CERAMIC INTEGRATION TEHNOLOGIES FOR ENERGY AND AEROSPACE APPLICATIONS

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Abstract

Robust and affordable integration technologies for advanced ceramics are required to improve the performance, reliability, efficiency, and durability of components, devices, and systems based on them in a wide variety of energy, aerospace, and environmental applications. Many thermochemical and thermomechanical factors including joint design, analysis, and optimization must be considered in integration of similar and dissimilar material systems.

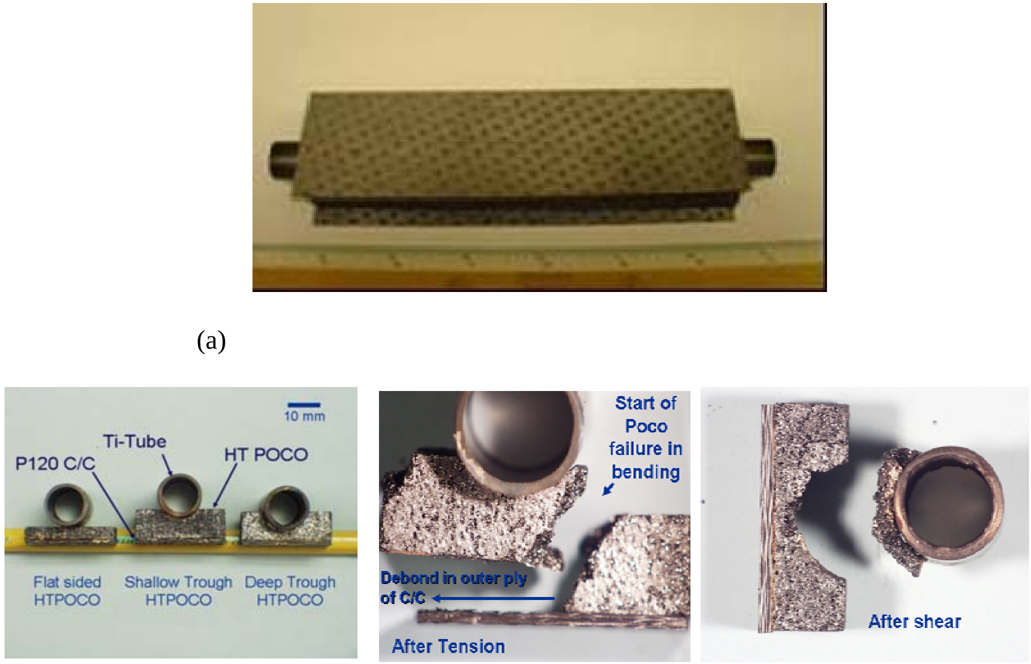
Introduction

Advanced ceramic integration technologies dramatically impact the energy and environment landscape due to wide scale application of ceramics in all aspects of alternative energy production, storage, distribution, conservation, and efficiency. Examples include fuel cells, thermoelectrics, photovoltaics, gas turbine propulsion systems, distribution and transmission systems based on superconductors, nuclear power generation, nuclear waste disposal, NOx and COx reduction technologies, and a wide variety of manufacturing processes and technologies. Some challenges in ceramic integration include joint design and analysis, selection of appropriate joining techniques, thermomechanical issues and residual stress management, non-destructive evaluation, mechanical testing, and long term performance.

Results and Discussion

Some examples of ceramic integration in solid oxide fuel cells (SOFCs), energy efficient fuel injectors for aero engines, and thermal management applications have been presented here. For the SOFCs, active metal brazing has been used for bonding of YSZ/steel. Diffusion bonding has been used for bonding of silicon carbide interlayers for fuel injectors. In addition, high conductivity carbon-carbon composites have been bonded with titanium and Cu-clad-Mo for thermal management applications. Figure 1 shows selected examples of C-C/Ti and Poco foam (from Poco Graphite, Inc.)/Ti-tube joints made using Ti-containing Ag-Cu active braze alloys (ABA). The results show that active braze alloys produce void- and crack-free interfaces with sound metallurgical bond due to reactions/wetting with Ti which promote braze flow and increase the joint strength.

In C-C/Ti joints for lightweight heat rejection systems, a joint strength of 1.5-9.0 MPa was tested and found to be adequate, and in Poco foam/Ti joints (Fig. 1 a-d), the foam matrix rather than the joints failed. Active brazing was also used to join YSZ and Al_2O_3 to steel, Ti, and Ni alloys, and ceramic matrix composites (SiC/SiC, C/SiC, C/C, ZrB_2-based CMCs) to themselves, and to Ti, Cu-clad-Mo, and Ni-alloys (Inconel 625 and Hastealloy) for a wide variety of applications [1-6]. The braze fillers included Ag-, Cu-, Pd-, and Ni-base alloys containing active fillers (e.g., Ti or Cr). Joint strength, hardness, and braze oxidation behavior (for SOFC applications) have been characterized for several of the above brazed joints. Braze alloys containing Ti produced sound joints with excellent integrity in monolithic ceramics (YSZ and Al_2O_3) and CMC’s. Fig. 1(a) show a heat pipe subelement bonded using active metal brazing approach.



(a)

(b) (c) (d)

Fig. 1 (a) Photograph of heat pipe subelement, (b) Ti-tube/Poco foam/P120 C-C composite mechanical test specimens, (c) & (d) failed specimens after tube-tensile and shear tests.

Conclusions

Ceramic integration technologies are critical for the use of advanced ceramics and composites in energy and environmental applications. Active metal brazing results in strong, hermetically sealed joints but braze composition must be judiciously selected to meet the diverse requirements such as resistance to grain growth, creep and oxidation, and small mismatch of CTE. Braze alloys must wet and adhere to the substrates. Joint design optimization and characterization of multi-axial stress distribution, stress-rupture, and oxidation behavior is critical. Considerable progress is envisioned in ceramic integration and optimization in such applications over the next 5-10 years.

