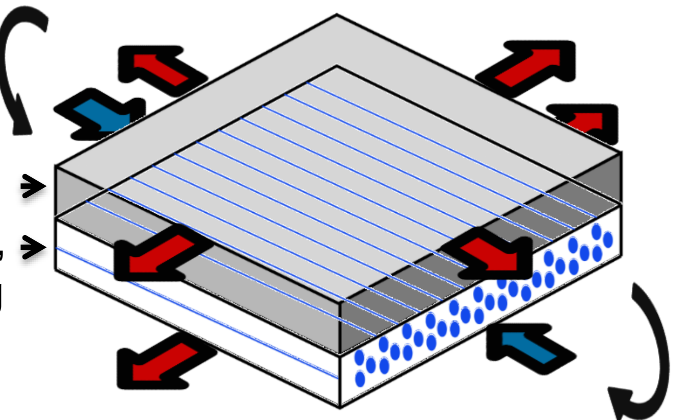
High expansion layer
Low expansion layer

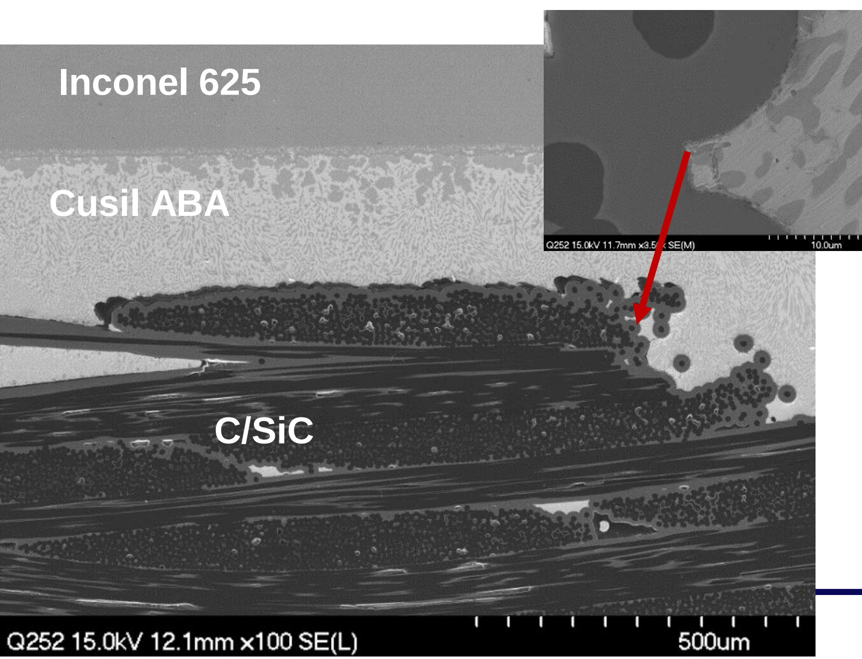


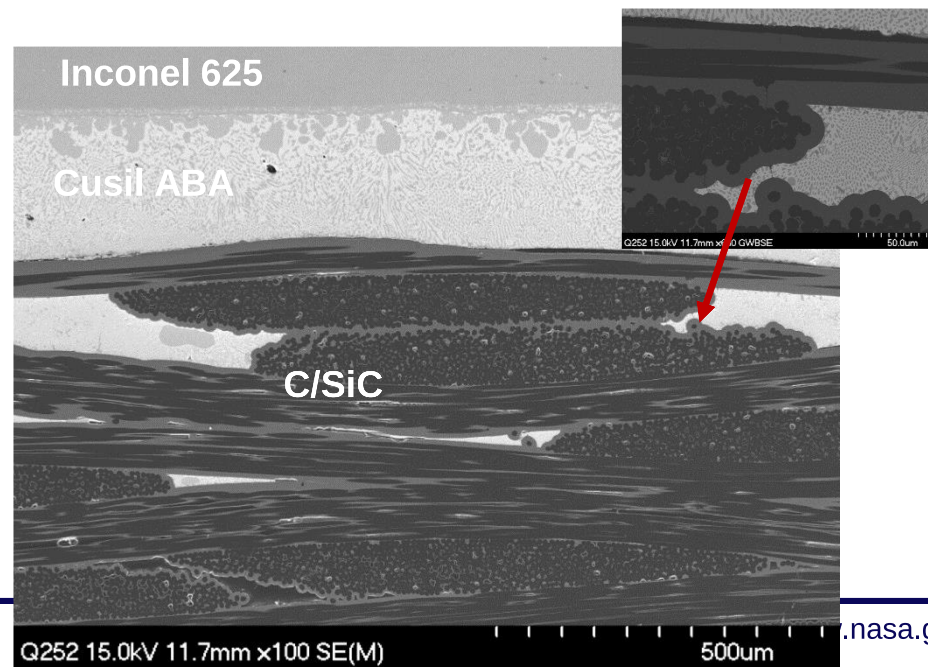
Courtesy of Eric Eckstein, University of Bristol, U.K.

Composite Construction Allows General Planforms

Metal, high CTE
UD composite, low CTE along fibers

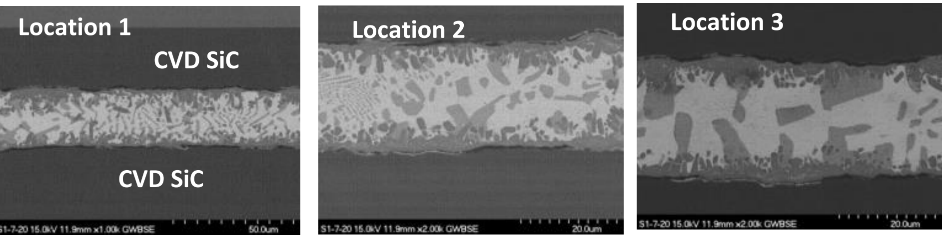


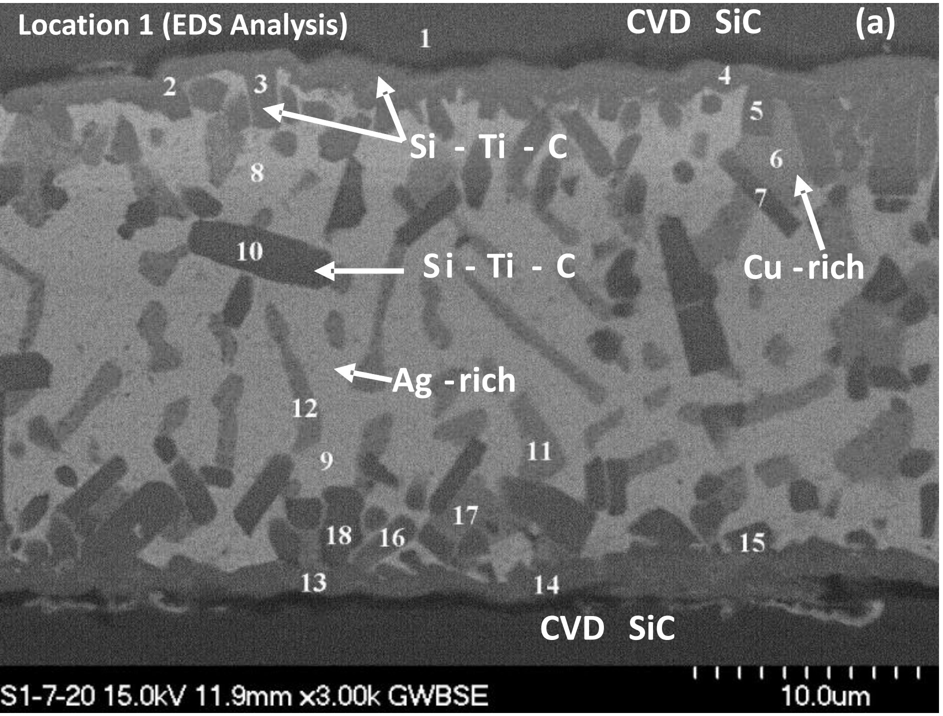




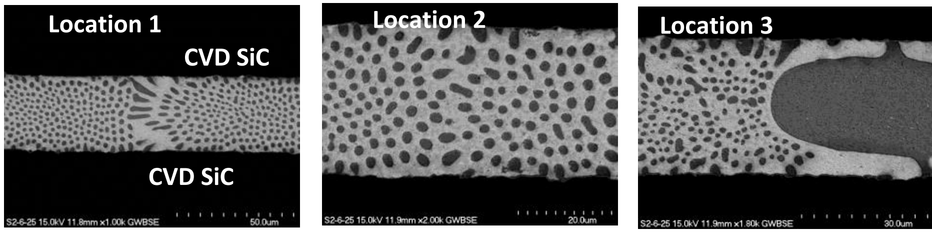
Brazing of CVD SiC to CVD SiC

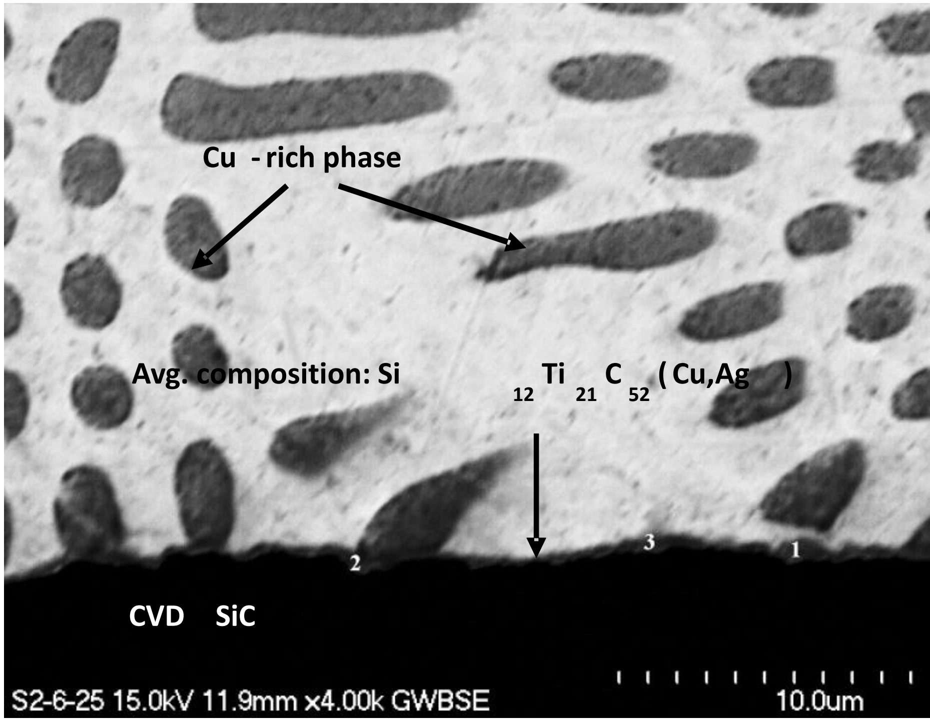
Joining CVD SiC to CVD SiC with – **Ticusil (Ag-26.7Cu-4.5Ti) paste**





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



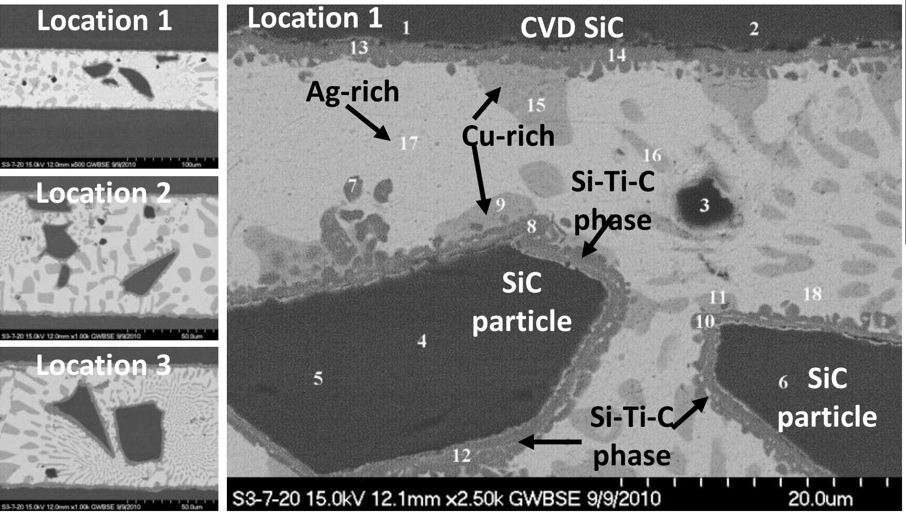


Uniform and crack-free joints are observed.
Relatively low temperature capability and extra challenges in brazing to metals.

