

## **DIFFUSION BONDING OF SILICON CARBIDE CERAMICS USING TITANIUM INTERLAYERS**

Michael C. Halbig, Army Research Laboratory, Vehicle Technology Directorate, Cleveland, OH; Mrityunjay Singh and Tarah P. Shpargel, QSS Group, Inc., Cleveland, OH; James D. Kiser, NASA Glenn Research Center, Cleveland, OH

Robust joining approaches for silicon carbide ceramics are critically needed to fabricate leak free joints with high temperature mechanical capability. In this study, titanium foils and physical vapor deposited (PVD) titanium coatings were used to form diffusion bonds between SiC ceramics using hot pressing. Silicon carbide substrate materials used for bonding include sintered SiC and two types of CVD SiC. Microscopy results show the formation of well adhered diffusion bonds. The bond strengths as determined from pull tests are on the order of several ksi, which is much higher than required for a proposed application. Microprobe results show the distribution of silicon, carbon, titanium, and other minor elements across the diffusion bond. Compositions of several phases formed in the joint region were identified. Potential issues of material compatibility and optimal bond formation will also be discussed.

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**VEHICLE TECHNOLOGY DIRECTORATE**



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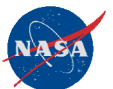




# Acknowledgements



- This effort was supported by the NASA Glenn Research Center under the Intelligent Propulsion Systems Foundation Technology Sub-Project / Ultra-Efficient Engine Technology Project / Vehicle Systems Program.
- The authors would like to thank the following:
  - Dr. Dan L. Bulzan and Robert R. Tacina at NASA GRC for their support and for providing the injector design and requirements.
  - James Smith of QSS Group, Inc. at NASA GRC for conducting electron microprobe work.
  - Dr. Robert Okojie of NASA GRC for providing PVD Ti Coated CVD SiC.





# Outline



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**1. Application** – Micro-Electro-Mechanical Systems Lean Direct Injector (MEMS LDI) for Advanced Aircraft Gas Turbines

**2. Joining Approach** – Diffusion Bonding of Silicon Carbide Ceramics With a Titanium Interlayer

A. Benefits of Approach

B. Processing Matrix for Joining Technology Development

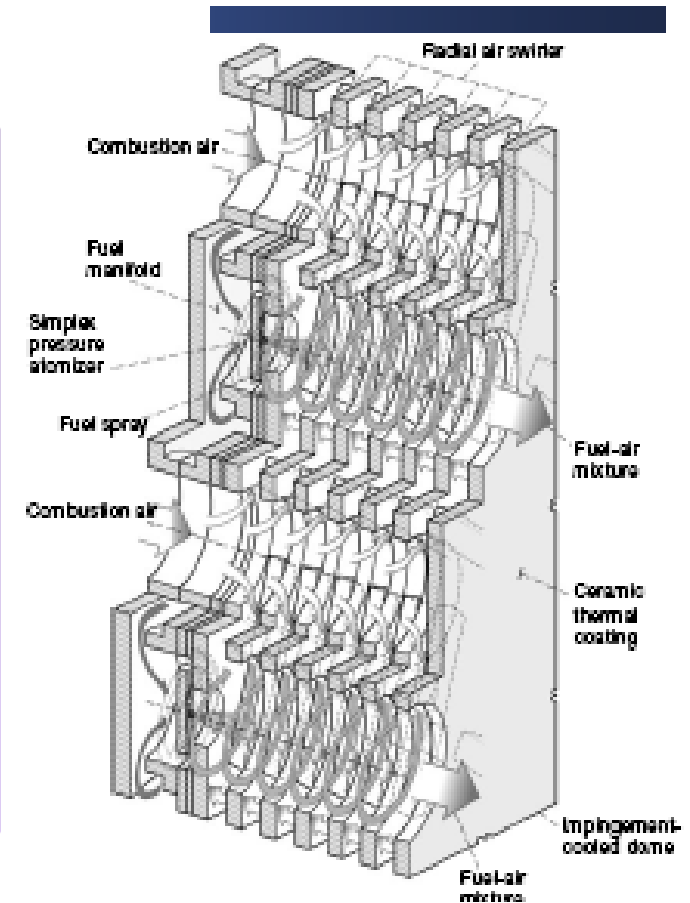
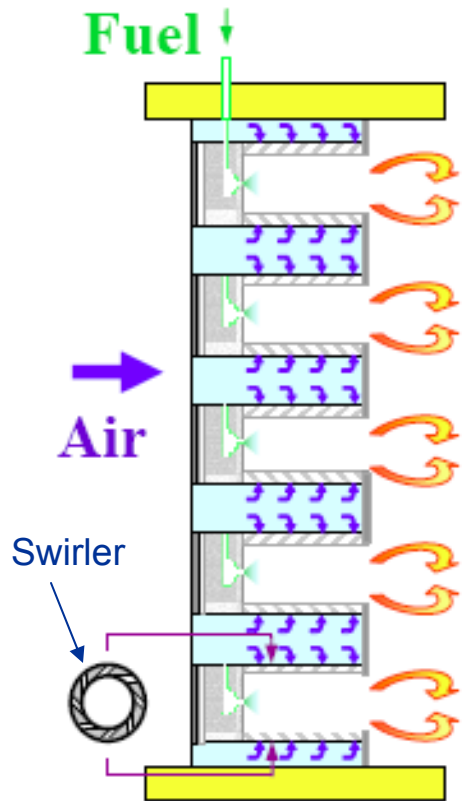
C. Results - Microscopy

**3. Summary and Conclusions**





# Multi-Point Lean Direct Injector



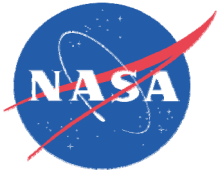
(Left) Multi-Point Lean Direct Injector accelerates fuel-air mixing and has small recirculation zones with short residence time that reduces NO<sub>x</sub> emission.

(Center) 3-inch square metal MP-LDI with 45 injectors.

(Right) Detail of fuel and airflow.

From Robert Tacina, et al., "A Low Lean Direct Injection, Multi-Point Integrated Module Combustor Concept for Advanced Aircraft Gas Turbines," NASA/TM-2002-211347, April 2002.