References

[1] M. Singh, T.P. Shpargel, R. Asthana, *Int. J. App. Ceram. Tech.* 4(2), 119-133 (2007).
[2] R. Asthana and M. Singh, *J. European Ceram. Soc.* (in press).
[3] M. Singh and R. Asthana, *Mater. Sci. Eng.*, 460-461, 153-162 (2007).
[4] M. Singh, R. Asthana, T.P. Shpargel, *Mater. Sci. Eng.*, 452-453, 699-704 (2007).
[5] G.N. Morscher, M. Singh, T.P. Shpargel, R. Asthana, *Mater. Sci. Eng.*, 418(1-2), 19-24 (2006).
[6] M. Singh, T.P. Shpargel, G.N. Morscher, R. Asthana, *Mater. Sci. Eng.*, 412, 123-128 (2005).

Ceramic Integration Technologies for Energy and Aerospace Applications

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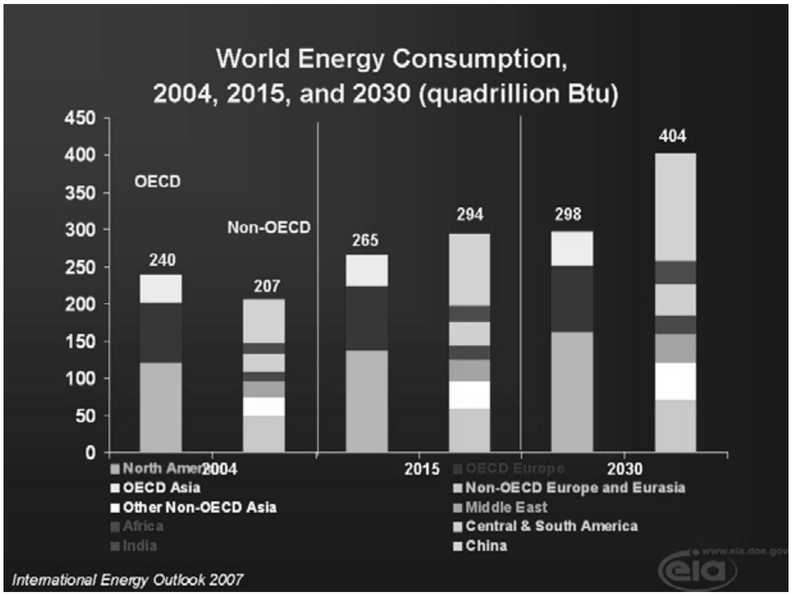
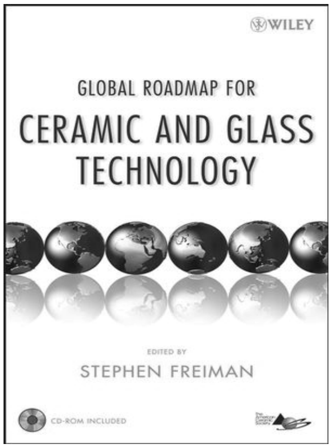
Overview

- **Introduction and Background**
  - ***Global Energy Issues and Role of Ceramics***
- **Technical Challenges in Integration**
  - ***Ceramic-Metal Systems***
  - ***Ceramic-Ceramic Systems***
- **Ceramic Integration Technologies**
  - ***Improved Efficiency and Low Emissions:*** *MEMS-LDI Fuel Injector*
  - ***Thermal Management Systems*** *(Heat Exchangers, Recuperators, etc.)*
  - ***Alternative Energy:*** *SOFC Systems*
- **Concluding Remarks**
- **Acknowledgments**



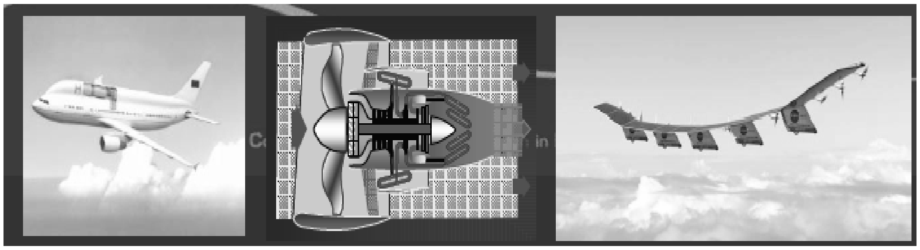
Critical Role of Advanced Ceramic Technologies in Energy and Aerospace Applications

- **Energy Production**
  - Fuel Cells, Thermoelectrics, Photovoltaics
  - Nuclear, Wind, Biomass
- **Energy Storage and Distribution**
  - Batteries, Capacitors, Hydrogen Storage Materials
  - High Temperature Superconductors
- **Energy Conservation and Efficiency**
  - Ceramic Components (Gas Turbines, Heat Exchangers, etc.), Coatings, Bearings



Stephen Freiman, Mrityunjay Singh, Gary Fischman, et al, ACerS-Wiley (2007).

Vision of Future Aircraft and Engine Configurations
[Broichhausen (2005), Szodruch (2005)]



Hydrogen **Intercooler/Recuperator** **Solar/Fuel Cells**

Lower
&
Slower

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

Bonding and Integration of MEMS-LDI Fuel Injector

Objective: Develop Technology for a SiC Smart Integrated Multi-Point Lean Direct Injector (SiC SIMPL-DI)

- 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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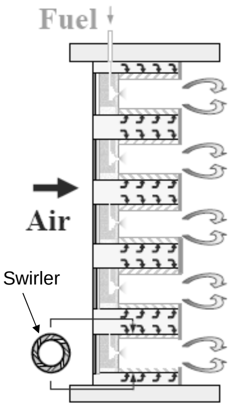
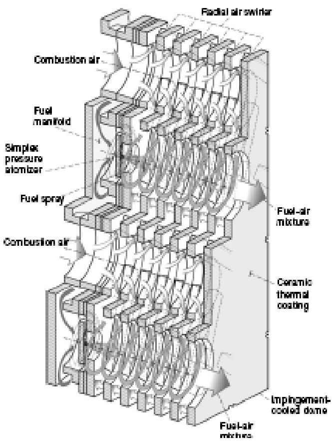
Multi-Point Lean Direct Injector





(Left) Multi-Point Lean Direct Injector accelerates fuel-air mixing and has small recirculation zones with short residence time that reduces NOx emission.