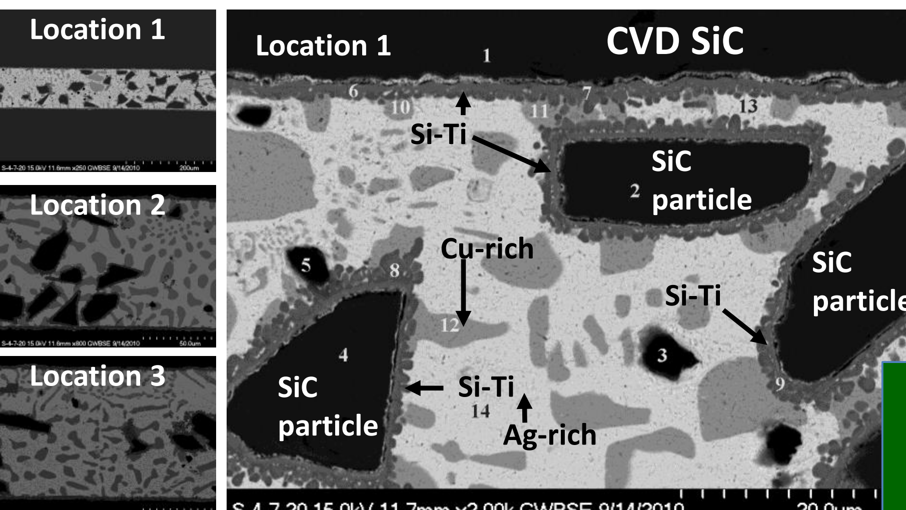
M.C. Halbig, B.P. Coddington, R. Asthana, and M. Singh, Ceram. Int., 39, 4 (2013) 4151-4162.

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

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

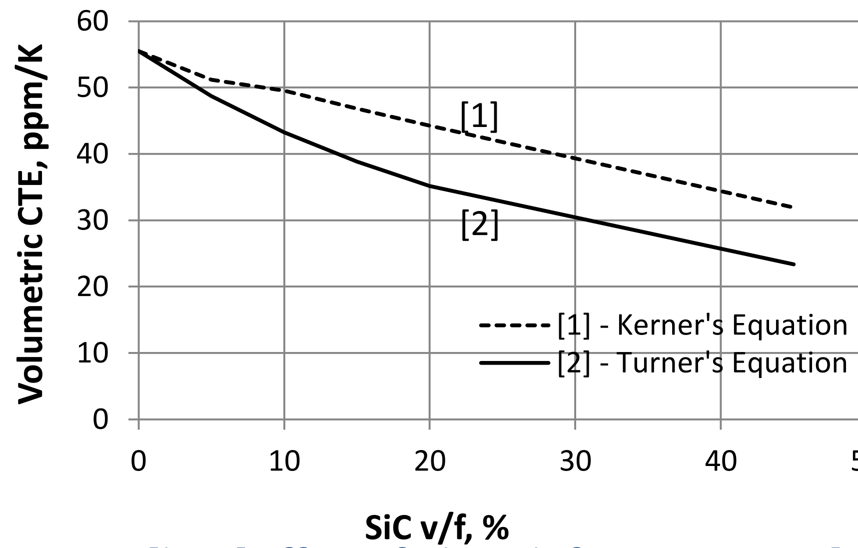


CVD SiC/Ticusil (15vol% SiCp)/CVD SiC



	Ticusil Paste			
	0 wt% SiCp	5 wt% SiCp	10 wt% SiCp	15 wt% SiCp
	μ ± σ	μ ± σ	μ ± σ	μ ± σ
CVD SiC	3442 ± 71	3304 ± 86	3134 ± 117	3305 ± 119
Braze	**252 ± 58**	**86 ± 5**	**117 ± 52**	**106 ± 31**
CVD SiC	3286 ± 71	3287 ± 95	3241 ± 51	3239 ± 111

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



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

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.

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

↓

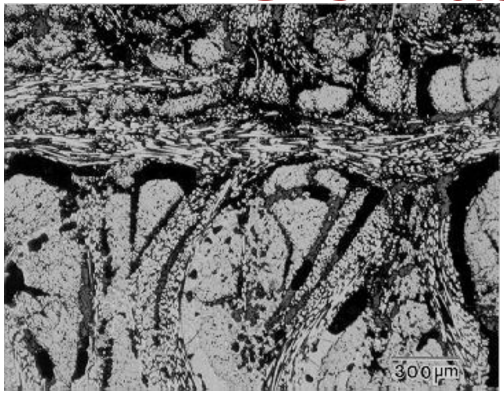
Affordable and Robust Ceramic Joints with Tailorable Properties

1999 R&D 100 Award
2000 NorTech Innovation Award
(M. Singh)

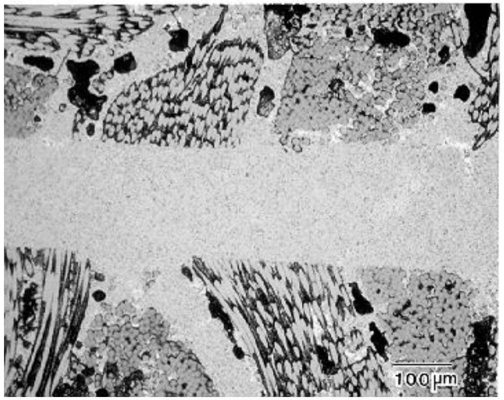
Advantages

- 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

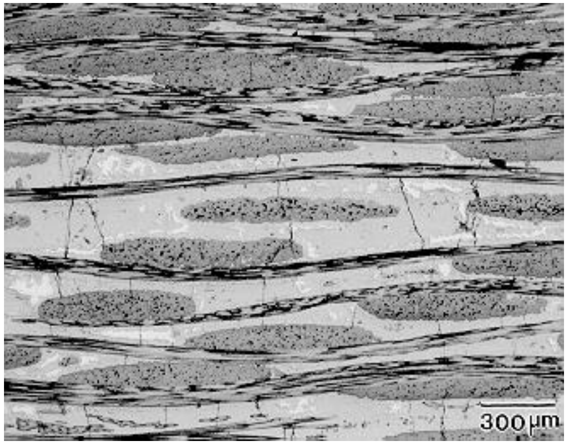


Novoltex® C/SiC Composite with as-processed porosity

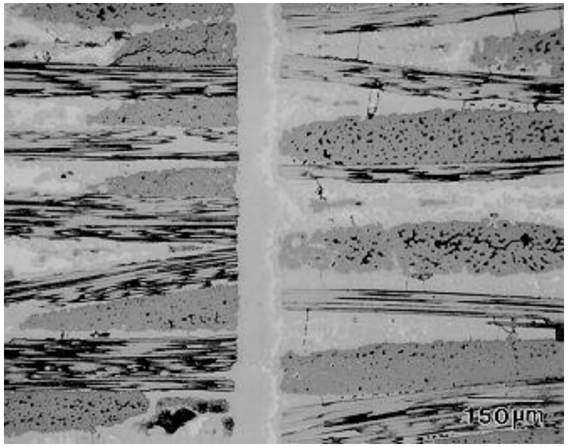


Joined Novoltex® Composite

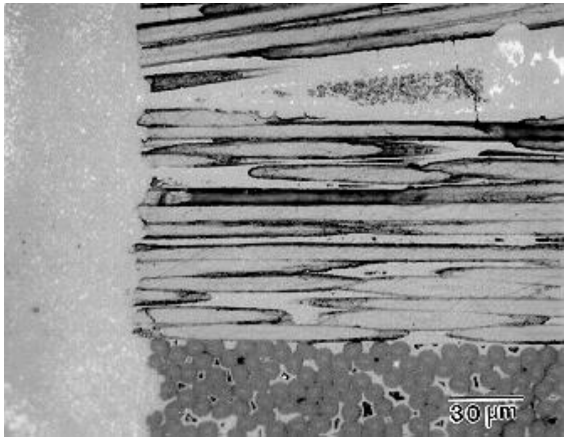
Good quality joints and the ability to fix CMC material processing flaws such as porosity and microcracking.



MI C/SiC Composite with as-processed microcracks



Joined MI C/SiC Composite



Joint-Composite Interface

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

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)**

Ceramic substrates were ultrasonically cleaned in Acetone for 10 minutes

Substrates were sandwiched around braze and foil layers

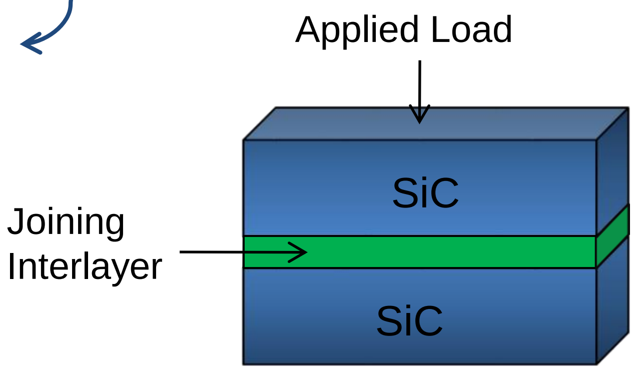
Materials (dimensions 0.5" x 0.5")

- 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.**

Diffusion Bonding

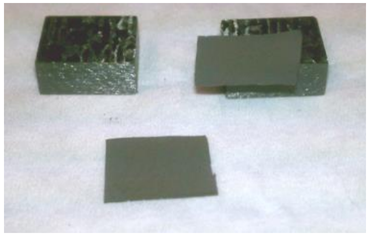
- Atmosphere: Vacuum
- Temperature: Ti 1200ºC, B-Mo 1400ºC
- **Pressure: 30MPa**
- Duration: Ti 4 hr, B-Mo 4 hr
- Cool down: 2 ºC/min



REABond

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

Mounted in epoxy, polished, and joints characterized using optical microscopy and scanning electron microscopy with energy dispersion spectroscopy analysis



Joining prep with CMC substrates and Si-Hf REABond tapes with 30-35% solid loading.