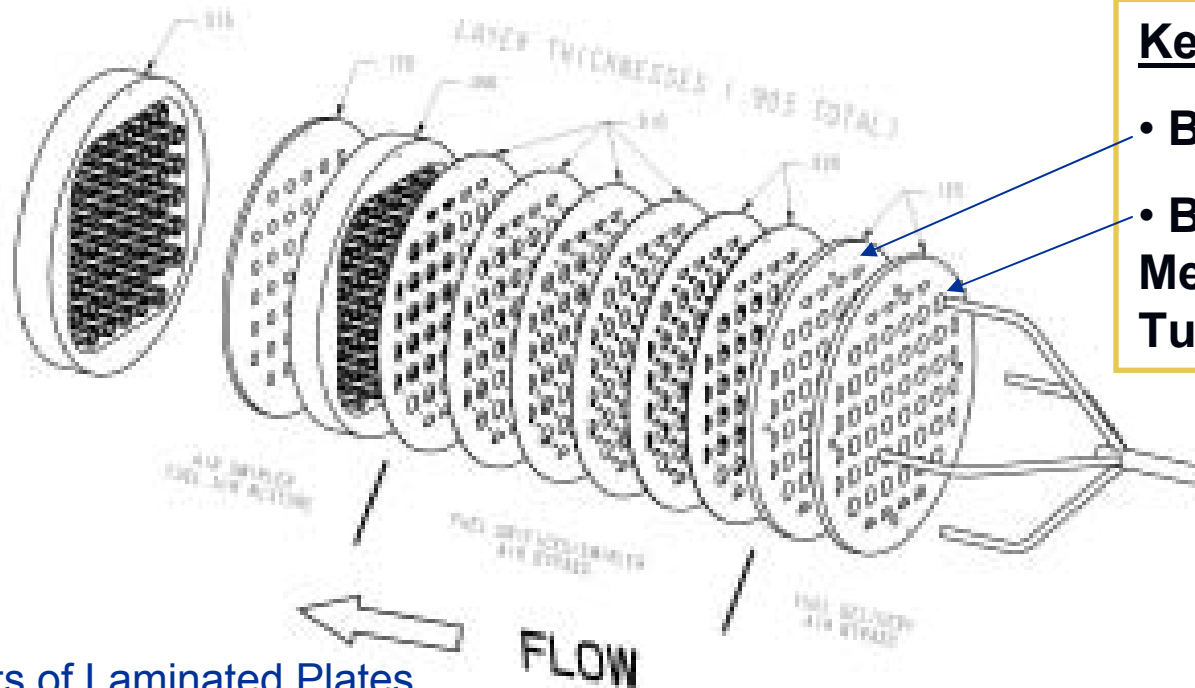




# Lean Direct Injector Fabricated by Laminates



SiC laminates can be used to create intricate and interlaced passages to speed up fuel-air mixing to allow lean-burning, ultra-low emissions.

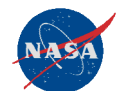


## Key Technologies:

- 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





# Joining SiC to SiC



## **Disadvantages of Previous Method of Joining with a Silicate Glass Layer**

- Difficult to achieve a uniform layer
- Relatively low strength
- Silicate glass flows and fills in holes and edges where it is not desired
- Due to these disadvantages, previous glass joints were not leak-free

## **Advantages of Ti Layer Joining**

- Uniform Ti layers can be applied
- Ti can be applied by different methods (foil, PVD, and other coating approaches)
- High strength and leak free bonds
- Good high temperature stability

## **The objective is to develop joining technology that has the following capabilities:**

- Joining of relatively large geometries (i.e. 4" diameter disks)
- Leak-free at an internal pressure of 200 psi (1.38 MPa)
- Stability and strength retention at 800°F (427°C)





# SiC-Ti-SiC Diffusion Bond Processing Matrix

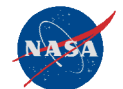


## SiC and Ti Material Combinations:

1. 1.75" diameter  $\alpha$ -SiC (CRYSTAR from Saint-Gobain) disks joined with a 1.5 mil (38 micron) foil
2. 1.75" diameter CVD SiC (TREX Enterprises) disks joined with a 1.5 mil (38 micron) foil
3. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with ~10 micron PVD Ti coating on one of the surfaces
4. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with a 1.5 mil (38 micron) foil
5. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with ~10 micron PVD Ti coating on both of the surfaces

Condition	Temp. (°C)	Pressure* (MPa)	Time (hr)	Atmosphere	Cooling Rate (°C/min)	Status
<b>A (materials 1, 2, and 3)</b>	1250	24, 24, 31	2	vacuum	5	Microscopy & Microprobe
<b>B (materials 1 and 3)</b>	1300	24, 31	2	vacuum	2	Microscopy
<b>C (materials 1 and 3)</b>	1250	50	2	vacuum	2	Microscopy
<b>D (materials 1, 4 and 5)</b>	1250	24, 31	2	vacuum	2	Microscopy

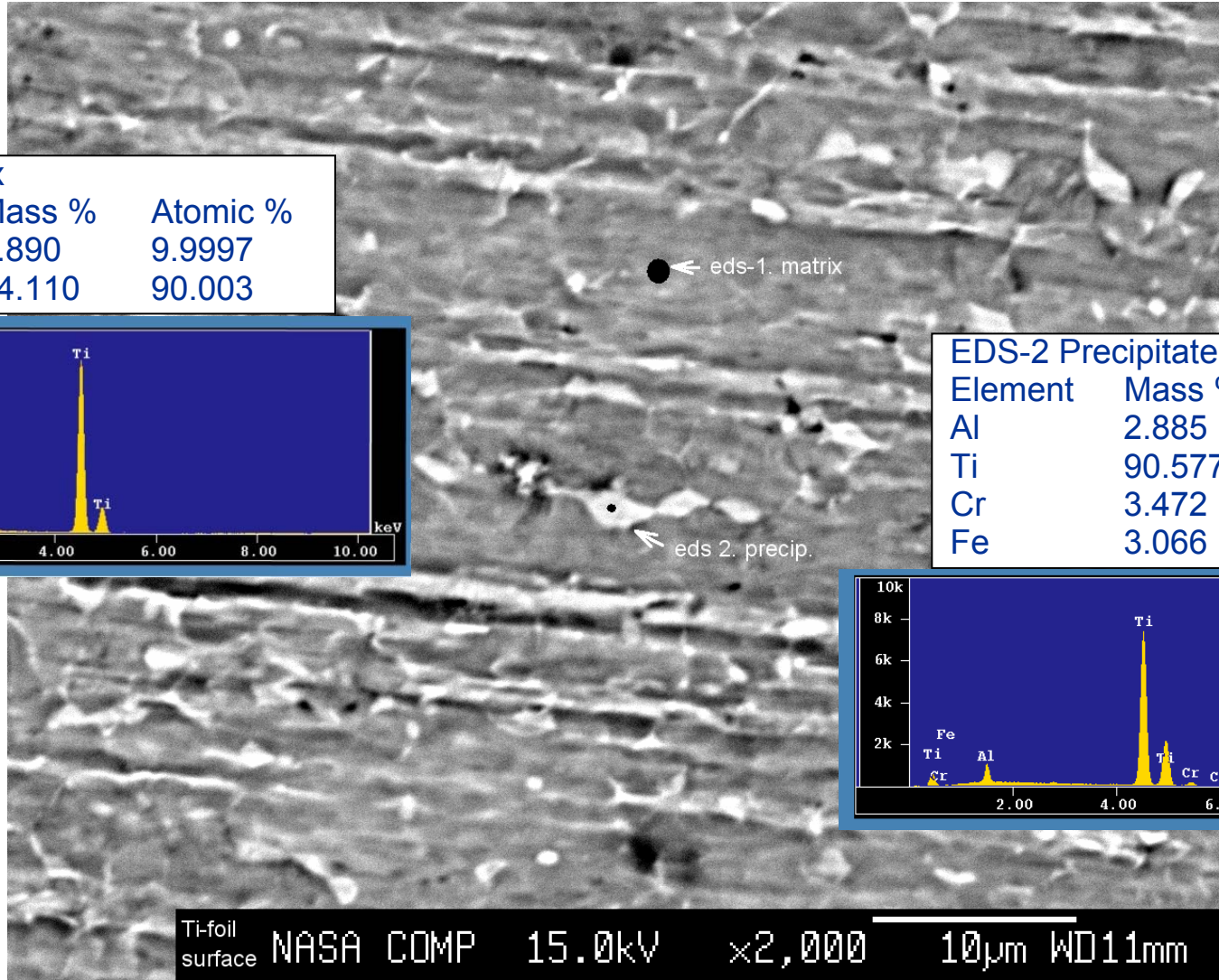
\*at the minimum clamping pressure for the hot press (except for processing at 50 MPa)