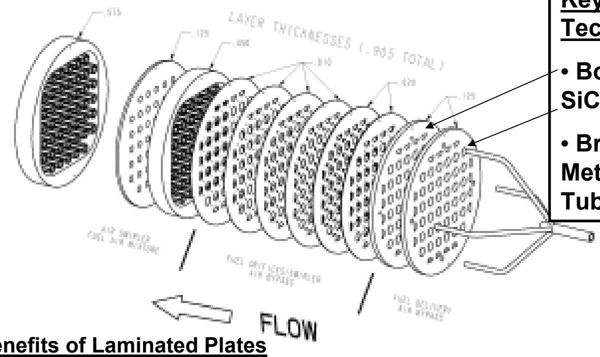
(Center) 3-inch square metal MP-LDI with 45 injectors.

(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 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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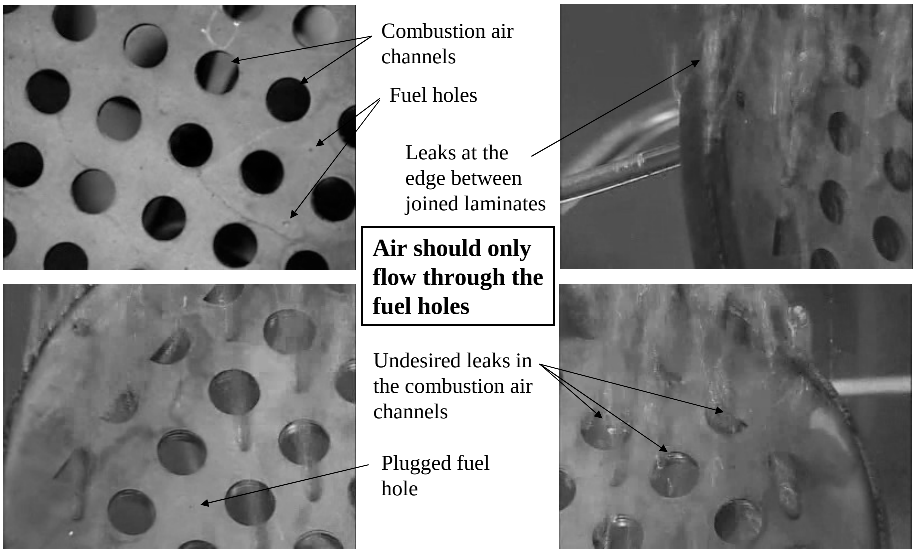
Leak Test of SiC Laminates Joined with Silicate Glass



Combustion air channels

Fuel holes

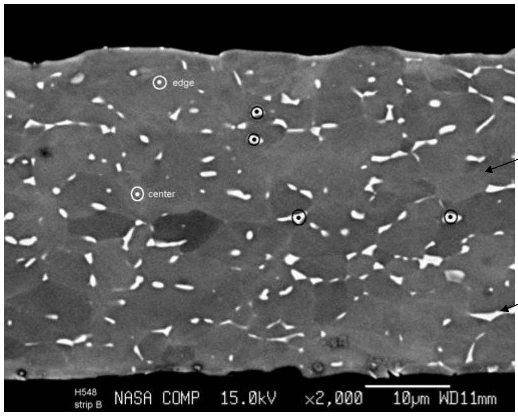
Leaks at the edge between joined laminates

Air should only flow through the fuel holes

Undesired leaks in the combustion air channels

Plugged fuel hole

Microprobe Analysis of Alloyed Ti Foil



Ti-6Al-4V (weight %)

Grey phase – Alpha alloy

White phase – Beta alloy

Microprobe from the cross-section of alloyed Ti foil (averages taken from several points near the edge and at the center of the foil)

	Phase	Al	Fe	Ti	V	Total
Atomic Ratio	Grey Phase	10.196	0.042	86.774	2.988	100.000
Weight (%)	Grey Phase	5.999	0.051	90.632	3.318	100.000
Atomic Ratio	White Phase	4.841	1.850	76.507	16.803	100.000
Weight (%)	White Phase	2.748	2.172	77.084	17.997	100.000

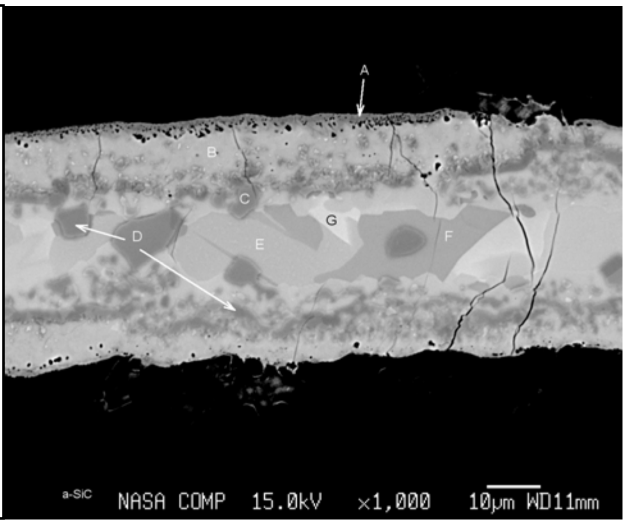
Microprobe of α-SiC Bonded Using Ti Foil

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

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

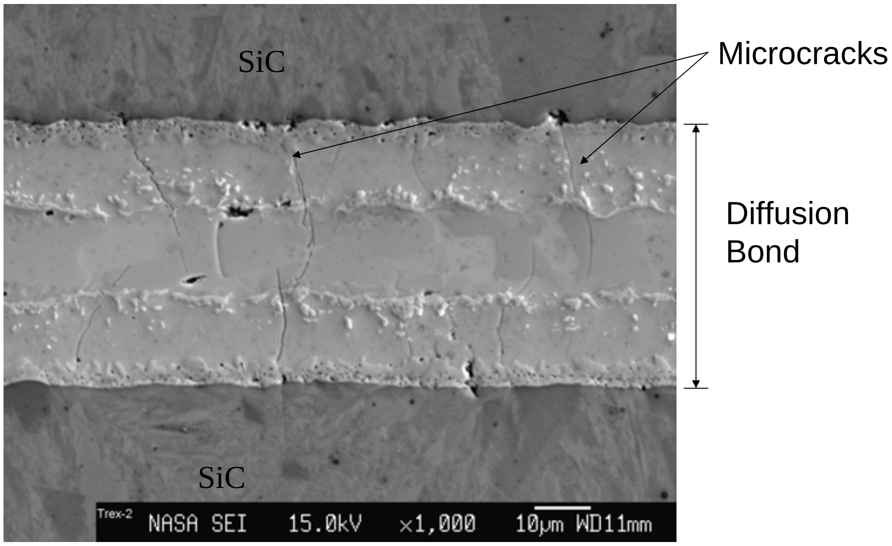
- Phase B $Ti_5Si_3C_X$ – Ti_5Si_3 is highly anisotropic in its thermal expansion where CTE(c)/CTE(a) = 2.72 (Schneibel et al).
- Phase E – Ti_3Al has low ductility at low temperatures. Al can be in the range of 23-35 atm % (Djanarthany et al).