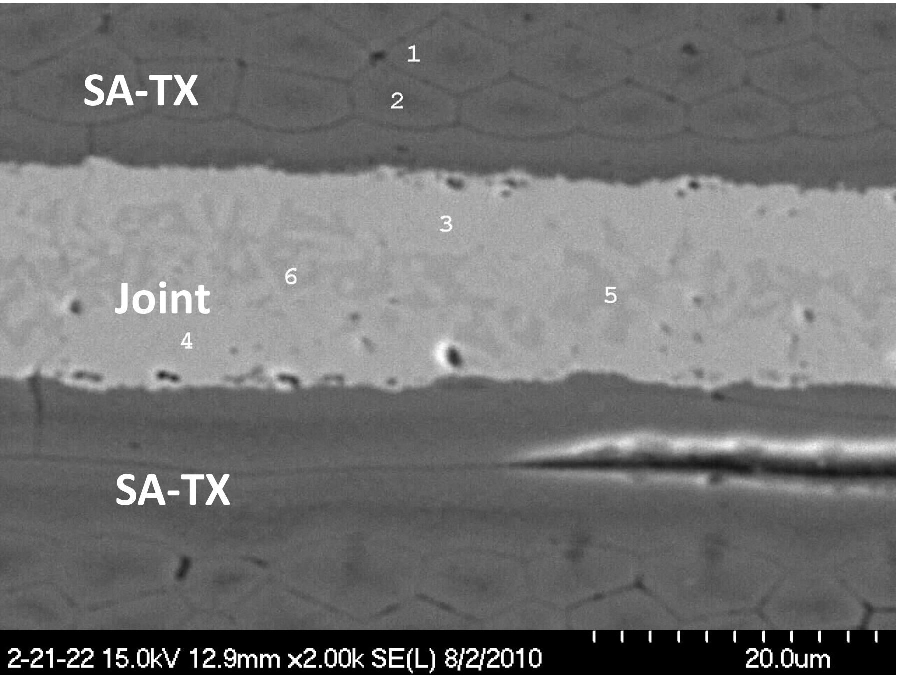
Materials

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

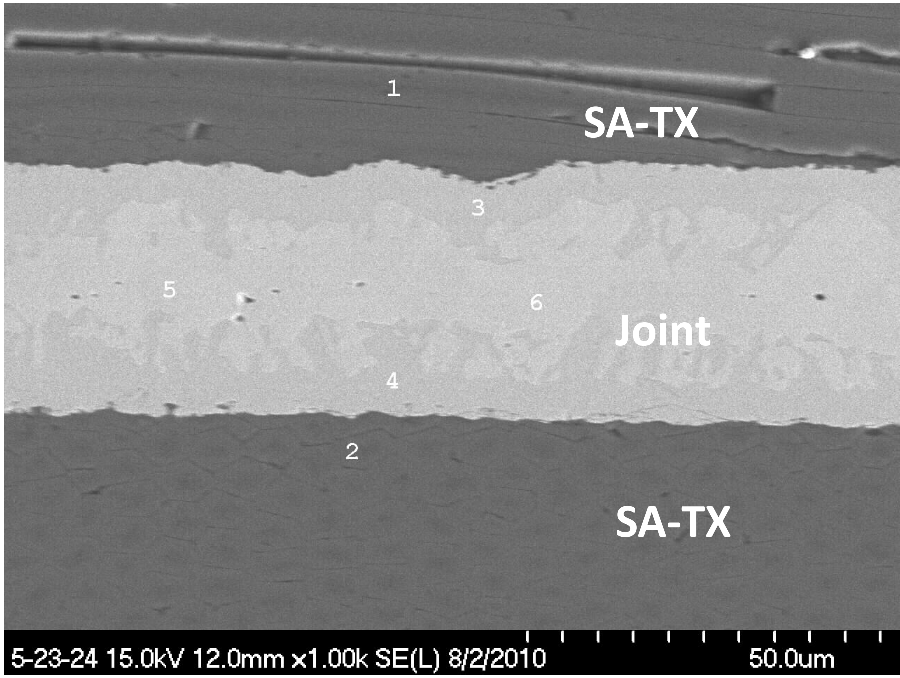
SA-Tyrannohex / **Ti** / SA-Tyrannohex



	C	Si	Ti
1	54.28%	45.72%	0%
3	44.89%	15.79%	39.33%
5	0%	69.39%	30.61%

Percents are atomic %

SA-Tyrannohex / **B-Mo alloy** / SA-Tyrannohex



	C	Si	B	Mo	O
1	58.34%	41.66%	0%	0%	0%
3	19.09%	5.51%	63.96%	8.25%	3.19%
5	0%	0%	89.18%	10.82%	0%

Percents are atomic %

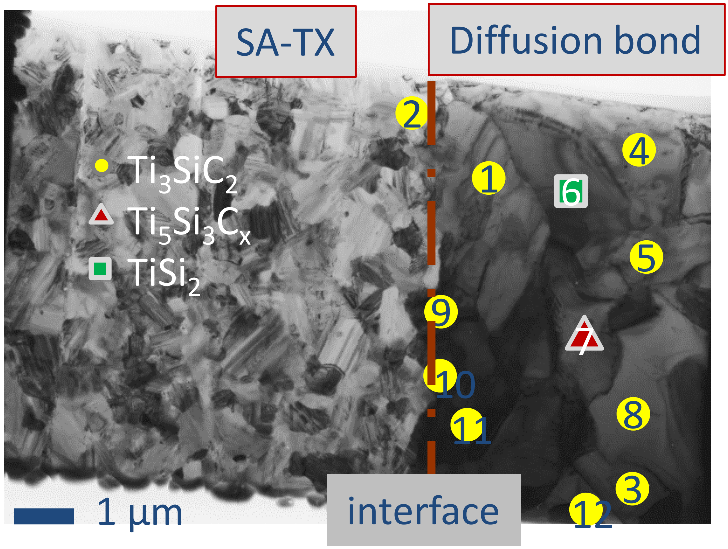
Very good quality bonds are obtained that are uniform and crack free.
However, the joining process requires high applied loads and flat sub-elements for joining.

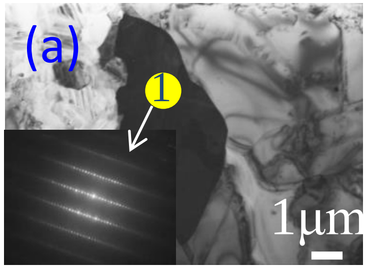
Advanced Analysis - Transmission Electron Microscopy (TEM)

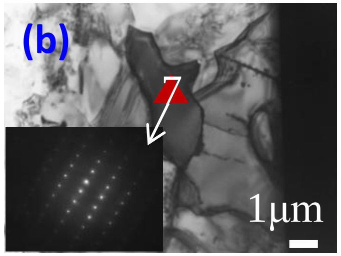
Calculated Volume Fraction of Phases Formed During Diffusion Bonding (%)

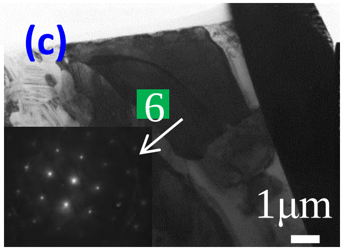
Substrate	CVD-SiC				SA-THX	
Interlayer	PVD-Ti		Ti foil		Ti foil	
thickness (µm)	10	20	10	20	10	10
fiber direction	—	—	—	—	Parallel	Perpen-dicular
Ti_3SiC_2	91.4	75.9	63.5	37.5	84.2	63.7
$Ti_5Si_3C_x$	2.9	13.8	18.2	43.7	5.3	9.1
$TiSi_2$	5.7	10.3	6.1	3.1	10.5	13.6
TiC	0	0	6.1	9.4	0	0
unknown	0	0	6.1	6.3	0	13.6
Total	100	100	100	100	100	100

Representative TEM image of 10 µm-Ti foil (parallel to SA-THX fiber)









Phases determined by selected area diffraction spot analysis.

(a) Ti_3SiC_2 (B=[11-20])

(b) $Ti_5Si_3C_x$ (B=[411]=[-72-53])

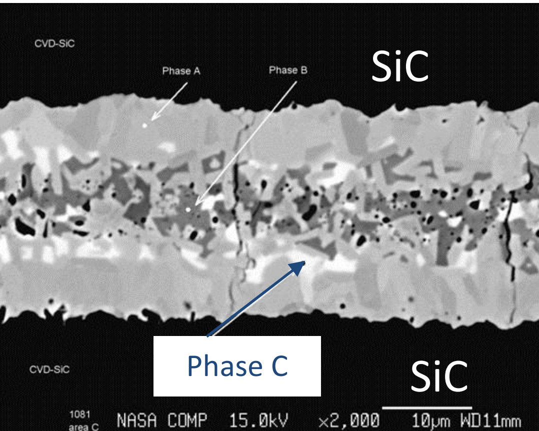
(c) $TiSi_2$ (B=[102])

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

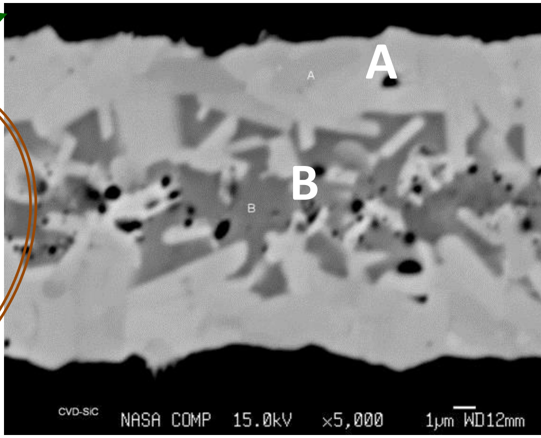
Volume fraction of formed phases and crack existence