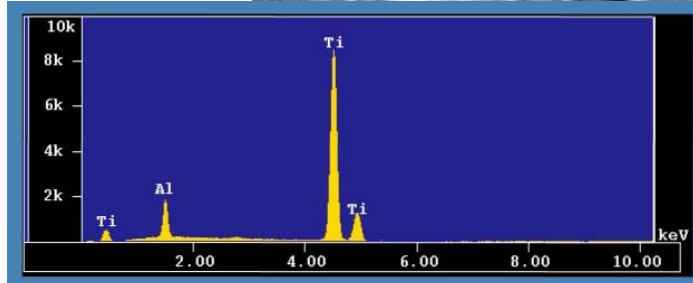


# Electron Microprobe Analysis of the "Titanium" Foil



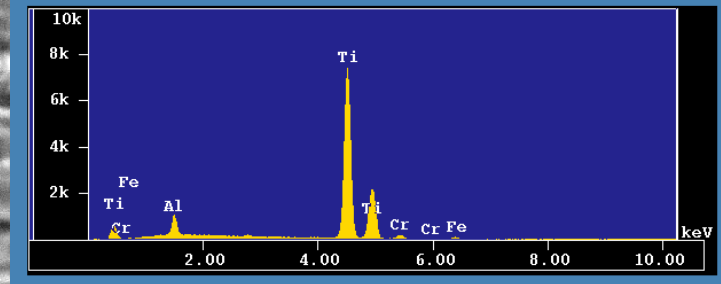
EDS-1 Matrix

Element	Mass %	Atomic %
Al	5.890	9.9997
Ti	94.110	90.003

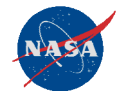


EDS-2 Precipitate

Element	Mass %	Atomic %
Al	2.885	5.0450
Ti	90.577	89.2144
Cr	3.472	3.1504
Fe	3.066	2.5901



Ti-foil surface NASA COMP 15.0kV x2,000 10µm WD11mm



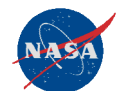


# Diffusion Bonds Analysis: Microscopy and Microprobe



Effect of Material Combinations and Processing Parameters (to be shown on the following slides):

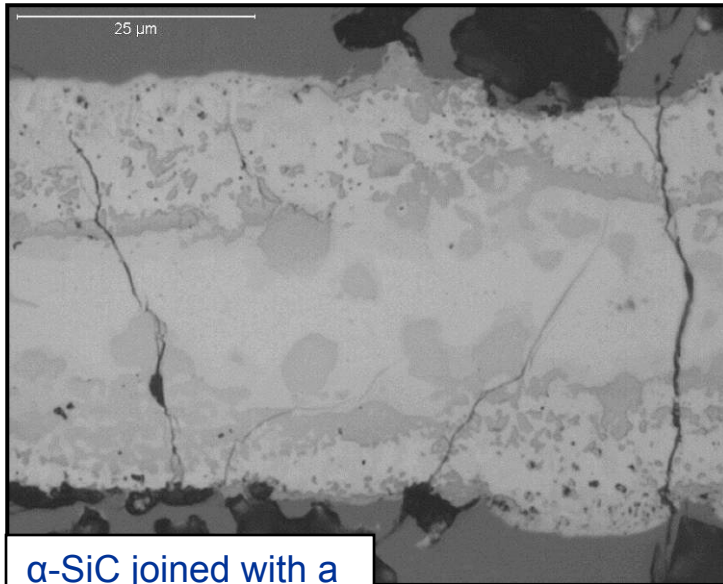
1. Material Combinations of Ti and Substrate (1250°C and minimum clamping pressure)
  - $\alpha$ -SiC (CRYSTAR from Saint-Gobain) discs joined with a 1.5 mil (38 micron) foil
  - CVD  $\beta$ -SiC (TREX) joined with a 1.5 mil (38 micron) foil
  - CVD  $\beta$ -SiC (Rohm & Hass) joined with ~10 micron PVD Ti coating on one of the surfaces
2. Effect of Cooling Rate (1250°C and minimum clamping pressure)
  - 5° C/min and 2° C/min
3. Effect of Higher Processing Temperature
  - 1300°C
4. Effect of a Higher Hot Press Load and Resulting Stress
  - 50 MPa
5. Effect of Ti Type and Thickness
  - 38 micron Ti foil, and ~10 and ~20 micron PVD Ti interlayers





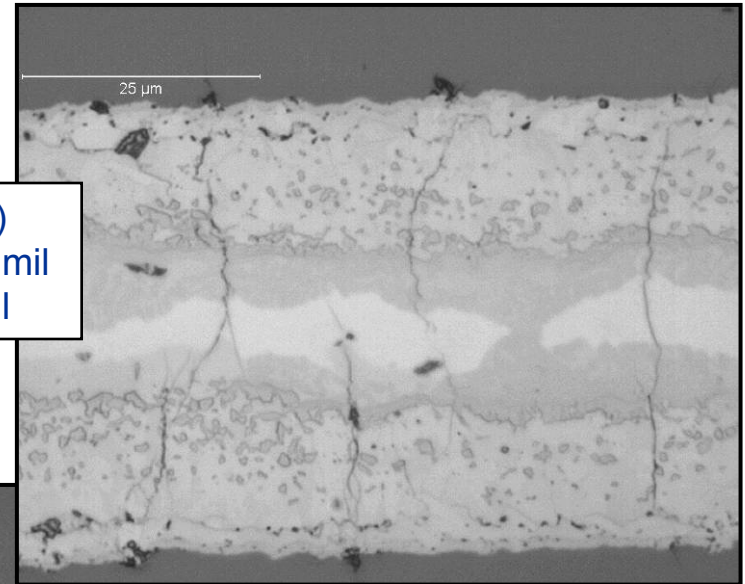
# Effects-Slide 1 - Material Combinations of Ti and Substrate

Conditions: 1250 °C, Minimum Clamping Pressure,  
2 hr hold, Vacuum, 5 °C/min Cooling Rate

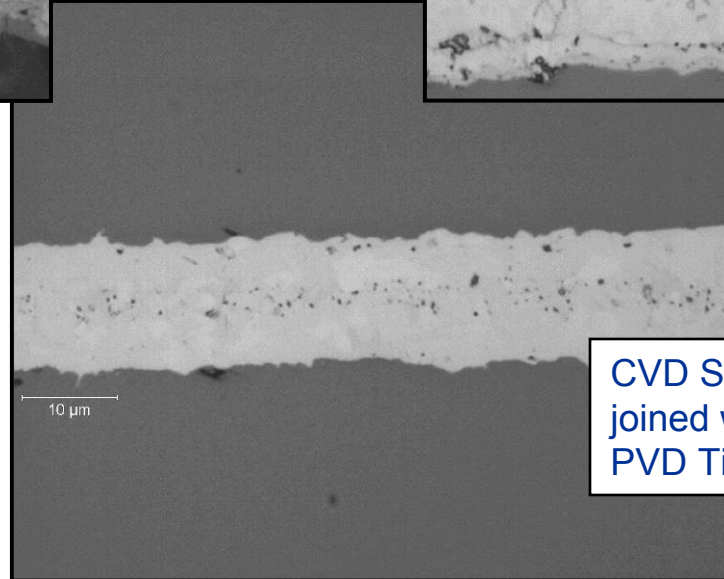


$\alpha$ -SiC joined with a  
1.5 mil (38 micron)  
Ti foil

CVD SiC (TREX)  
joined with a 1.5 mil  
(38 micron) Ti foil

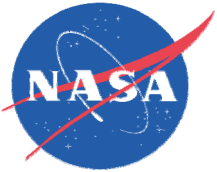


Microcracks are present in  
bonds formed with the Ti foil.  
**Cracks are submicron.**  
No microcracks in bonds formed  
with the PVD Ti interlayer.