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



M. Singh and M.C. Halbig, Key Engineering Materials Vol. 352 (2007) pp. 201-206

Secondary Electron Image of the Diffusion Bond - Alloyed Ti Foil and Trex CVD SiC

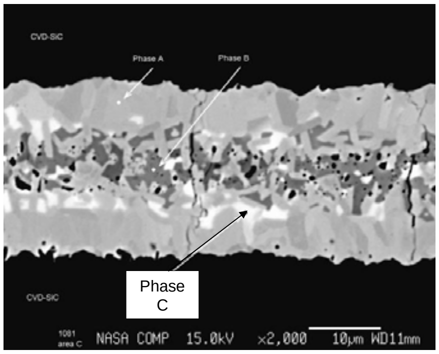


Diffusion Bonding of CVD-SiC Using PVD Ti Interlayer

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.



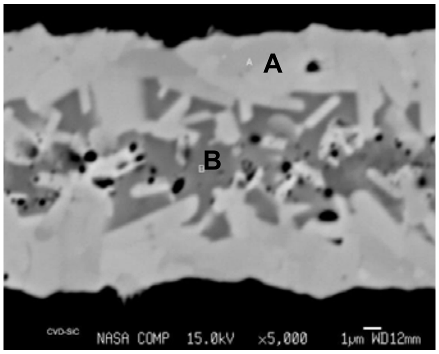
Phases in bond with the 20 µ Ti Interlayer – Atomic Ratios

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.

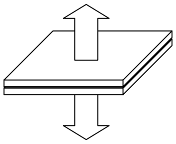


Phases in bond with the 10 µ Ti Interlayer – Atomic Ratios

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

High Strength of Bonds Greatly Exceeds the Application Requirements

1" x 1" Bonded Substrates



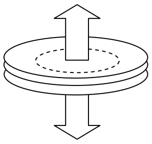
Pull test tensile strengths:

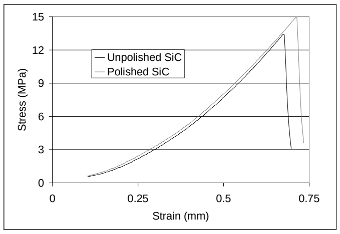
> 23.6 MPa (3.4 ksi)*

> 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)

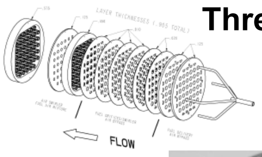
15.0 MPa (2.2 ksi)

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

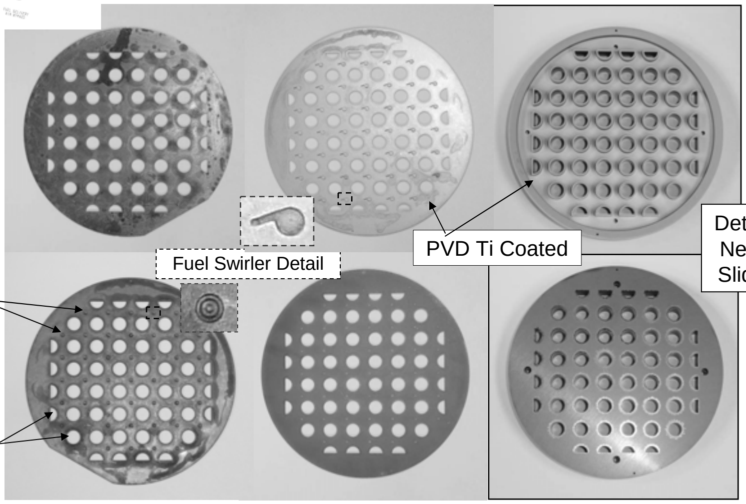
Failures are primarily in the SiC substrate rather than in the bond area.