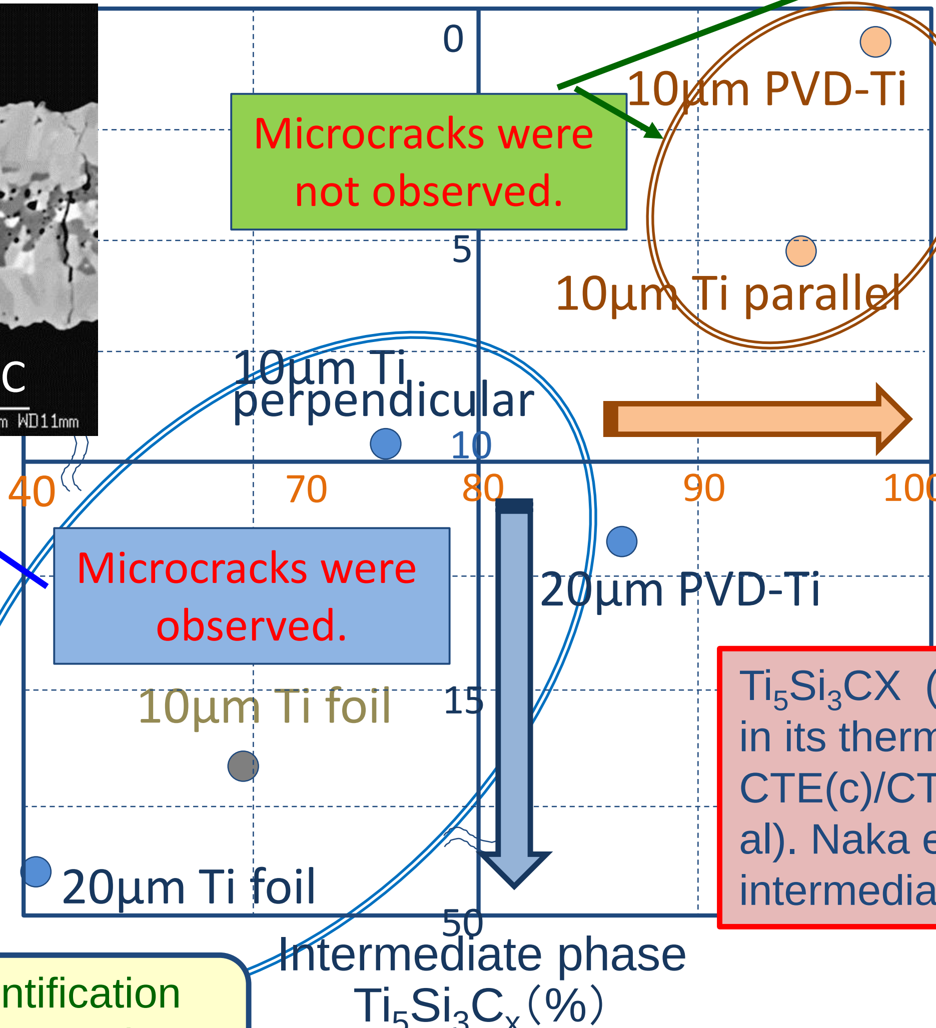
Substrates : CVD-SiC and SA-THX
Interlayer : PVD-Ti, Ti foil

20 Micron Ti Interlayer, 1250°C, 2 Hr



10 Micron Ti Interlayer , 1250°C, 2 HR

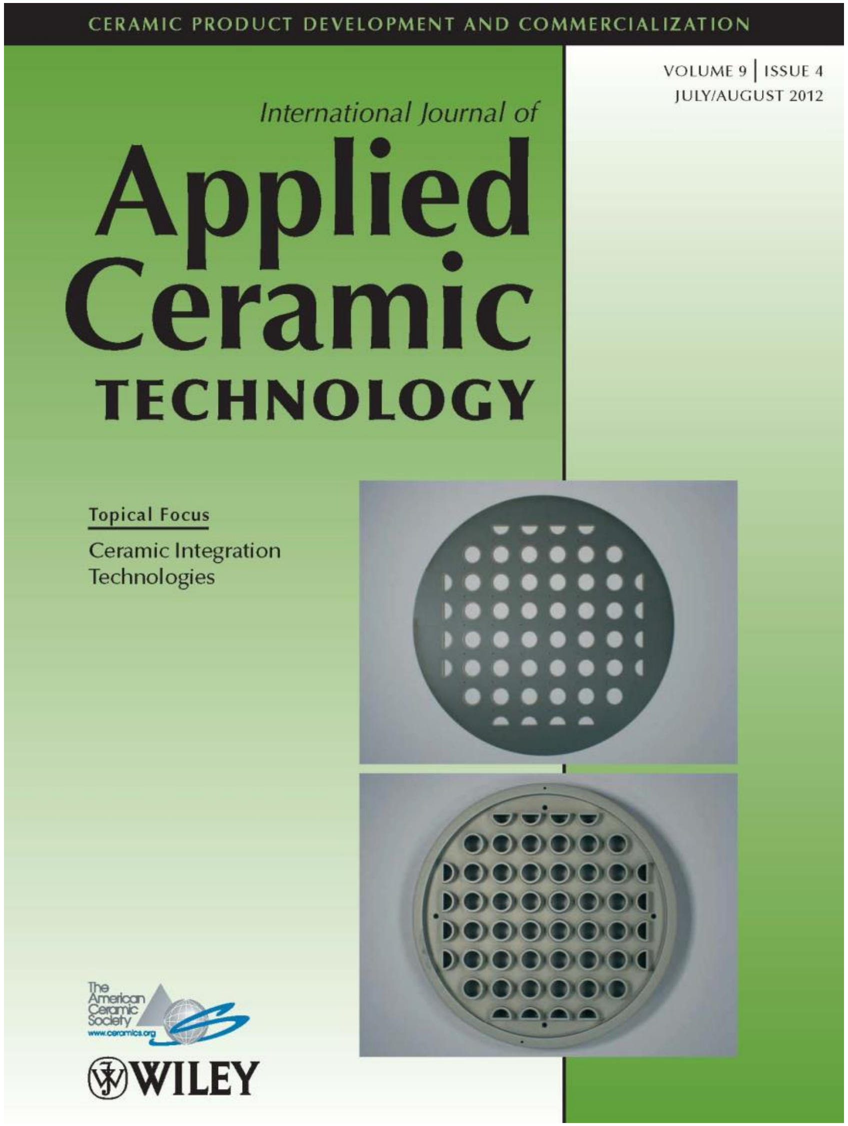




Ti_5Si_3CX (Ti_5Si_3) is highly anisotropic in its thermal expansion where CTE(c)/CTE(a) = 2.72 (Schneibel et al). Naka et al suggest that this is an intermediate phase.

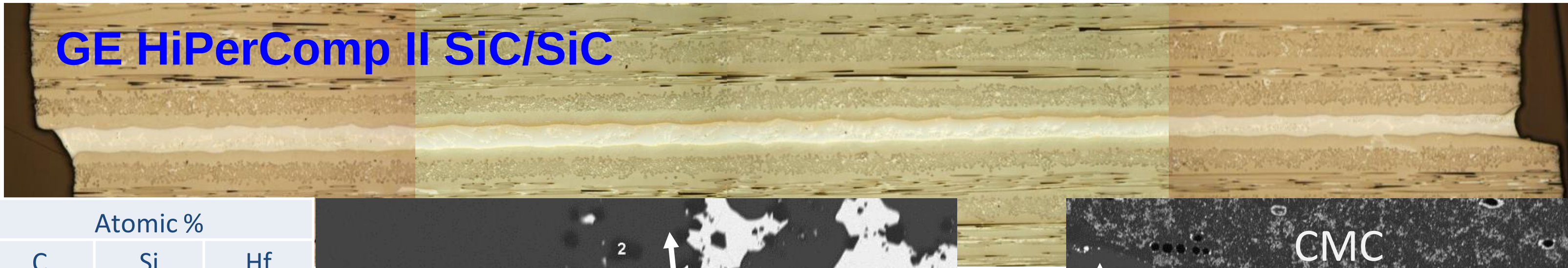
Phase and trend identification leads to optimized processing and avoidance of crack formation.

More Detail on the Diffusion Bonding Approach and Characterization Can be Found in a Previous Publication

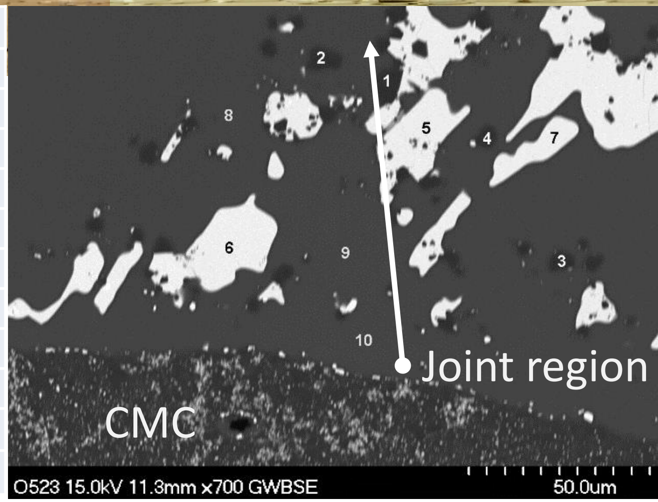


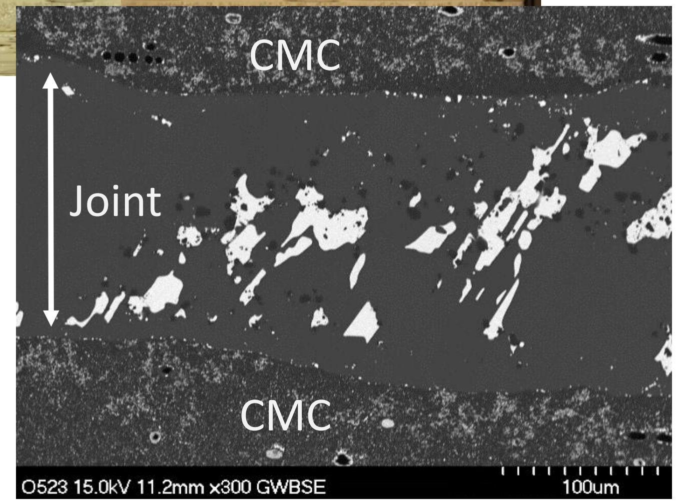
ACT topical issue on "Ceramic Integration Technologies": Michael C. Halbig, Mrityunjay Singh, and Hiroshi Tsuda, "Integration Technologies for Silicon Carbide-Based Ceramics for MEMS-LDI Fuel Injector Applications" *International Journal of Applied Ceramic Technology*, Volume 9, Number 4, 2012, p. 677-687. (July/August 2012 issue)

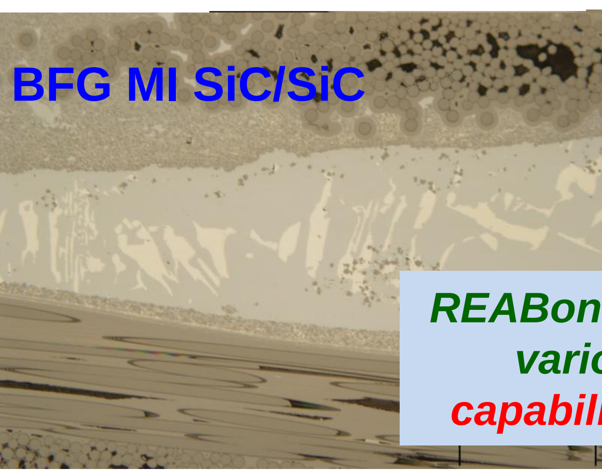
REABond: Joined with Two Si-8.5Hf Eutectic Tapes [210 microns each]