CVD SiC (Rohm & Hass)  
joined with ~ 10 micron  
PVD Ti Interlayer

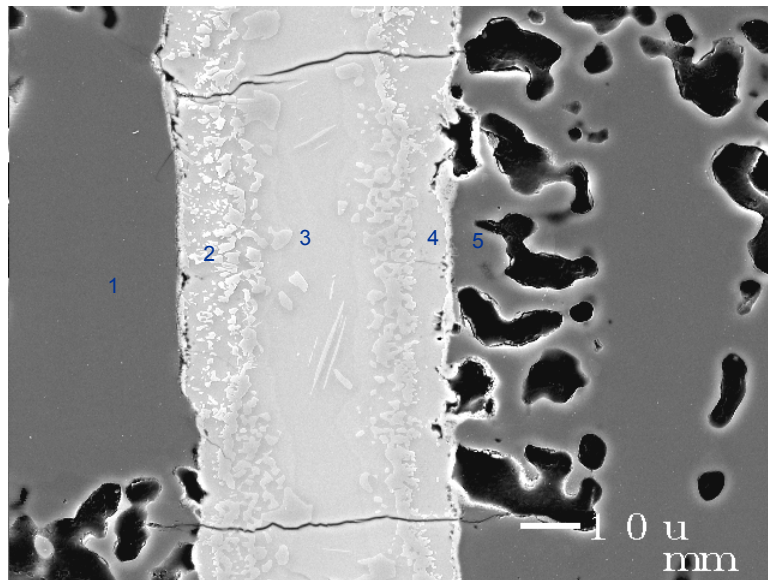




## Effects-Slide 2 – Effect of Cooling Rate: 2 and 5 °C/min Conditions: 1250 °C, Minimum Clamping Pressure, 2 hr hold, Vacuum

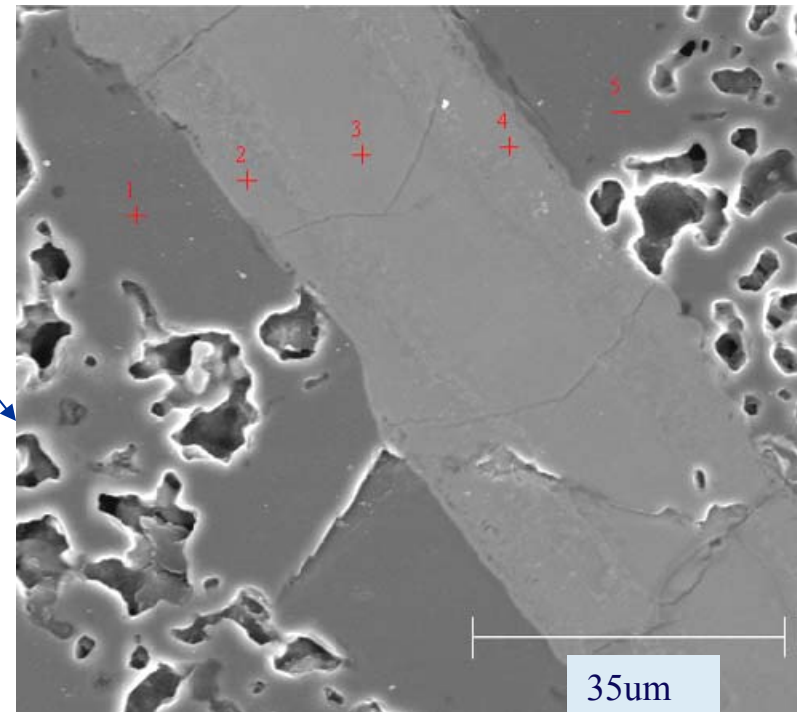


$\alpha$ -SiC joined with a 1.5 mil (38 micron) Ti foil



2 °C/min

5 °C/min



A slower cooling rate of 5 °C/min did not alleviate the microcracking.

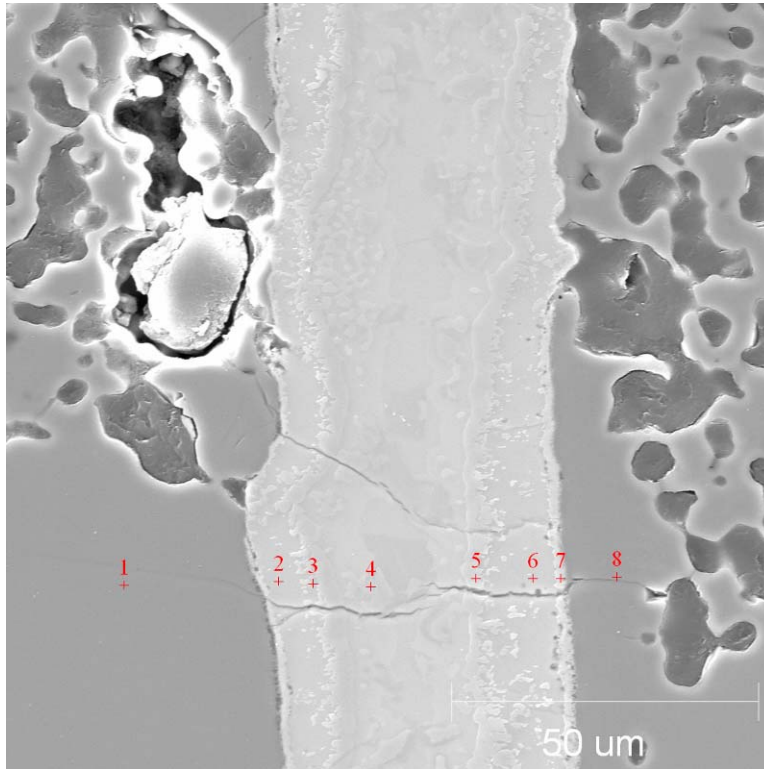


# Effects-Slide 3 – Effect of Higher Processing Temperature

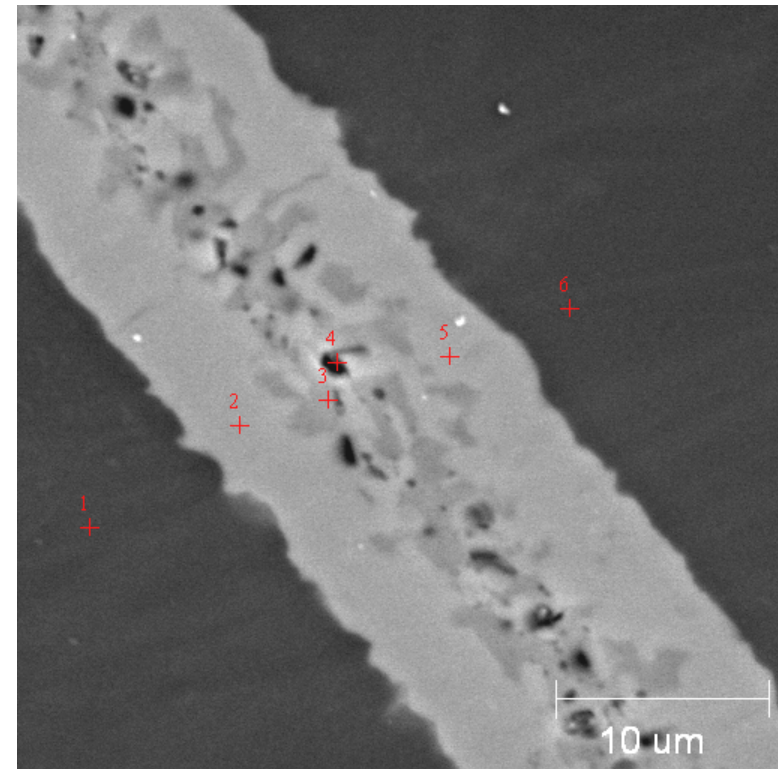
Conditions: 1300 °C, Minimum Clamping Pressure, 2 hr hold, Vacuum, Cooling Rate 2 °C/min



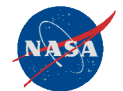
$\alpha$ -SiC joined with a 1.5 mil (38 micron) Ti foil

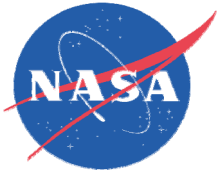


CVD SiC (Rohm & Hass) joined with a 10 micron PVD Ti Interlayer



Minimal difference from processing at the higher temperature of 1300°C.