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

Three Part 10 cm (4") Diameter SiC Injector



Stacking Sequence
Top to Bottom



Top Surfaces

Bottom Surfaces

Fuel Swirler Detail

PVD Ti Coated

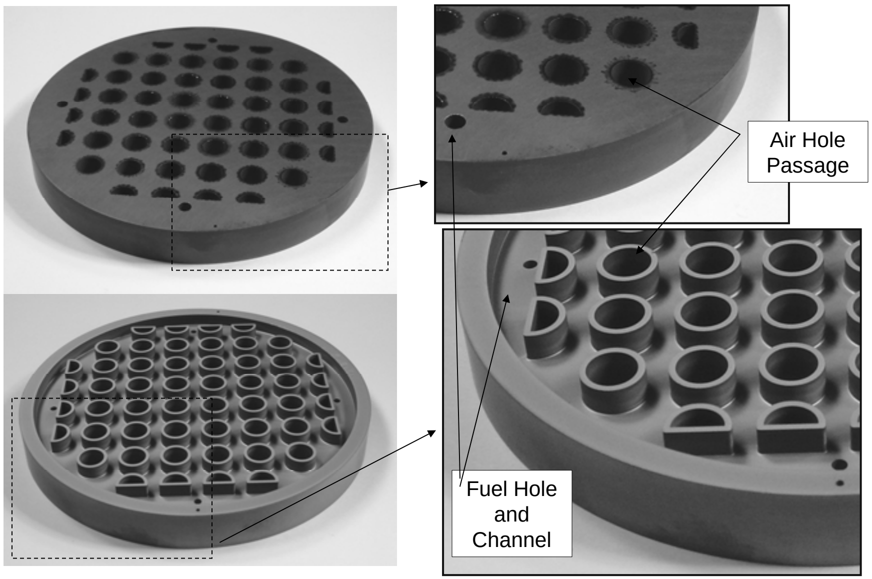
Detail Next Slide

Small Fuel Holes

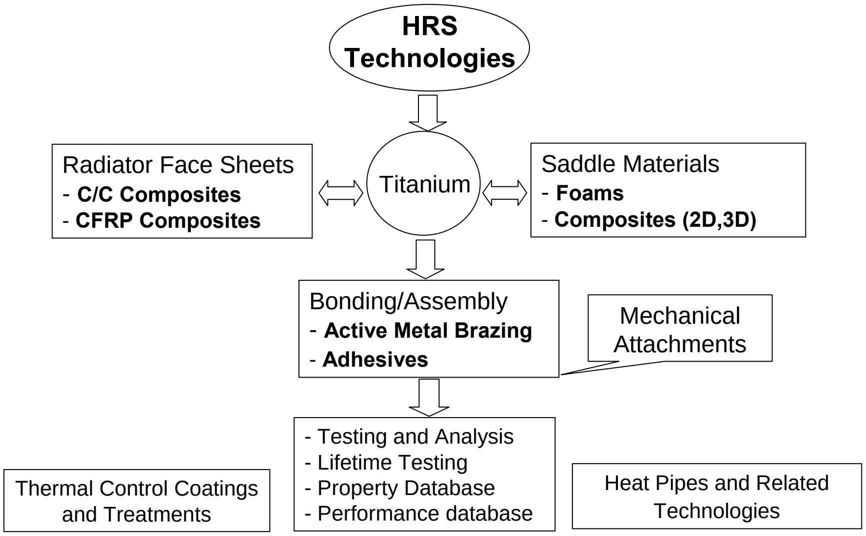
Large Air Holes

Detail of the Thickest Injector Substrate

(~0.635 cm thick)



Integration Needs in Heat Rejection System



HRS Technologies

Titanium

Radiator Face Sheets
- **C/C Composites**
- **CFRP Composites**

Saddle Materials
- **Foams**
- **Composites (2D,3D)**

Bonding/Assembly
- **Active Metal Brazing**
- **Adhesives**

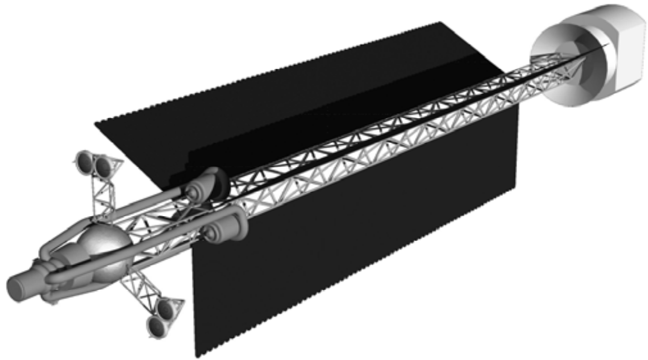
Mechanical Attachments

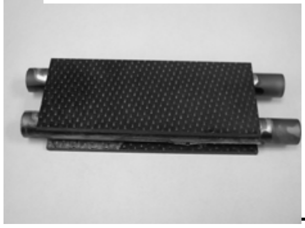
- Testing and Analysis
- Lifetime Testing
- Property Database
- Performance database

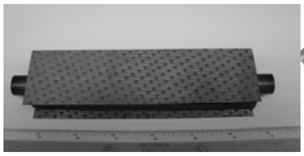
Thermal Control Coatings and Treatments

Heat Pipes and Related Technologies

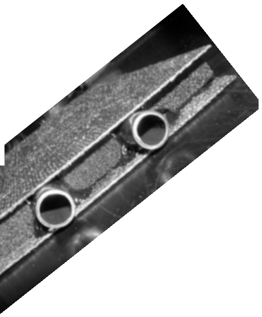
Integration of Sub-elements for Heat Rejection System Using Brazing and Adhesive Bonding





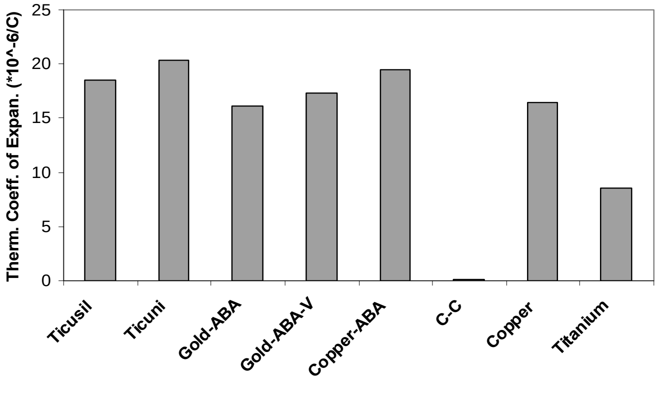


Brazed Radiator Sub-elements



Adhesive Bonded Radiator Sub-element

Thermal Expansion Mismatch Issues are Critical in Brazing of Metal-Composite System



Innovative joint design concepts, new braze materials, and robust brazing technology development are needed to avoid deleterious effects of thermal expansion mismatch.

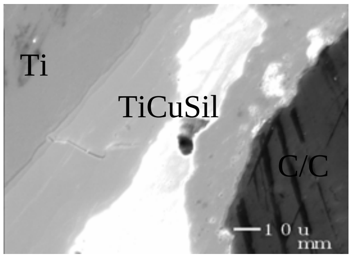
Active Metal Brazing

- **Ti tubes and plates brazed to P120 CVI C/C composite**
- **Several braze/solder compositions compared (processing Temp):**
  - TiCuSil (910 C) foil and paste
  - CuSil-ABA (820 C) foil and paste
  - CuSin-1ABA foil (810 C)
  - Incusil foil (725 C)
  - S-Bond solder (~ 400 C)
- **Two tests have proved successful:**
  - Butt Strap Tension (BST)
  - Tube-Plate Tensile Test

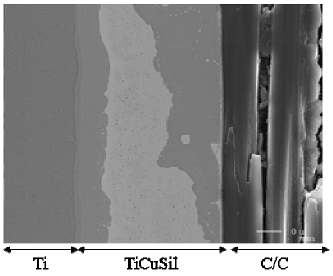
- ***Require*** ***good wetting, bonding and spreading properties***
- ***Desire*** ***minimal residual stress induced cracking in C/C***

