Ceramic Integration Technologies for Advanced Energy Systems:
Critical Needs, Technical Challenges, and Opportunities

Abstract
Advanced ceramic integration technologies dramatically impact the energy 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 and waste disposal. Ceramic integration technologies play a key role in fabrication and manufacturing of large and complex shaped parts with multifunctional properties. However, the development of robust and reliable integrated systems with optimum performance requires the understanding of many thermochemical and thermomechanical factors, particularly for high temperature applications.

In this presentation, various needs, challenges, and opportunities in design, fabrication, and testing of integrated similar (ceramic-ceramic) and dissimilar (ceramic-metal) material systems have been discussed. Experimental results for bonding and integration of SiC based Micro-Electro-Mechanical-Systems (MEMS) LDI fuel injector and advanced ceramics and composites for gas turbine applications are presented.
Ceramic Integration Technologies for Advanced Energy Systems

Critical Needs, Technical Challenges, and Opportunities

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Overview

- Introduction and Background
  - Global Energy Issues and Role of Ceramics
- Technical Challenges in Integration
  - Similar vs Dissimilar Systems
    - Role of Interfaces
    - Thermal Expansion Mismatch and Residual Stresses
    - Design and Testing
- Ceramic Integration Technologies
  - Improved Efficiency and Low Emissions:
    - Gas Turbine Components
    - MEMS-LDI Fuel Injector
  - Thermal Management Systems
    - Heat Exchangers and Recuperators
  - Alternative Energy Systems
- Concluding Remarks
Energy Use Grows with Economic Development


Source: UN and DOE EIA

World Energy Consumption, 2004, 2015, and 2030 (quadrillion Btu)

International Energy Outlook 2007
**Advanced Materials and Technologies Play a Key Role in Improving Energy Efficiency**

![Graph showing global energy efficiency over time](image1)

Source: Millennium Project, 2020 Global Energy Delphi Round 2

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**Critical Role of Advanced Ceramic Technologies in Energy Systems**

- **Energy Production**
  - Fuel Cells
  - Thermoelectrics
  - Photovoltaics
  - Nuclear Systems
  - Wind Energy
  - Biomass

- **Energy Storage and Distribution**
  - Batteries
  - Supercapacitors
  - Hydrogen Storage Materials
  - Thermal Energy Storage/PCMs
  - High Temperature Superconductors

- **Energy Conservation and Efficiency**
  - Ceramic Components (Gas Turbines)
  - Heat Exchangers and Recuperators
  - Coatings, Bearings

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**Ceramic Integration Technologies**
Overview of Key Ceramic Integration Technologies

Joining Technologies
- Ceramic-Ceramic
- Ceramic-Metal

Component & System Level Integration

Repair/Refurbishment
- In-Situ Repair
- Ex-Situ Repair

Mechanical Fastening
- Ceramic-Ceramic
- Ceramic-Metal
- Rivets/Bolts

Robust Manufacturing
- Large Components
- Complex Shapes
- Multifunctional

Robust Design and Testing Requirements for Integrated Ceramic Components

Supporting Technologies Analysis
- Full-Scale Tests
- Component Tests
- Subcomponent Tests
- Element Tests
- Coupon Tests

Design Considerations

Opportunities to Utilize Building-Block Approach to Design and Manufacturing of Large Ceramic and Composite Structures
**Technical Challenges in Integration of Ceramic-Metal vs Ceramic-Ceramic Systems**

<table>
<thead>
<tr>
<th>Ceramic-Metal System</th>
<th>Ceramic-Ceramic System</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Flow and wettability</td>
<td>• Reaction and diffusion</td>
</tr>
<tr>
<td>• Roughness</td>
<td>• Roughness</td>
</tr>
<tr>
<td>• Residual stress (ΔCTE)</td>
<td>• Residual stress (ΔCTE)</td>
</tr>
<tr>
<td>• Multi-axial stress state</td>
<td>• Multi-axial stress state</td>
</tr>
<tr>
<td>• Joint design</td>
<td>• Joint design</td>
</tr>
<tr>
<td>• Joint stability in service</td>
<td>• Joint stability in service</td>
</tr>
</tbody>
</table>

**Common Issues**

- • Metal – forgiving
- • Elastic-plastic system
- • Lower use temperatures
- • Less aggressive environment