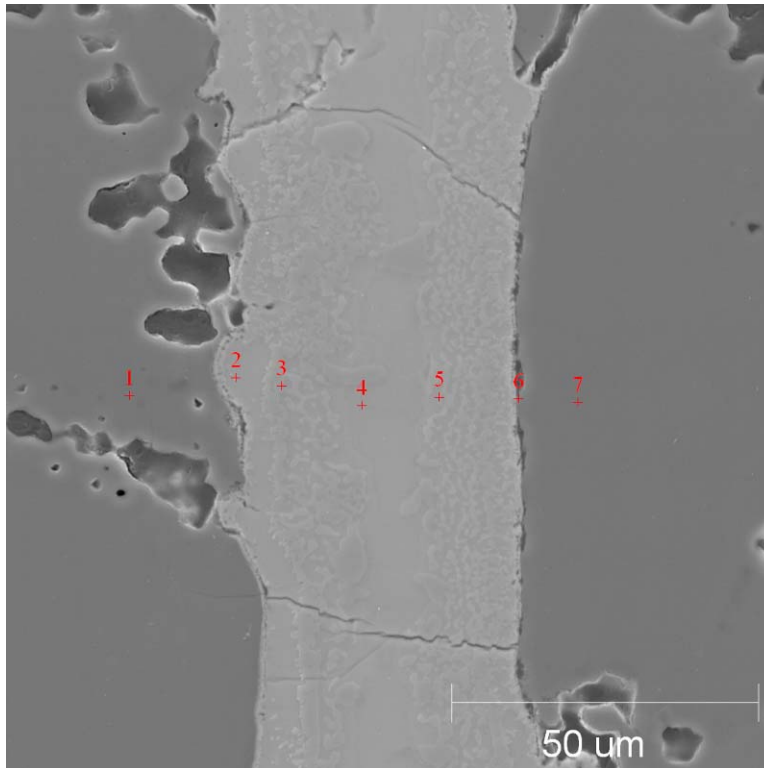


## Effects-Slide 4 – Effect of Higher Processing Stress

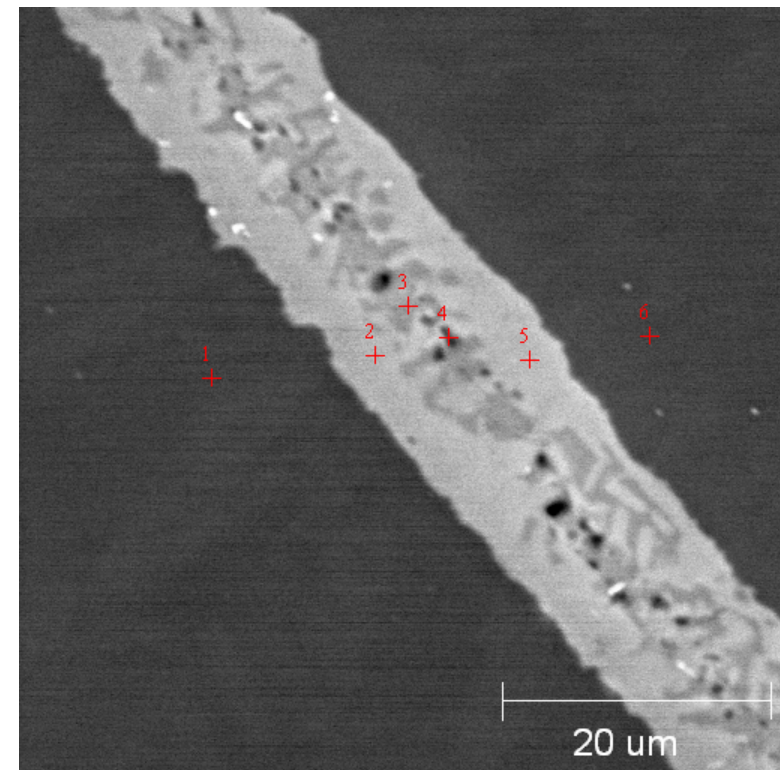
Conditions: 1250 °C, 50 MPa, 2 hr hold, Vacuum,  
Cooling Rate 2 °C/min



$\alpha$ -SiC joined with a 1.5 mil (38 micron) Ti foil



CVD SiC (Rohm & Hass) joined with ~ 10 micron PVD Ti Interlayer



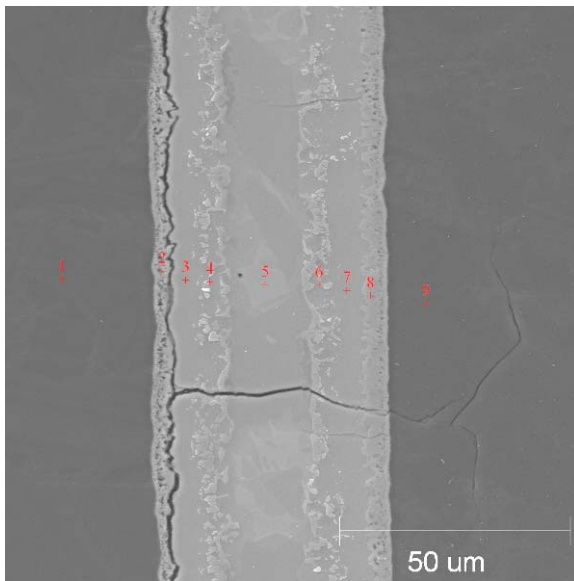
Minimal difference from processing at the higher stress of 50 MPa.



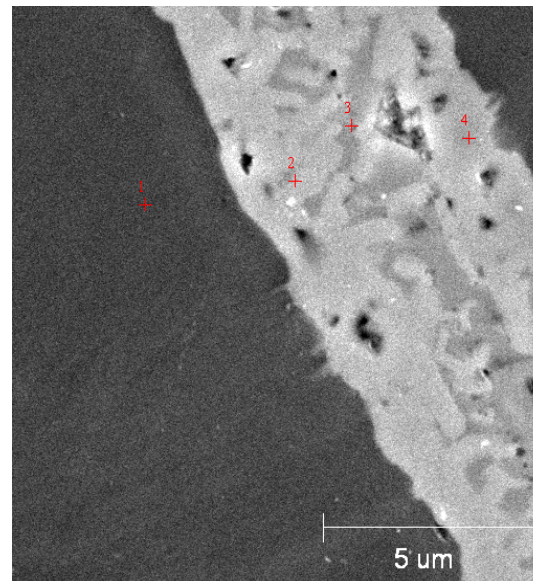
## Effects-Slide 5 – Effect of Ti Type and Thickness Conditions: 1250 °C, 31 MPa, 2 hr hold, Vacuum, Cooling Rate 2 °C/min