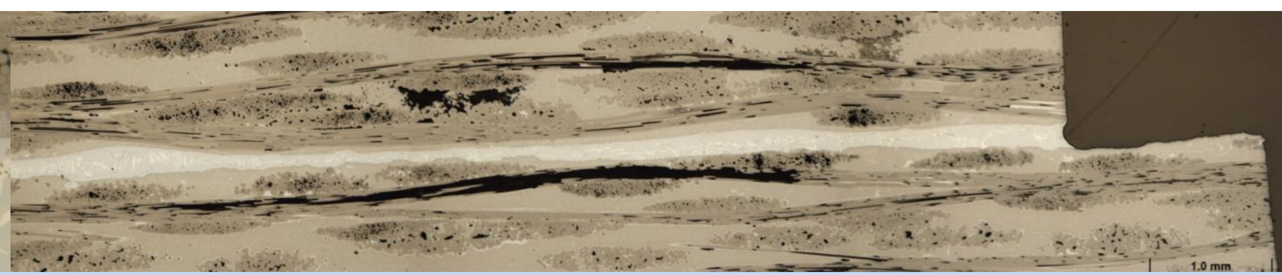


O523	Atomic %		
	C	Si	Hf
1	49.6	50.4	
2	49.5	50.5	
3	29.1	60.9	
4	47.6	52.4	
5	19.0	53.4	27.6
6	16.6	56.5	26.9
7	18.2	53.8	28.0
8	25.1	74.5	0.4
9	24.5	75.2	0.3
10	11.5	88.4	





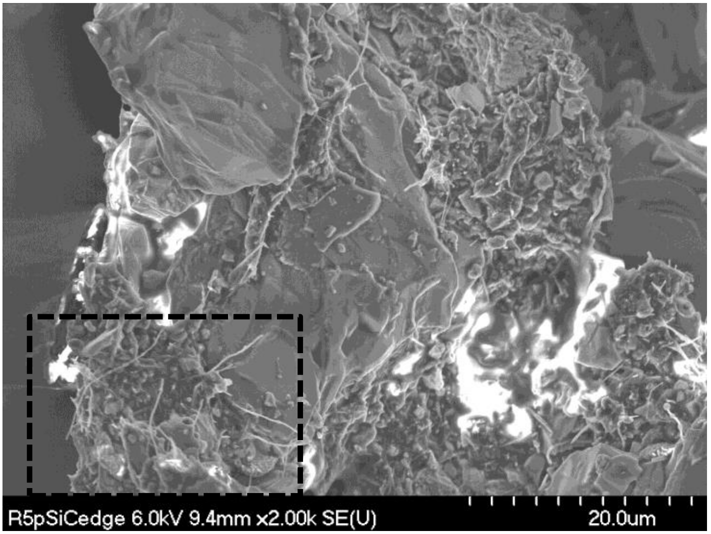


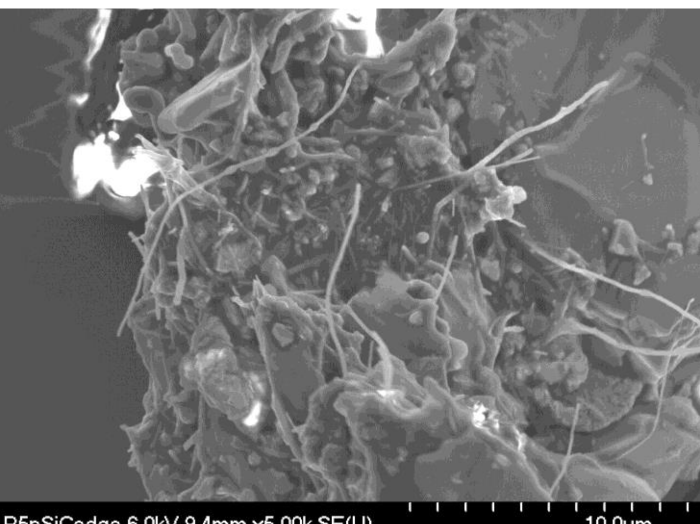


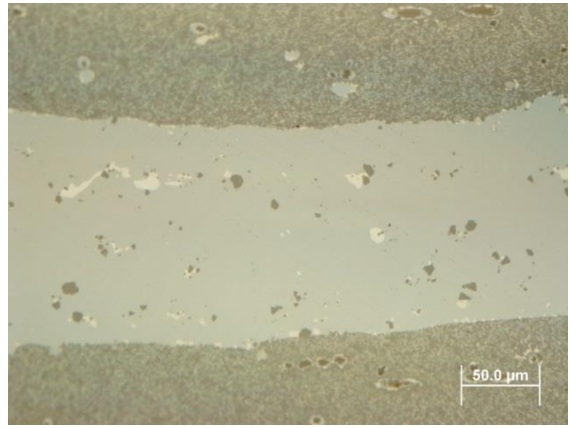
REABond provides simple processing with very good results for joining various CMCs even with uneven surfaces. Relatively high temp. capability, but limited to below the use temperature of the free silicon.

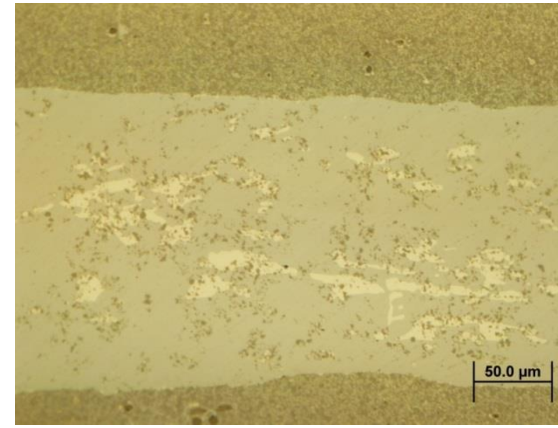
Joint Modification: SiC Nanotube Interlayer Integration for "Composite-Like" Joint Properties

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



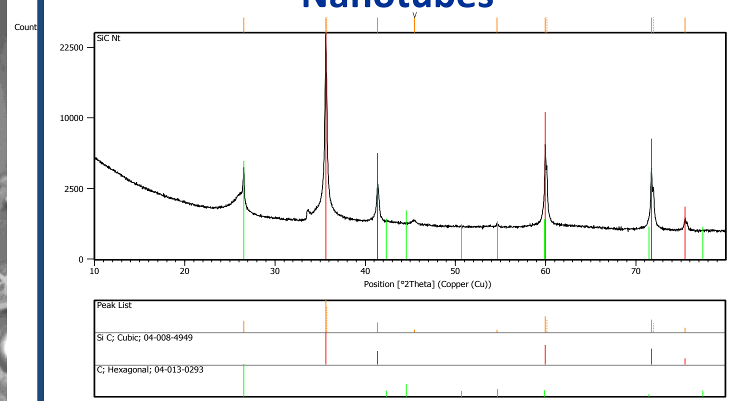






Cross-sections of as processed joint: REABOND (left) and REABOND w/5vol.% nano (right).

X-Ray Diffraction of "SiC" Nanotubes



Nonotubes contained residual carbon which may affect their reactivity with the Si-Hf REABond joining interlayer.

High Temperature Joining Approaches

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

- **Carbon**
  - Carbon Sources
    - Solid, liquid
- **SiC**
  - Particle Size Effect
  - Micro and Nano sizes (Nano 1 and Nano 2)
- **Silicon**
  - Particle Size Effect
  - Weight Percent Effect
- **Surface Modifiers**
  - Surfactants
  - Dispersants
  - Coupling agents

Furnace Weight Loss Studies

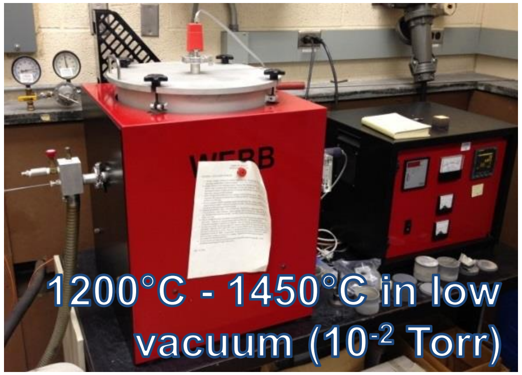
Materials:
J5A, J5A Nano 1, and J5A Nano 2 + 10, 20, 30 wt% Silicon

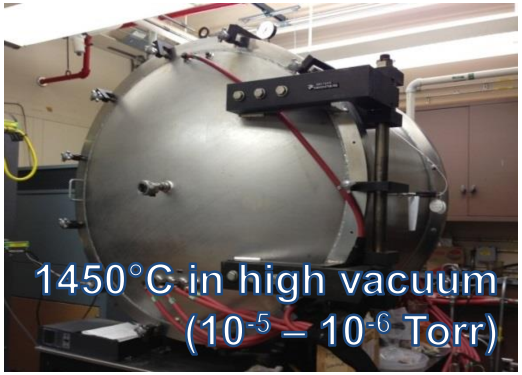
Procedure:

Cure
90°C overnight

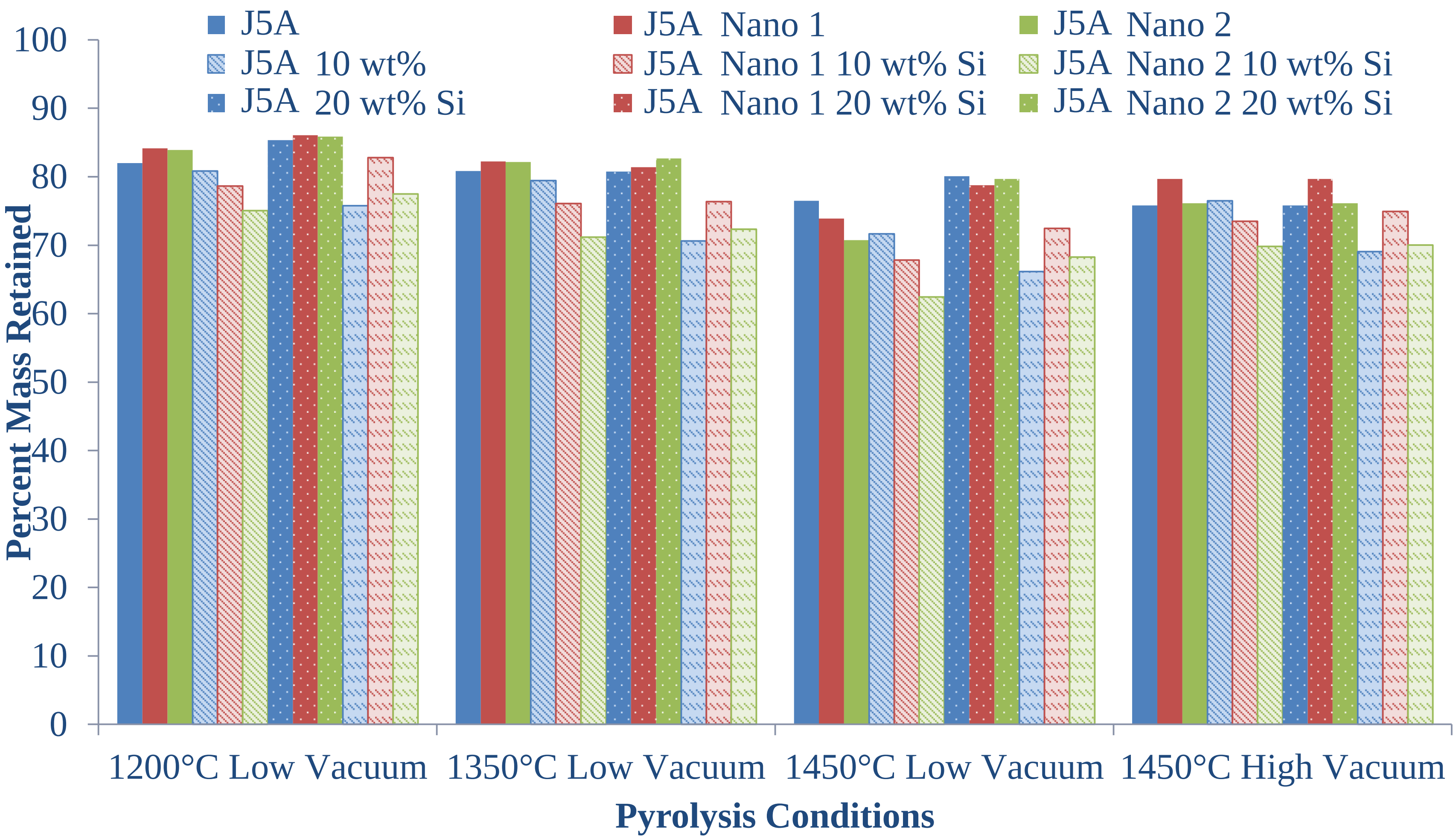
Binder burnout
1000°C in Argon

Pyrolysis
1200°C, 1350°C, or 1450°C





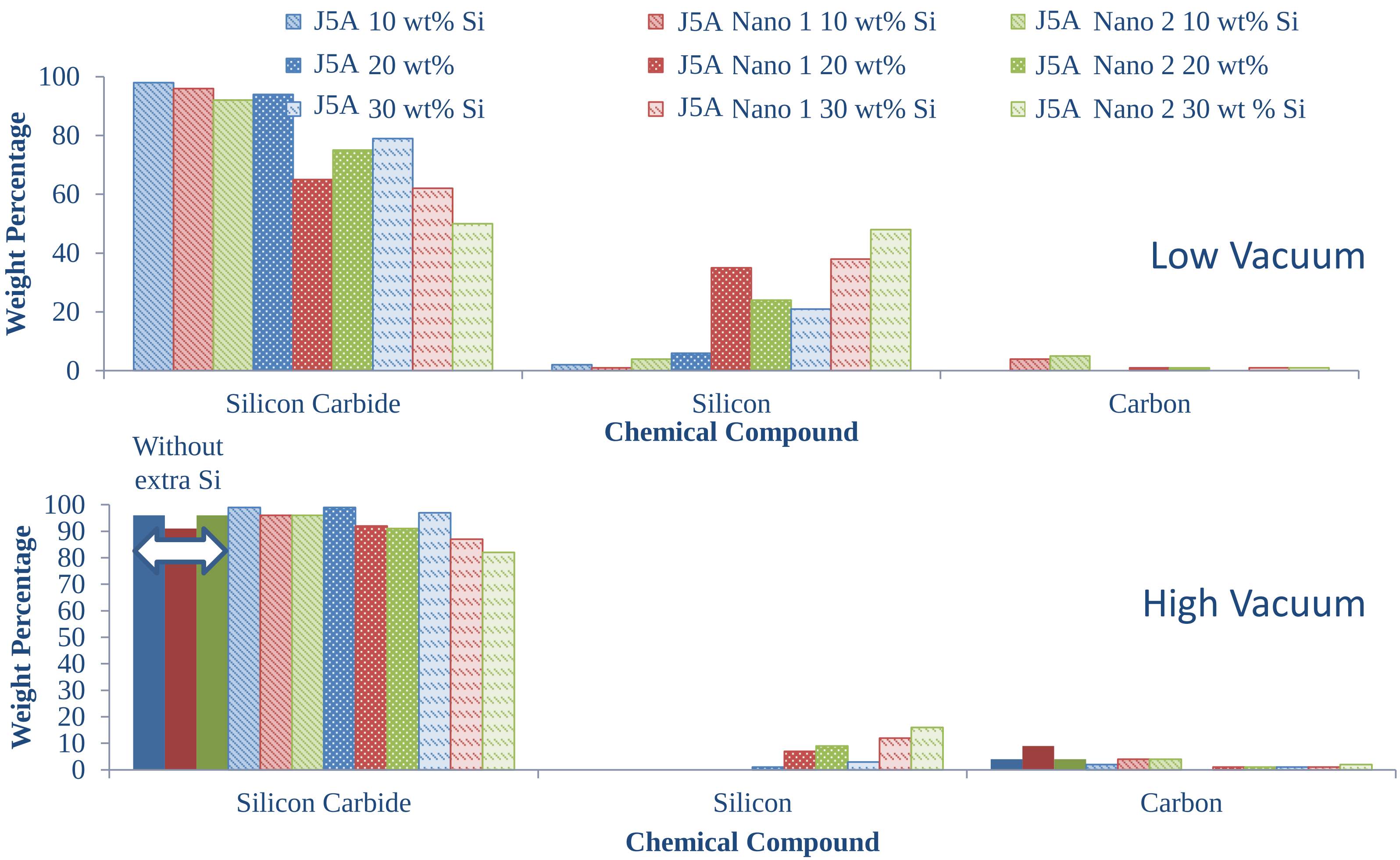
Weight Retention of Pre-Ceramic Pastes



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

Chemical Composition of Heat-treated Pastes at 1450°C (from X-Ray Diffraction Analysis)

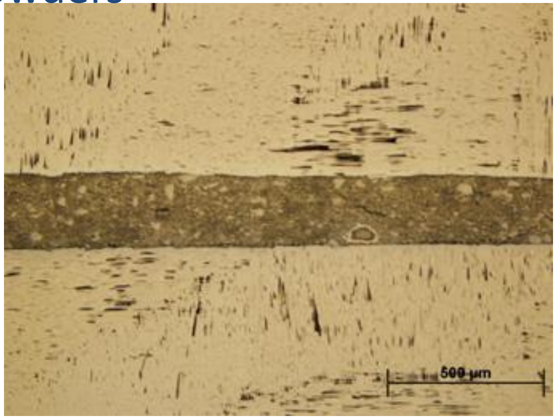


- **All compositions after pyrolysis show a high yield of SiC.**
- **Vaporization of Si occurs in vacuum due to its high vapor pressure.**

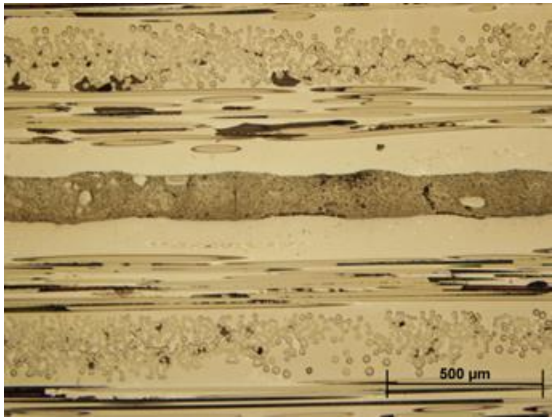
Single-Step Elevated Temperature Joining: Higher Temperature Capable C, Si, and SiC-Based Pastes

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.

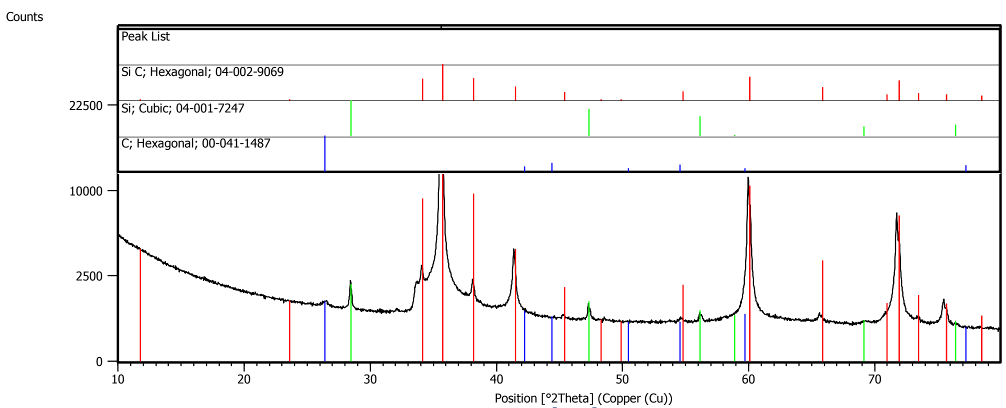


J5A+N2+Si Joining of SA-THX (⊥orientation)



J5A+N1+Si Joining of SiC/SiC

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



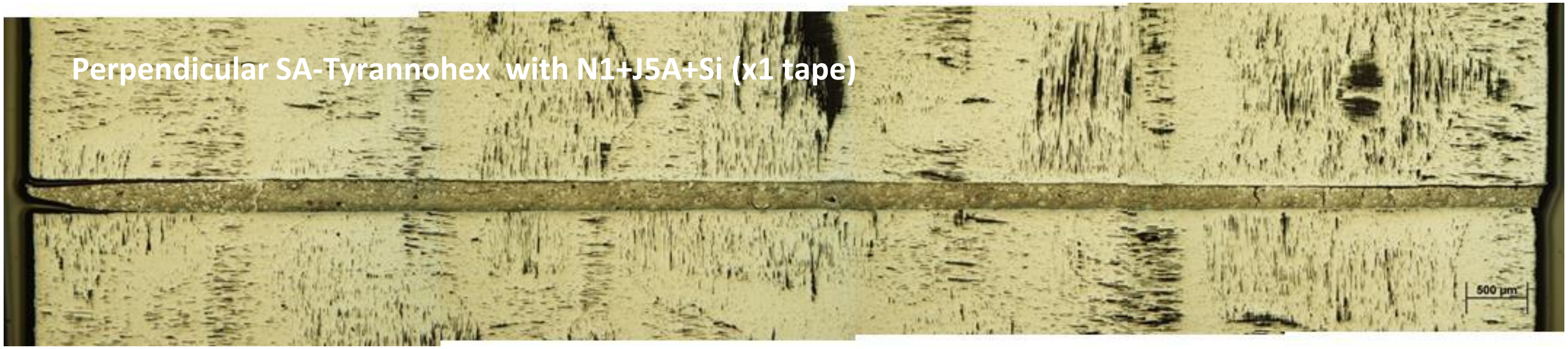
SemiQuant (%)