- • Ceramic – unforgiving
- • Elastic-elastic system
- • Higher use temperatures
- • More aggressive environment

**Challenges in Design and Testing of Integrated Structures**

Typical Integrated Systems will have Combination of Stresses Under Operating Conditions

**Different Types of Shear Tests**

- (a) Compression; (b) Tension; (c) Shear; (d) Peel; (e) Cleavage
Wetting and Interfacial Phenomena in Ceramic-Metal System

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

Wettability is Important Factor in Brazing

Young's equation

\[ \sigma_L - \sigma_T = \sigma_v \cos \theta \]

Contact angle of braze should be small

Braze layer melts and spreads between the substrates to form the joint

Must use ‘active’ brazes that wet and bond with both metal and ceramics
Integration of Metals to Ceramics and Composites
Using Metallic Interlayers

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

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 Technologies for Improved Efficiency and Low Emissions
- Gas Turbine Components
Advanced Silicon Nitride Based Components for Propulsion Systems

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

Integration Technologies for Silicon Nitride Ceramics to Metallic Components

Issues with Ceramic Inserted Blades

There are contact stresses at the metal-ceramic interface. Compliant layers (i.e. Ni-alloy+Pt) are used to mitigate the stress and damage. Failures can occur in the compliant layer.

Mark van Roode, “Advances in the Development of Silicon Nitride and Other Materials”, Environmental Barrier Coatings Workshop, November 6, 2002, Nashville, TN.
Integration Technologies for Silicon Nitride Ceramics to Metallic Components

INTEGRAL ROTORS
• No Compliant Layer with Disk
• Attachment of Ceramic Rotor to Metal Shaft
• Primarily Small Parts
• Ability to Fabricate Larger Parts Has Improved
• Integral Rotors are Replacing Metal Disks with Inserted Blades

Industry Direction

INTEGRAL ROTORS

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

Mark van Roode, Solar Turbines

Integration of Silicon Nitride to Metallic Systems

Approach: Use multilayers to reduce the strain energy more effectively than single layers.

Challenge: Multiple interlayers increase the number of interfaces, thus increasing the probability of interfacial defects.

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE x10^6/K</th>
<th>Yield Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon nitride</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td>Ta</td>
<td>6.5</td>
<td>170</td>
</tr>
<tr>
<td>Mo</td>
<td>4.8</td>
<td>500</td>
</tr>
<tr>
<td>Ni</td>
<td>13.4</td>
<td>14-35</td>
</tr>
<tr>
<td>Nb</td>
<td>7.1</td>
<td>105</td>
</tr>
<tr>
<td>Kovar</td>
<td>5.5-6.2</td>
<td>270</td>
</tr>
<tr>
<td>W</td>
<td>4.5</td>
<td>550</td>
</tr>
</tbody>
</table>

Various combinations of Ta, Mo, Ni, Nb, W and Kovar to integrate Silicon nitride to Nickel-Base Superalloys
Microstructure of Silicon Nitride Joints Using Cu-ABA (92.75Cu-3Si-2Al-2.25Ti) Interlayers


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

Titanium Segregation at the Interface
TEM Analysis Silicon Nitride/Silicon Nitride Joints Using Cu-ABA Interlayers

(a) Reaction layer at the Si3N4/braze interface and dislocations in braze, (b) titanium silicide formation, and (c) a higher magnification image of region shown in (b).

Details of joint microstructure (fine grains < 50 nm) form the reaction layer. b) Electron diffraction patterns of the Si3N4 reaction layer and joint interior (Cu-ABA).


Typical Shear Behavior of Joints at Different Temperatures

- Si3N4 JOINT
- INCONEL JOINT
Microstructure of Silicon Nitride/Inconel 625 Multilayer Joints

Si₃N₄/W/Mo/Inconel 625 (Cu-ABA, brazed at 1044C, 30 min.).

Si₃N₄/Ni/W/Ni/Inconel 625 (with Cu-ABA on SN side and MBF on Inconel side) (brazed at 1044C, 30 min.).