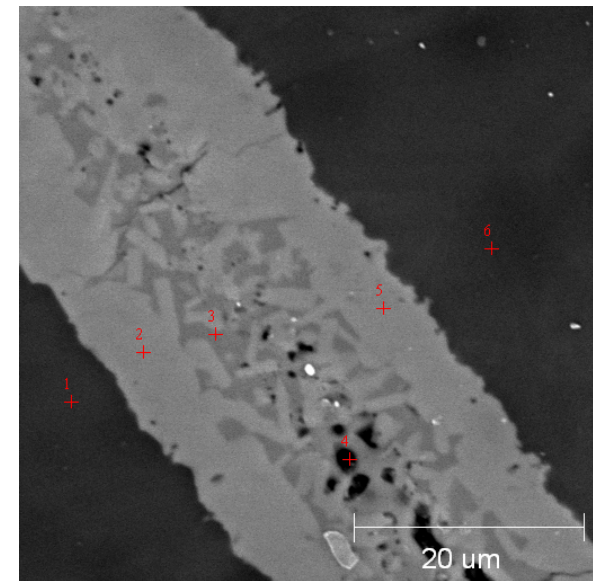
CVD SiC (Rohm & Hass) joined with a 1.5 mil (38 micron) Ti foil



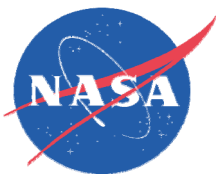
CVD SiC (R & H) joined with ~10 micron PVD Ti Interlayer



CVD SiC (R & H) joined with ~20 micron PVD Ti Interlayer



Debonding was observed in the material combination of Ti foil and CVD SiC.  
In all cases that the Ti foil was used as the interlayer, microcracking was observed.  
Minimal microcracking was observed when a PVD Ti interlayer was used. Well reacted diffusion bond formed when the thickness of the PVD Ti interlayer was doubled.



# Microprobe of $\alpha$ -SiC Reaction Bonded Using Ti Foil

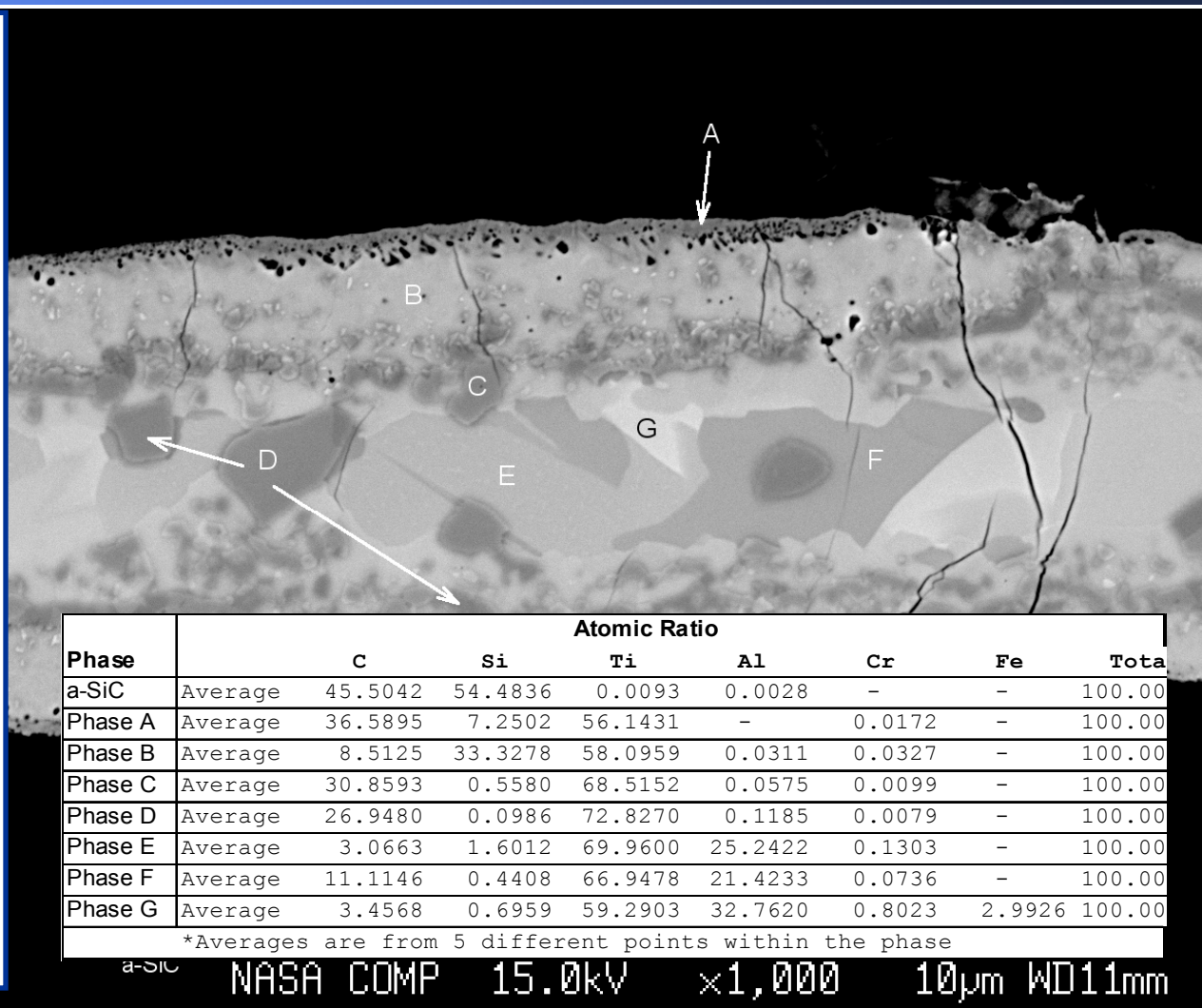
Conditions: 1250 °C, 24 MPa, 2 hr, vacuum, 5 °C/min



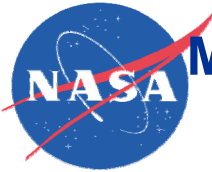
Microcracking may be due to the formation of two detrimental phases:

- Phase B  $Ti_5Si_3C_x - Ti_5Si_3$  if highly anisotropic in its thermal expansion where  $CTE(c)/CTE(a) = 2.72$  (Schneibel et al).
- Phase E –  $Ti_3Al$  has low ductility at low temperatures. Al can be in the range of 23-35 atm % (Djanarthany et al).