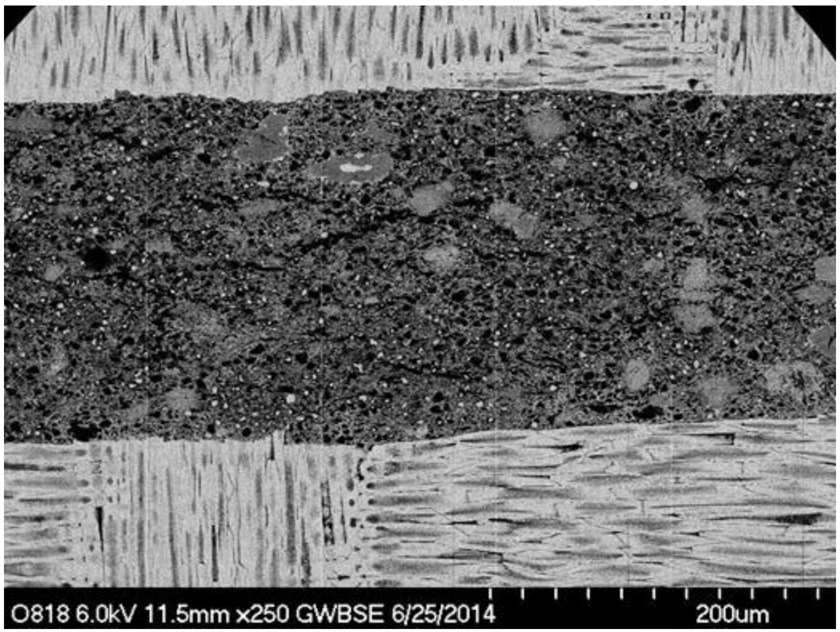
Composition	SiC	Si	C
J5A+Si	**99**	**1**	**0 -nearly complete SiC conversion**
J5A+N1+Si	91	9	1
J5A+N2+Si	92	7	1

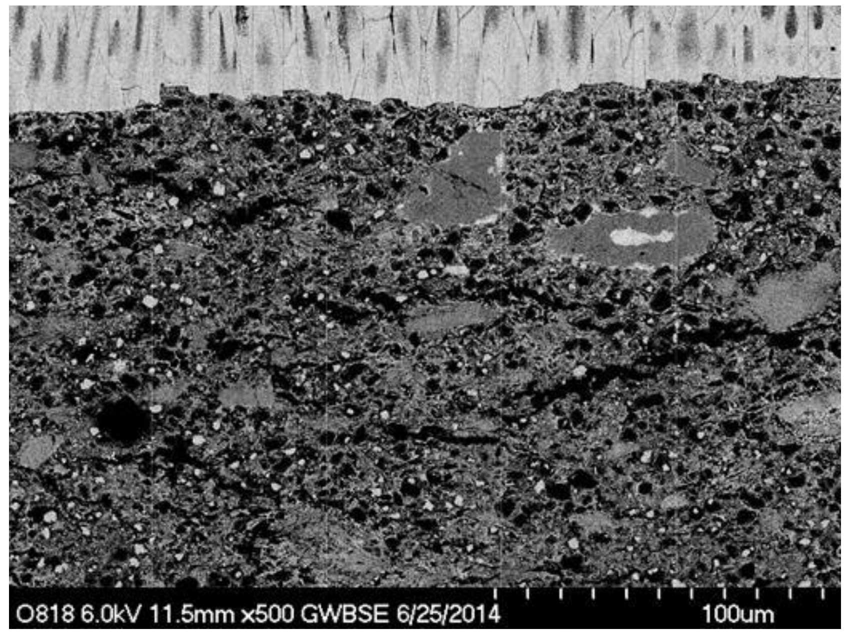
High conversion to SiC suggests the compositions will provide one-step SiC formation.

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







Comparison of CMC Joining Approaches

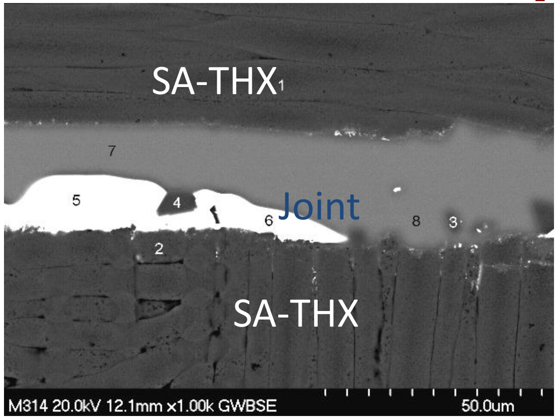
Characteristics	Joining Approach				
	Brazing (Cu-Si-Ti based)	ARCJoinT	Diffusion Bonding (Ti)	REABond (Si-Hf)	SET Joining (C,Si,SiC based)
Temperature limit	<1472°F (800°C)	<2400°F (1316°C)	~2373°F (1300°C)	<2400°F (1316°C)	>2400°F (1316°C)
Little or no processing pressure	√	√	x	√	√
Curved shape joining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

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

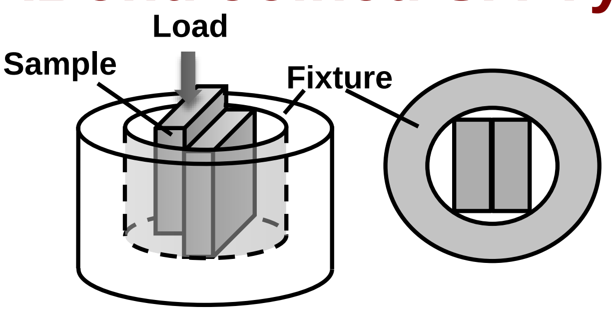
→

Second phase of development: advanced processing, analysis, and thermo-mechanical testing.

Mechanical Testing: Single Lap Offset - REABond Joined SA-Tyrannohex

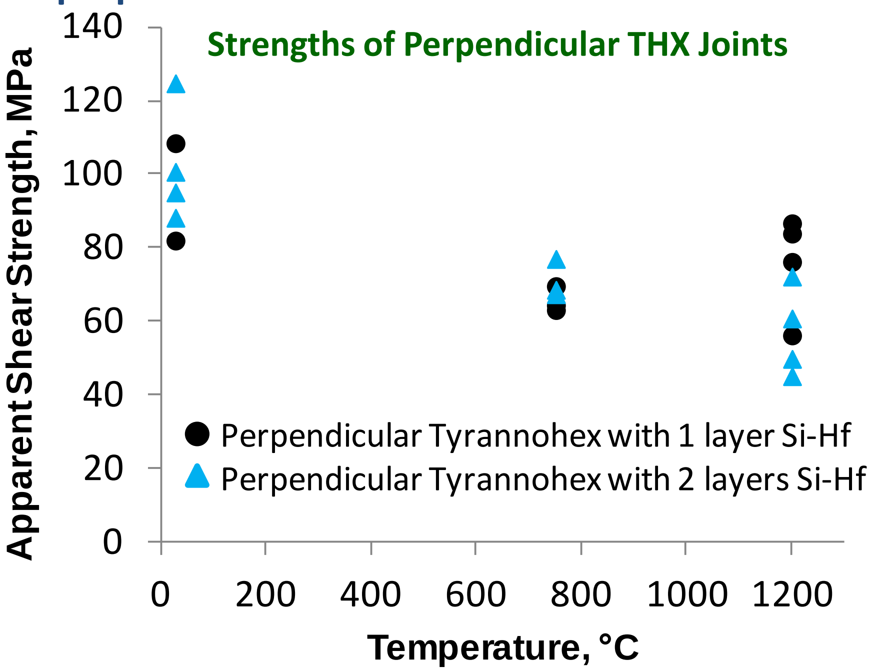


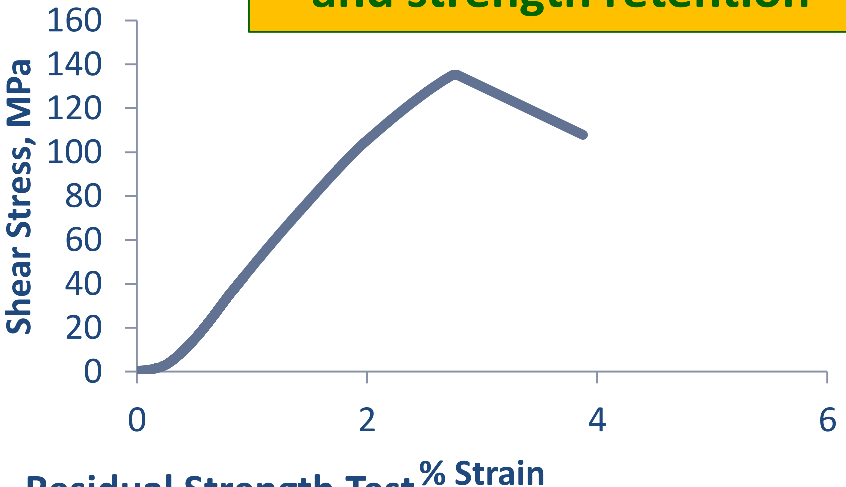
As-processed joint for SA-THX in **perpendicular** orientation



Test configuration for single lap offset shear test

Excellent joint stability and strength retention



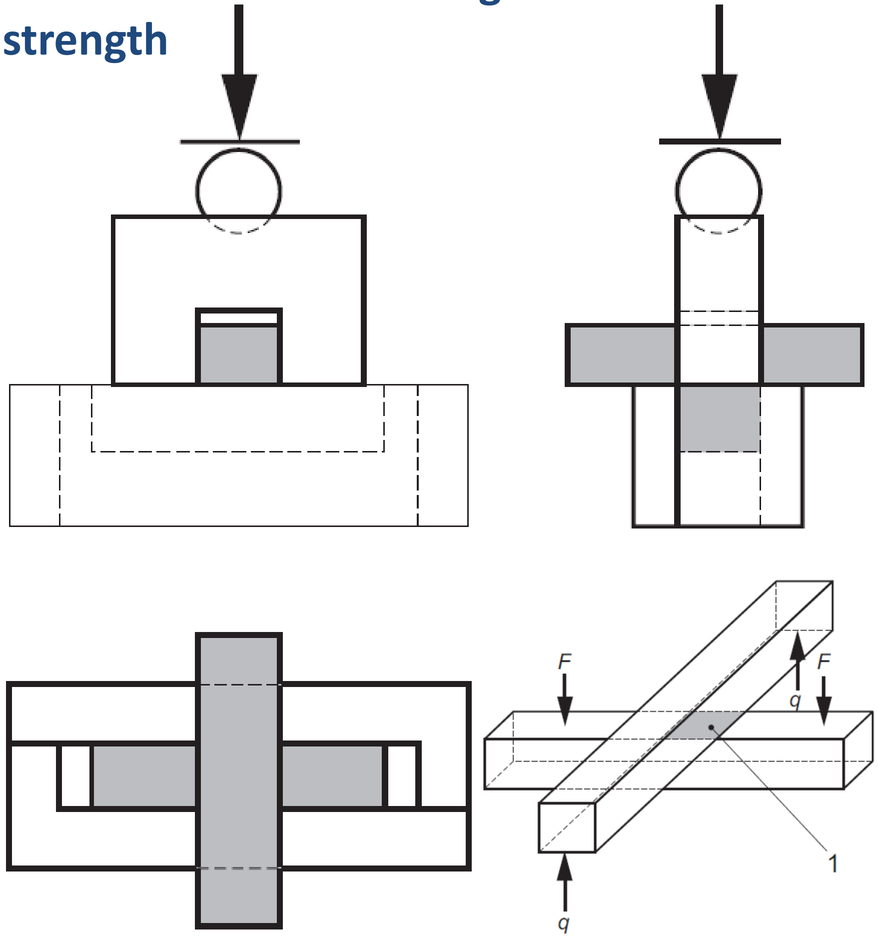


Residual Strength Test
- 350 hr run out at 1200°C and 25 MPa
- tested at 1200°C
- highest strength seen in a SLO test, 135 MPa