Microstructure of Brazed Ti and C-C Composites using TiCuSil and CuSil ABA Paste

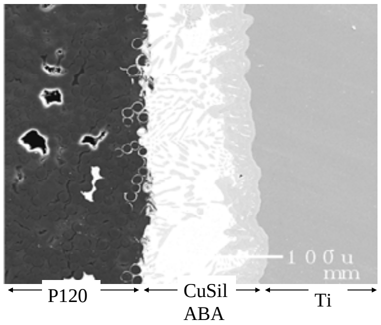
Ti- Tube



Ti- Plate

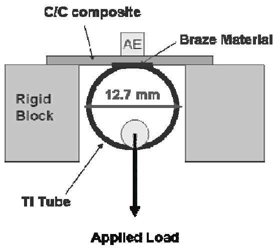


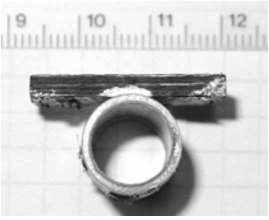
Titanium Plate



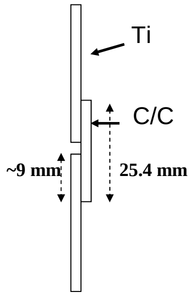
Mechanical Testing of Brazed/Soldered Joints

Tube Tensile Test



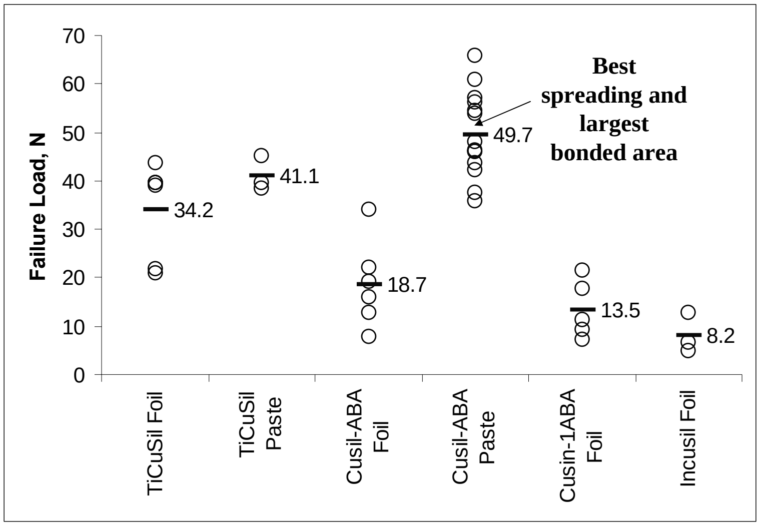


Butt Strap Tensile Test

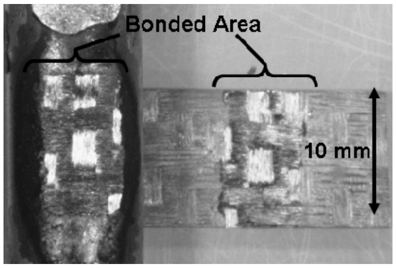


Factors to consider:
-Braze composition, Processing variables
-Bonded area, Location of failure
-Architecture effects

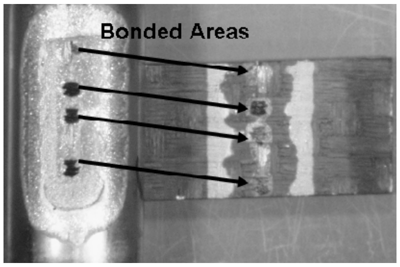
Tube Tensile Test Data for Brazed Joints



Failure Behavior of Ti Tube - C/C Composite Joints



Tube and C/C plate fracture surfaces for CuSil-ABA paste braze material showing the bonded area of the outer ply of C/C brazed to the Ti tube (left) and C/C plate (right).

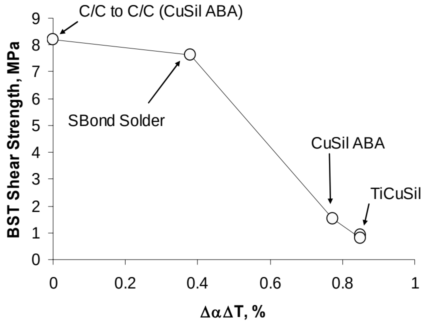


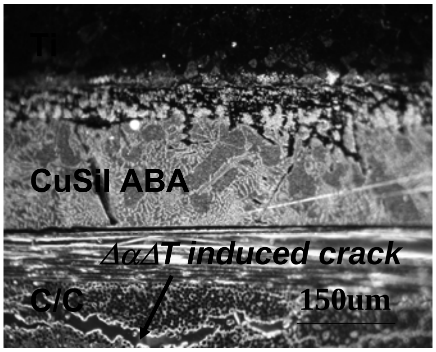
Tube and C/C plate fracture surfaces for Incusil ABA foil braze material showing the distinct bonded areas of the outer ply of C/C brazed to the Ti tube (left) and C/C plate (right).

Test data on a wide variety of brazes reported in Mater. Sci. Engg. A, 412 (2005) 123-128 and Mater. Sci. Engg. A., 418 (2006) 19-24.

Thermally-Induced Cracking in C/C Controls Shear Strength of Brazed Joints

For braze materials where there was strong bonding between the braze and the C/C and failure occurred in the outer-ply of the C/C





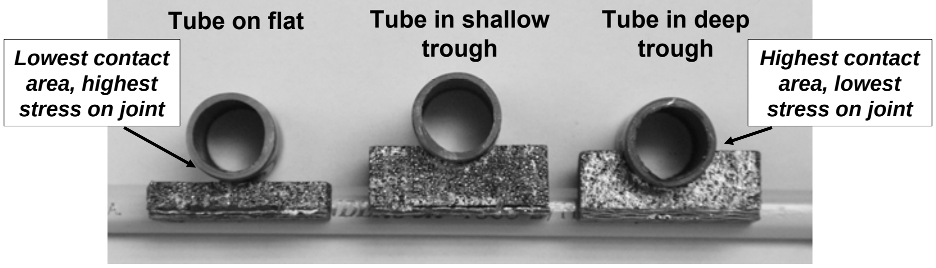
$\Delta\alpha = \alpha$ (Ti) – α (C/C)