**Both phases can contribute to thermal stresses and microcracking during cool down.**







# Microprobe of TREX CVD SiC Reaction Bonded Using Ti Foil

Conditions: 1250 °C, 24 MPa, 2 hr, vacuum, 5 °C/min

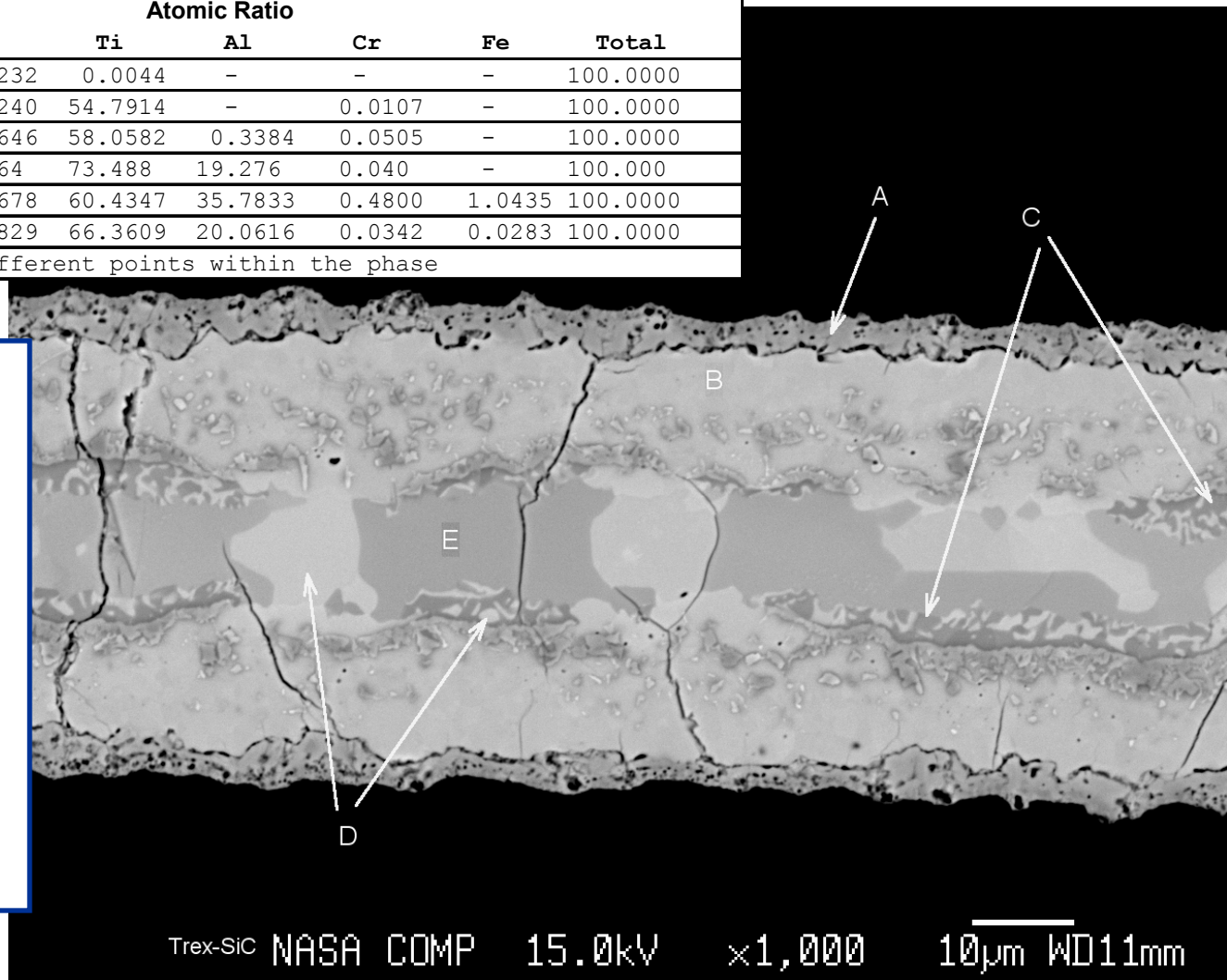


Phase	Atomic Ratio							
	C	Si	Ti	Al	Cr	Fe	Total	
CVD SiC	Average	45.0724	54.9232	0.0044	-	-	-	100.0000
Phase A	Average	27.6739	17.5240	54.7914	-	0.0107	-	100.0000
Phase B	Average	7.3882	34.1646	58.0582	0.3384	0.0505	-	100.0000
Phase C	Average	6.432	0.764	73.488	19.276	0.040	-	100.000
Phase D	Average	1.1908	1.0678	60.4347	35.7833	0.4800	1.0435	100.0000
Phase E	Average	12.9321	0.5829	66.3609	20.0616	0.0342	0.0283	100.0000

\*Averages are from 5 different points within the phase

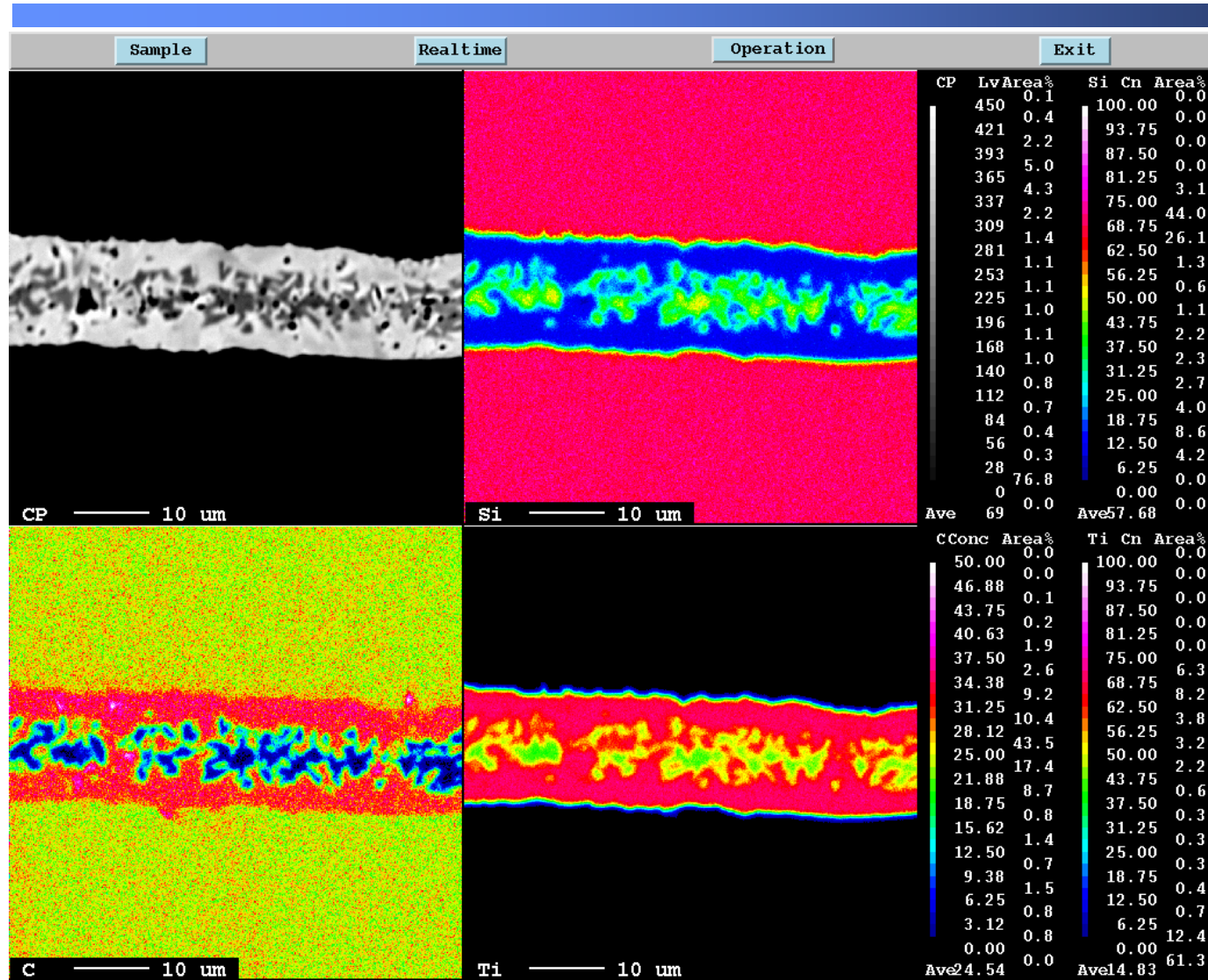
The same detrimental phases of  $Ti_5Si_3$  (B) and  $Ti_3Al$  (D) are formed which can contribute to microcracking during cool down.