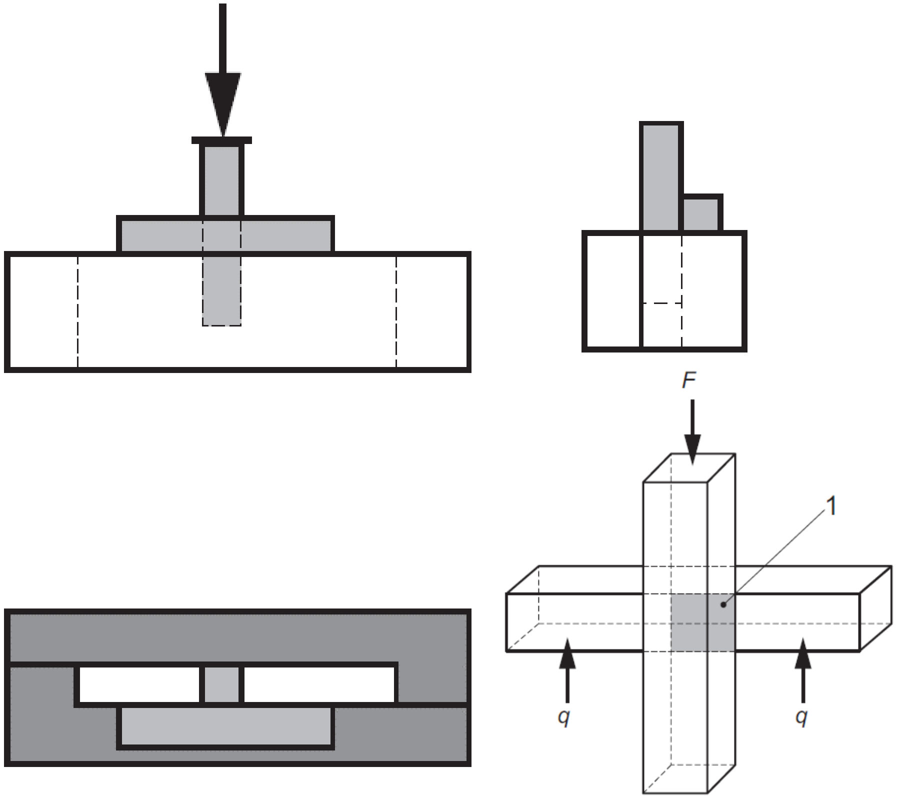
Single lap offset shear test to be used for in-house screening.

Mechanical Testing: In-House Capability for Testing According to ISO 13124

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



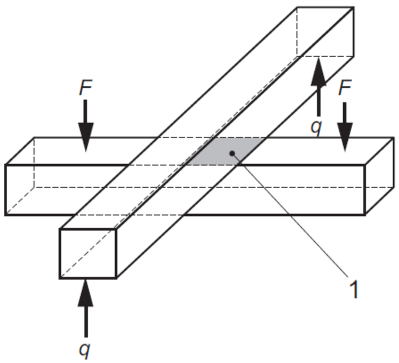
Schematic diagram of cross bonded sample and fixture for **measuring shear bond strength**

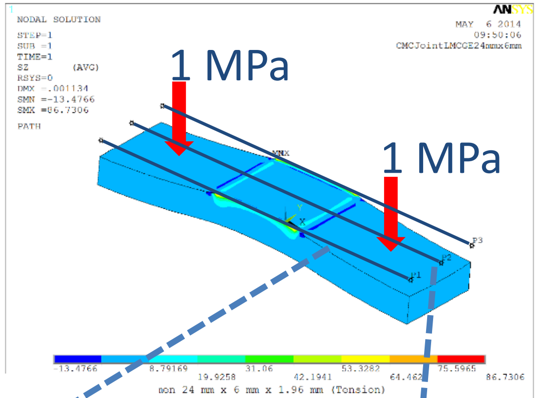


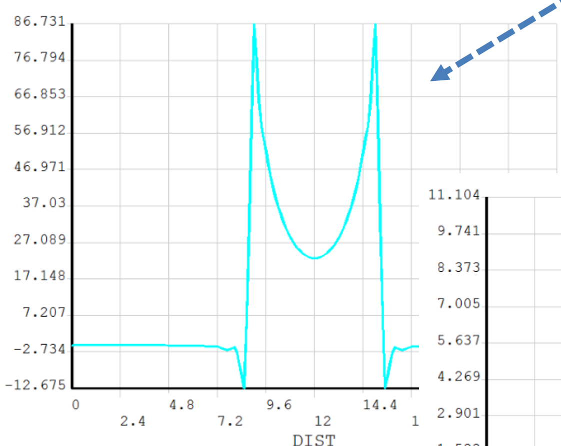
INTERNATIONAL STANDARD ISO 13124 First edition 2011-05-15: Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for interfacial bond strength of ceramic materials

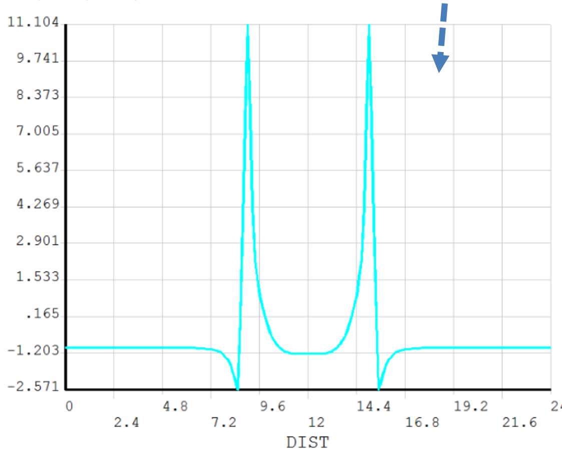
Results and Analysis for Testing to ISO 13124 (with REABond Joining)

Testing in Tension



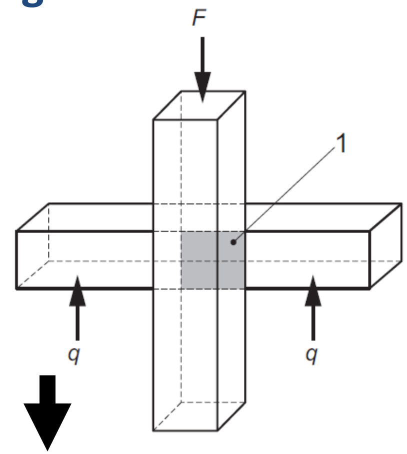


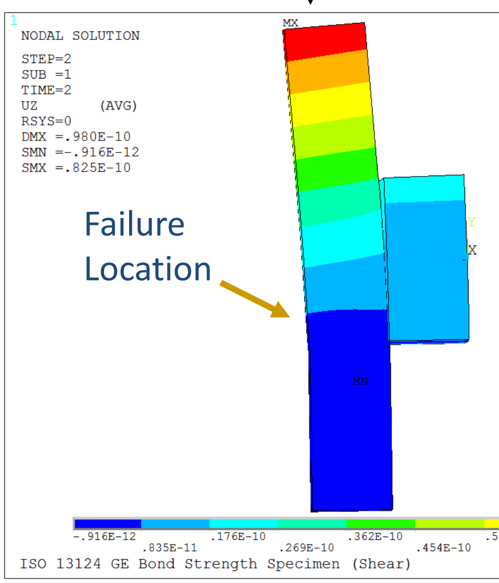


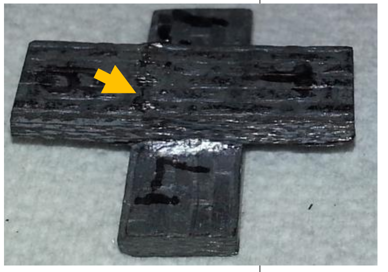


Stress (MPA) versus location

Testing in Shear



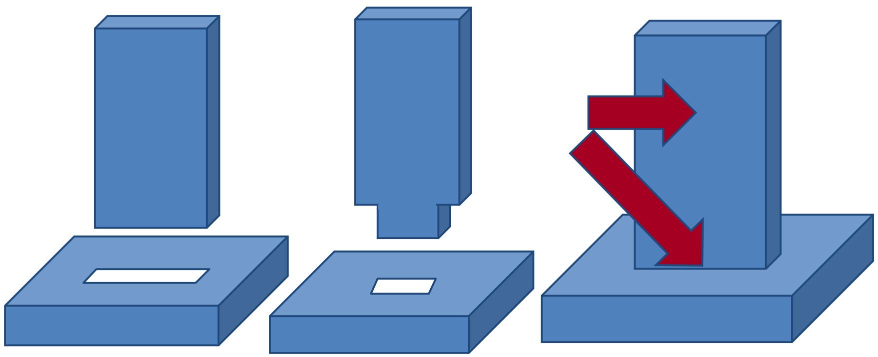


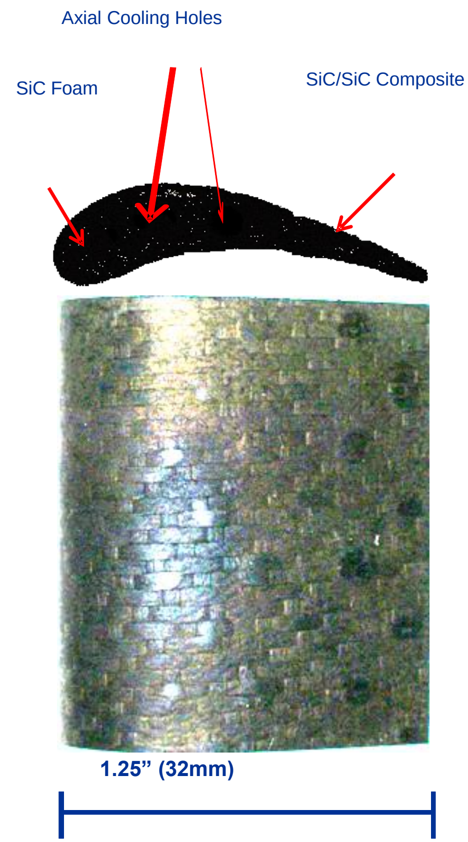


Results show the need for additional analysis and improved test methods.

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.





NASA environmental barrier coating applied

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.

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 is 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.