ΔT = T (liquidus ~ processing) – 25^{o}C

Joint Material	Proc. Temp., C
S-Bond	~ 400
CuSil ABA	830
TiCuSil	910

Brazed Structures with Woven K1100 and P120 C/C Facesheet/Foam/Titanium Tube

Specimens with different tube-foam contact areas were fabricated in order to vary braze contact area and stress applied to joints



Tube on flat

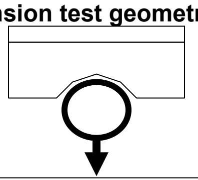
Tube in shallow trough

Tube in deep trough

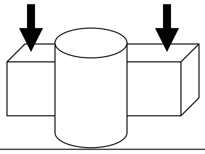
Lowest contact area, highest stress on joint

Highest contact area, lowest stress on joint

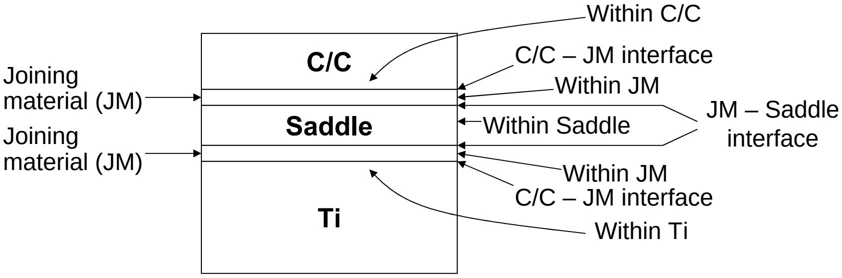
Tension test geometry



Shear test geometry



Locations of Potential Joint Failure in C/C Face Sheet/Poco Foam Saddle/Titanium



Within C/C

C/C

Joining material (JM)

C/C – JM interface

Within JM

Saddle

Within Saddle

JM – Saddle interface

Joining material (JM)

Within JM

C/C – JM interface

Ti

Within Ti

In addition the geometry of joining surfaces will affect strength of joint and influence spreading of joint material: flat to flat, flat to tube, curved surfaces…

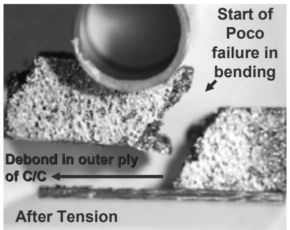
Therefore, knowing the location of joint failure is critical

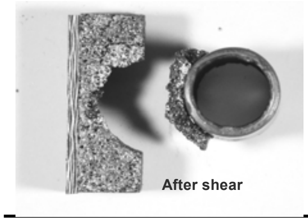
- **Weakest link requiring further improvement**
- **Affects interpretation of results (material or test-dependent property)**

Key factor: Bonded area dictated by braze composition and applied pressure, C/C constituent composition, fiber orientation, geometry of joined surface

Brazed Structures with Woven K1100 and P120 C/C Facesheet/Foam/Titanium Tube

- **Excellent bonding of CuSil-ABA Braze to Poco HTC, C-C Composite, and Ti Tube**
- **Failure always occurred in Poco HTC (Saddle Materials)**





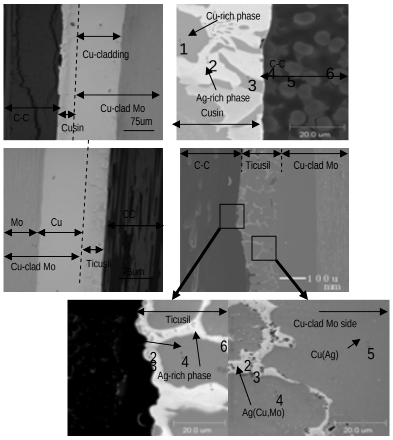
Observations:

- The Poco HTC (carbon foam saddle material) is the weak link in the sandwich structures and not the brazed joint.
- Failure in tension and shear always occurs in the foam regardless of (1) P120 or K1100 woven face sheet materials or (2) whether the Ti tube was brazed to a curved Poco surface to maximize bond area or a flat Poco surface to maximize stress in the joint.
  - Maximum *shear stresses* subjected to braze *exceeded 12 MPa* based on load applied and approximate braze area.
  - Maximum *tensile stresses* subjected to braze *exceeded 7 MPa* based on load applied and approximate braze area.

M. Singh, G. Morscher, R. Asthana, T. Shpargel, Mater. Sci. Eng., A 2007 in press.

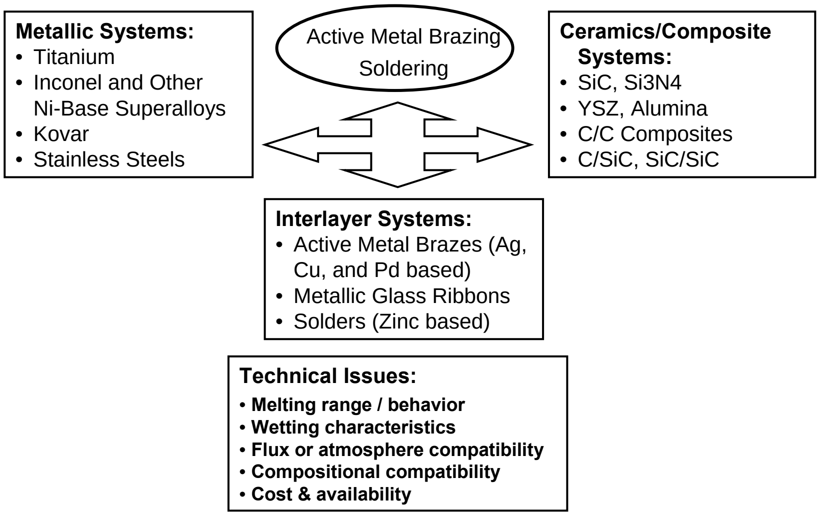
C-C Composite/Cu-Clad-Mo Joints for Thermal Management Applications

- C-C composites were brazed to Cu-clad Mo using four ABA's (Cu-ABA, Cusin, Ticusni and Ticusil).
- Good metallurgical bonding at joints, with some dissolution, diffusion, and solute redistribution.
- Ti preferentially segregated at the C-C/braze interface. Cu-ABA joints displayed the largest Ti concentrations at joint.
- Microhardness gradients exist at joint (peak HK is 300-350 in Cusin-1 ABA and Ticusil, and 200-250 HK in Cu-ABA and Ticuni).
- C-C/Cu-clad Mo systems are useful for thermal management applications.