Integration Technologies for Improved Efficiency and Low Emissions

• MEMS-LDI Fuel Injector
Integration Technologies for MEMS-LDI Fuel Injector

Objective: Develop Technology for a SiC Smart Integrated Multi-Point Lean Direct Injector (SiC SIMP-LDI)
- Operability at all engine operating conditions
- Reduce NOx emissions by 90% over 1996 ICAO standard
- Allow for integration of high frequency fuel actuators and sensors

Possible Injector Approaches

1. Lean Pre-Mixed Pre-Evaporated (LPP)
   - **Advantages**: Produces the most uniform temperature distribution and lowest possible NOx emissions
   - **Disadvantages**: Cannot be used in high pressure ratio aircraft due to auto-ignition and flashback

2. Lean Direct Injector (LDI)
   - **Advantages**: Does not have the problems of LPP (auto-ignition and flashback)
   - Provides extremely rapid mixing of the fuel and air before combustion occurs

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
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

Microcracking is still present due to the presence of Ti₅Si₃Cx.
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 25.767
Phase B 35.794 62.621 1.570
Phase C 58.767 33.891 7.140

Phases in bond with the 10 µ Ti Interlayer – Atomic Ratios
Phase Ti Si C
Phase A 56.621 18.690 24.686
Phase B 35.752 61.217 3.028

Diffusion Bonding of CVD-SiC Using PVD Ti Interlayer

20 Micron Ti Interlayer
Microcracking is still present due to the presence of Ti₅Si₃Cx.
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 25.767
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 Ti₅Si₃Cx 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
Phase A 56.621 18.690 24.686
Phase B 35.752 61.217 3.028
Non-Destructive Evaluation (NDE) Method of Ultrasonic Immersion Shows Very Good Bonding of 1" Discs

Less Polished SiC
Highly Polished SiC

Discs Before Bonding

0.65" Diameter PVD Ti Coating

Ultrasonic C-scan Image of Bonded Discs

Ultrasonic C-scan Image of Bonded Discs

Clay on backside of sample to verify that ultrasound reached backwall

Ti bonded region

High Strength of Bonds Greatly Exceeds the Application Requirements

1" x 1" Bonded Substrates
1" Diameter Discs with a 0.65" Diameter Bond Area

Pull test tensile strengths:
- > 23.6 MPa (3.4 ksi)*
- > 28.4 MPa (4.1 ksi)*

* failure in the adhesive to the test fixture

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

Top Surfaces (Facing the Flow Direction)
- Fuel Tube
- Fuel Swirler Detail
- PVD Ti Coated
- Detail
- Next Slide

Bottom Surfaces (Facing Opposite to the Flow Direction)
- Small Fuel Holes
- Large Air Holes
- Holes for Fuel Tube Integration
- Passage

Detail of the Thickest Injector Substrate (~0.635 cm thick)
- Air Hole Passage
- Fuel Hole and Channel
Integration Technologies for Improved Efficiency and Thermal Energy Storage Devices

- Thermal Management Systems
- Heat Exchangers/Recuperators
- Thermal Energy Storage

National Aeronautics and Space Administration

Bonding of Titanium to C/C Composites

- We had joined C-C composite to Ti tubes for lightweight heat exchanger applications.
- Both direct bonding using braze layers and indirect bonding using a porous carbon foam (saddle material) and braze layers were employed.
- Excellent bonding of active braze to foam, C-C Composite, and Ti Tube occurred.
- Failure always occurred in Poco HTC (Saddle Material) indicating that bond strength exceeded the fracture strength of foam.

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

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: Lowest contact area, highest stress on joint
- Tube in shallow trough: Tube in deep trough: 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 C/C Joining material (JM)

Within C/C

C/C – JM interface

Within JM

Foam Saddle

Within Saddle

JM – Saddle interface

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.

Ceramic Integration Technologies for Alternative Energy Systems
- Solid Oxide Fuel Cells

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.

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.


Transmission Electron Microscopy of Interfaces in YSZ/Ag-Cu-Pd/Steel System

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

• Professor Rajiv Asthana, University of Wisconsin-Stout
• Mr. Michael H. Halbig, NASA Glenn Research Center
• Prof. J.M. Fernandez, University of Seville, Spain
• Dr. Gregory N. Morscher, University of Akron
• Mr. Ron Phillips, ASRC Corp.
• Mr. Ray Babuder, Case Western Reserve University