Note how cracks appear to originate in Phase B or in the core, however they are absent from outer phase (Phase A)

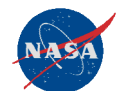




# Microprobe of CVD SiC (R & H) Bonded Using PVD Ti Conditions: 1250 °C, 31 MPa, 2 hr, vacuum, 5 °C/min

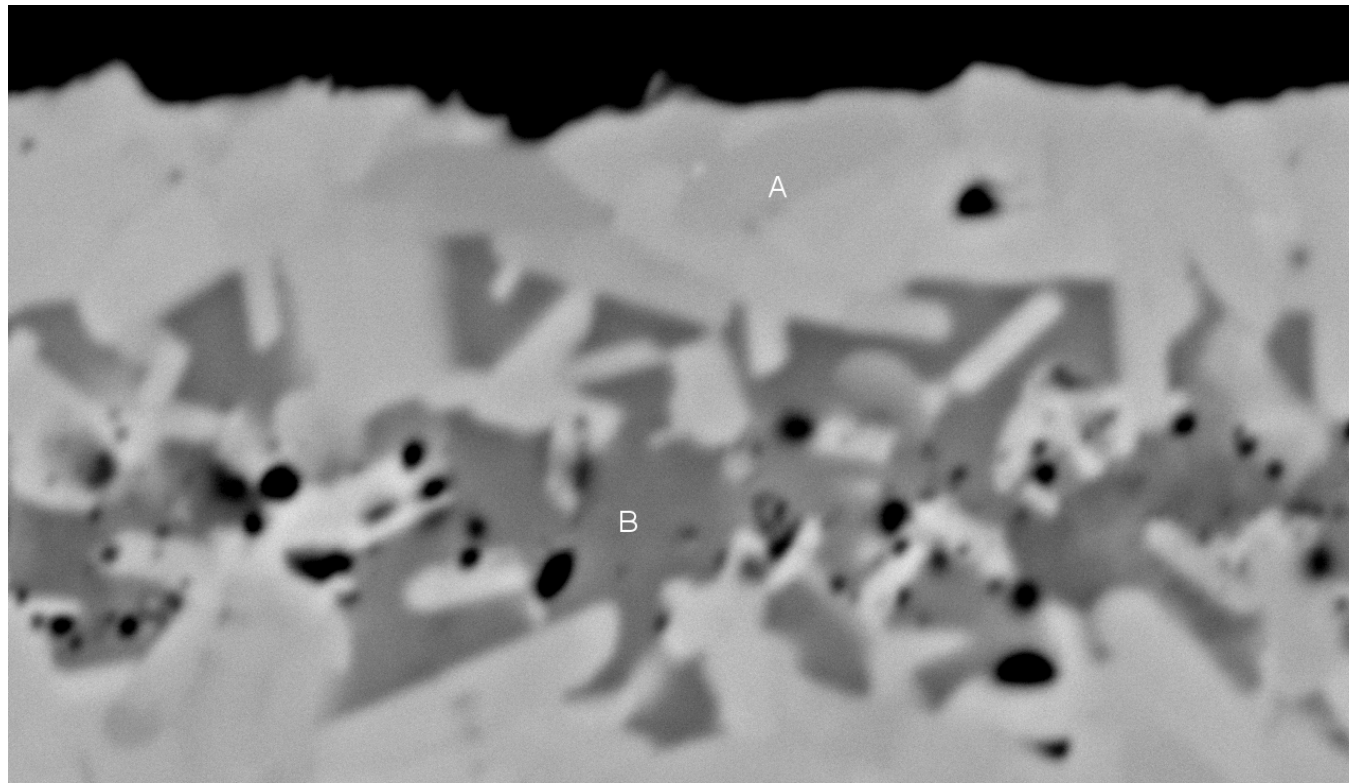


The use of a high purity Ti interlayer contributed to a less complex diffusion bond.





# Microprobe of CVD SiC Reaction Bonded Using PVD Ti Conditions: 1250 °C, 31 MPa, 2 hr, vacuum, 5 °C/min



The undesirable phases of  $Ti_5Si_3$  and  $Ti_3Al$  were not formed.

Identity/source of the black phase or voids still needs to be determined.

Phase	Atomic ratio						
		C	Si	Ti	Al	Cr	Total
CVD SiC	Average	45.8898	54.0955	0.0110	0.0002	0.0035	100.0000
Phase A	Average	24.6860	18.6901	56.6210	-	0.0029	100.0000
Phase B	Average	3.0282	61.2168	35.7521	-	0.0029	100.0000

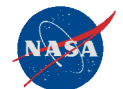
CVD-SiC

NASA COMP

15.0kV

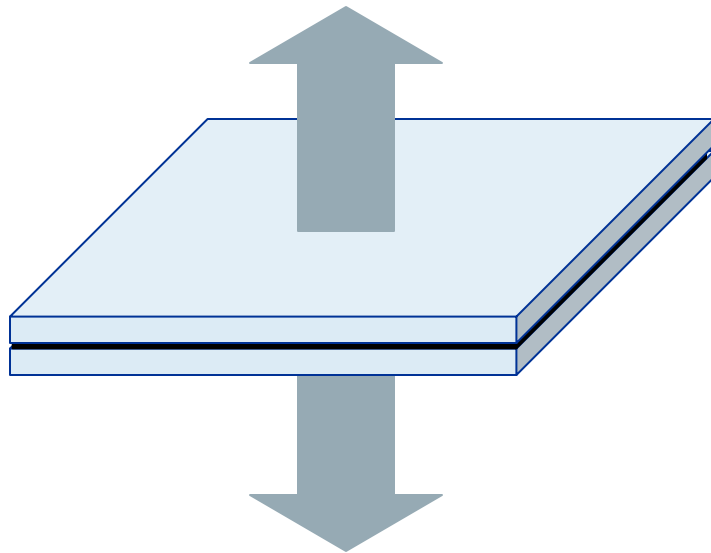
×5,000

1µm WD12mm





## Initial Strength Tests on Diffusion Bonded CVD SiC with a PVD Ti Interlayer



Initial pull test tensile strengths:

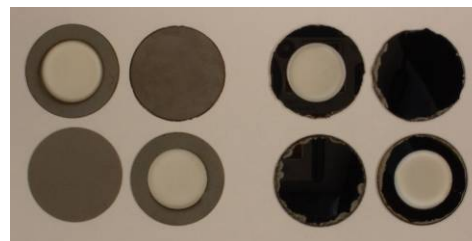
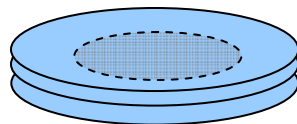
> 23.62 MPa (3.43 ksi)\*

> 28.38 MPa (4.12 ksi)\*

\* failure in the adhesive

The injector application requires a strength of about 3.45-6.89 MPa (0.5 - 1.0 ksi).

The new 1" sample design (partially coated disks) will allow for stresses of 62 MPa (9 ksi) to be applied (due to a large adhesive/pull area compared to the diffusion bond area).





## Summary and Conclusions



- A robust method of bonding SiC to SiC has been developed and optimized.
- Diffusion bonds fabricated with the alloyed Ti foil as the interlayer formed microcracks due to the formation of thermally anisotropic and low ductility phases.
- Diffusion bonds fabricated with the PVD Ti coating gave better diffusion bonds than the alloyed Ti foils
  - Bonds were uniform with no delaminations.
  - Preferred phases were formed which resulted in bonds without microcracks.
- The currently planned sub-element tests will further evaluate this bonding method to determine if it is fully capable of meeting the needs of the proposed injector application – uniform, leak-free bonds with stability and strength retention at temperatures up to 800°F.