M. Singh, R. Asthana, T. Shpargel, Mater. Sci. Eng., A 452-453, 2007, 699-704

Integration of Metals to Ceramics and Composites Using Metallic Interlayers



Metallic Systems:
- Titanium
- Inconel and Other Ni-Base Superalloys
- Kovar
- Stainless Steels

Active Metal Brazing
Soldering

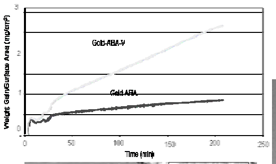
Ceramics/Composite Systems:
- SiC, Si3N4
- YSZ, Alumina
- C/C Composites
- C/SiC, SiC/SiC

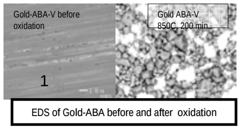
Interlayer Systems:
- Active Metal Brazes (Ag, Cu, and Pd based)
- Metallic Glass Ribbons
- Solders (Zinc based)

Technical Issues:
- **Melting range / behavior**
- **Wetting characteristics**
- **Flux or atmosphere compatibility**
- **Compositional compatibility**
- **Cost & availability**

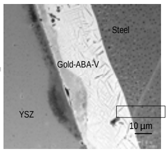
Integration of YSZ/Steel for SOFC Applications

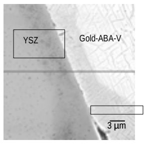
- **Gold-ABA and Gold ABA-V exhibit linear oxidation kinetics at 850 C. Gold-ABA-V shows faster oxidation kinetics than Gold-ABA.**
- **Ti in Gold-ABA and V in Gold-ABA V caused discoloration (darkening) of YSZ.**
- **The darkening is caused by Ti and V that act as oxygen getters and form oxygen-deficient YSZ. No reaction layers formed at joint.**
- **The oxygen-deficient YSZ is better wet by gold than stoichiometric YSZ.**

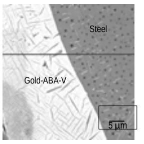


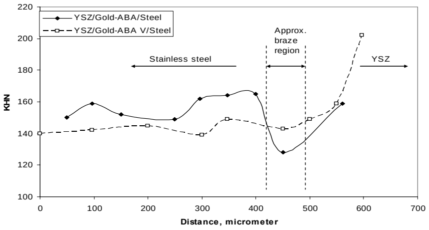


EDS of Gold-ABA before and after oxidation





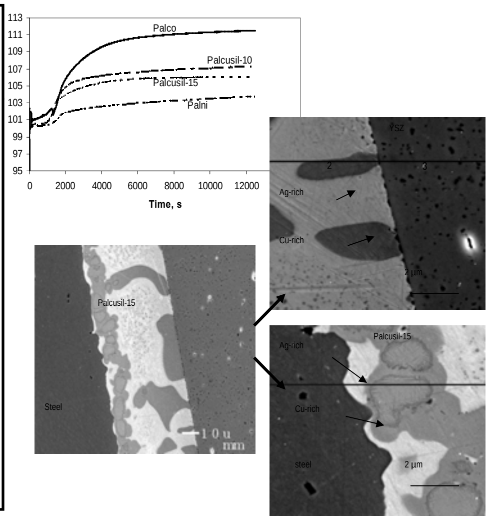




M. Singh, T. Shpargel, R. Asthana, Int. J. Appl. Ceram. Tech. 4(2), 2007, 119-133.

Integration of YSZ/Steel for SOFC Applications

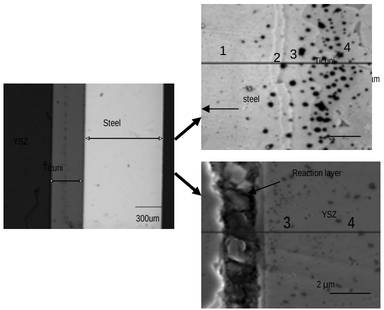
- **Pd-base brazes (Palco and Palni) and Ag-base brazes (Palcusil-10 and Palcusil-15) were characterized for oxidation at 750ºC.**
- **Structural changes accompany oxidation which is fastest for Palco, slowest for Palni, and intermediate for Palcusil-10 and Palcusil-15.**
- **All brazes were effective in joining yttria stabilized zirconia (YSZ) to stainless steel for solid oxide fuel cell (SOFC).**
- **Dissolution of YSZ and steel in braze, and braze constituents in YSZ and steel led to diffusion and metallurgically sound joints.**
- **Knoop hardness (HK) profiles are similar for all brazes, and exhibit a sharp discontinuity at the YSZ/braze interface.**

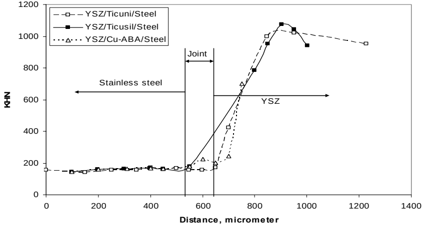


M. Singh, T. Shpargel, R. Asthana, Mater. Sci. Eng. A (2007 in press)

Integration of YSZ/Steel for SOFC Applications

- **Active braze alloys, Cu-ABA, Ticuni and Ticusil, were characterized for oxidation at 750-850ºC.**
- **Oxidation is fastest for Ticusil, slowest for Cu-ABA, and intermediate for Ticuni.**
- **Brazes were used for joining yttria-stabilized-zirconia (YSZ) to stainless steel for Solid Oxide Fuel Cell (SOFC) applications.**
- **Interdiffusion, compositional changes, and reaction layer formation led to high-integrity joints.**





M. Singh, T. Shpargel, R. Asthana, J. Mater. Sci (2007 in press)

Concluding Remarks

- Ceramic integration technologies are critically needed for the successful development and applications of ceramic components in a wide variety of energy and aerospace 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.
- There have been a number of short term design, development, and evaluation efforts in various parts of the world. However, a concerted and long term sustained effort is needed to make the significant progress in this area.

Acknowledgements

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