FABRICATION AND CHARACTERIZATION OF BRAZED JOINTS FOR SiC-METALLIC SYSTEMS UTILIZING REFRACTORY METALS

ABSTRACT
Metal to ceramic joining plays a key role for the integration of ceramics into many nuclear, ground and aero based technologies. In order to facilitate these technologies, the active metal brazing of silicon carbide (CVD β-SiC, 1.1 mm thick, and hot-pressed α-SiC, 3 mm thick) to the refractory metals molybdenum and tungsten using active braze alloys was studied. The joint microstructure, composition, and microhardness were evaluated by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Knoop hardness testing. The braze alloys, Cusil-ABA, Ticusil and Copper-ABA, all formed sound joints with excellent wetting and chemical bonding with the SiC substrate. Despite the close thermal expansion match between the metal substrates and SiC, hairline cracks formed in α-SiC while β-SiC showed no signs of residual stress cracking. The use of ductile interlayers to reduce the effect from residual stresses was investigated and joints formed with copper as an interlayer produced crack free systems utilizing both CVD and hot-pressed SiC.
Fabrication and Characterization of Brazed Joints for SiC-Metallic Systems Utilizing Refractory Metals

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Outline

• **Application**
  – Nuclear, Electronic, Ground and Aero Based Technologies

• **Experimental Procedure / Joint Processing**
  – Tungsten to SiC Brazing
  – Molybdenum to SiC Brazing
  – Challenges Encountered

• **Characterization**
  – Optical Microscopy
  – Knoop Microhardness Testing
  – Scanning Electron Microscopy (SEM) coupled with Energy Dispersion Spectrometry (EDS)

• **Summary and Conclusions**
Joining Applications for SiC Based Components

Applications for Mo & W Materials
- Electronic Components
  - Electrodes
  - Contacts
- Nuclear Applications
  - Radiation Shielding
  - Heat Shielding
- Aerospace Industries
  - Turbine Engine Components
    - Injectors
    - Turbines
  - Rocket Nozzles
- Ground Based Industries
  - Heating Elements
  - Medical Equipment

Fabrication and Testing of a MEMS Lean Direct Injector

Key Enabling Technologies:
- Brazing of SiC to Metallic Fuel Tubes
- Bonding of SiC to SiC

R. Tacina et al., TM-2002-211347

Develop and characterize the joining and integration technologies required for injector fabrication:
- Brazing Metallic Tubes to SiC
Key Enabling Technology – Metal/Ceramic Joining

• Experimental Procedure
  – Substrates and braze foils were ultrasonically cleaned in Acetone for 10 minutes
  – Substrates were sandwiched together with a 100g load applied to the assembly
  – Heated to 10°C above the braze liquidus temperature
  – Isothermally held for 5 minutes under vacuum
  – Cooled to room temperature at 2°C/min
  – Mounted in epoxy, polished and the joints were characterized
# Key Enabling Technology – Metal/Ceramic Joining

### Selected Substrate and Braze Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (GPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>U.T.S. (MPa)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>CTE ($x10^{-6}$ m/m*K)</th>
<th>Electrical Conductivity ($x10^6$ /Ωm)</th>
<th>% Elongation</th>
</tr>
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<tbody>
<tr>
<td>Copper ABA</td>
<td>96</td>
<td>279</td>
<td>520</td>
<td>398</td>
<td>19.5</td>
<td>5.1</td>
<td>42</td>
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<tr>
<td>Cusil ABA</td>
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<td>271</td>
<td>346</td>
<td>180</td>
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<td>23</td>
<td>20</td>
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<tr>
<td>Ticusil</td>
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<td>292</td>
<td>339</td>
<td>219</td>
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<td>29</td>
<td>28</td>
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<tr>
<td>SiC</td>
<td>466</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>4.0*</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Molybdenum</td>
<td>330</td>
<td>-</td>
<td>350</td>
<td>138</td>
<td>6.5*</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tungsten</td>
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<td>590</td>
<td>758</td>
<td>33</td>
<td>4.4**</td>
<td>-</td>
<td>7</td>
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<tr>
<td>Nickel</td>
<td>190</td>
<td>150</td>
<td>345</td>
<td>67</td>
<td>13.5</td>
<td>-</td>
<td>47</td>
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<tr>
<td>Copper</td>
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<td>70</td>
<td>220</td>
<td>391</td>
<td>16.9</td>
<td>-</td>
<td>42</td>
</tr>
</tbody>
</table>

* 0 - 1000°C
** 20 - 400°C
Key Enabling Technology – Metal/Ceramic Joining

Challenges

• Wetting of the Ceramic Substrate
  – Active Braze Alloys – Ti
    • Cusil ABA – 63Ag 35.25Cu 1.75Ti
    • Ticusil – 68.8Ag 26.7Cu 4.5Ti
    • Copper ABA – 92.75Cu 3.0Si 2.0Al 2.25Ti

• Managing residual stresses due to differing Coefficients of Thermal Expansion (CTE)
  – Warping, Delamination, Cracking in SiC Substrate
  – Ductile Interlayer Approach

• Formation of Silicides
  – Nickel and Titanium
All three brazes exhibited excellent wetting of the ceramic.

Nickel within the W alloy and the constituents of Ticusil interdiffused allowing nickel to react with the SiC substrate.

Samples brazed with Copper ABA also exhibited diffusion of the nickel within the W alloy allowing an interaction with SiC.

Samples formed with Hexoloy-SA showed nearly identical microstructure but with some minor stress cracking.
Nickel from the tungsten alloy diffused through the braze layer to form a possible nickel silicide at the SiC-braze interface.

EDS analysis detected Ag along the grain boundaries of W.
Energy Dispersive Spectroscopy (EDS) Analysis of Braze Reaction Layer at W - Copper ABA Interface

<table>
<thead>
<tr>
<th>Point Marker</th>
<th>Si</th>
<th>Ti</th>
<th>Ni</th>
<th>Cu</th>
<th>W</th>
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<td>2</td>
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<td>0.261</td>
<td>8.279</td>
<td>75.169</td>
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</table>

EDS Analysis at Braze Reaction Layer

![Image of EDS Analysis and Micrograph](image-url)
Microstructures of Brazed Mo-SiC Joints

- Cusil ABA appeared to wet both substrates very well.
- Ticusil effectively wet the molybdenum substrate but a large gap was observed between the SiC substrate and the braze.
- Copper ABA wet both the Molybdenum and the SiC very well.
Microstructures of Brazed Mo/Hexoloy-SA Joints

Despite relatively close CTE, residual stresses caused extensive cracking within the Hexoloy-SA substrate.

Samples brazed with Cusil ABA & Copper ABA fractured within the Hexoloy-SA substrate.

Large crack in Hexoloy-SA substrate.
Knoop Microhardness Profiles for SiC-Mo Joints

**CVD SiC - Braze - Molybdenum Hardness Profiles**

<table>
<thead>
<tr>
<th>Material</th>
<th>Cusil ABA</th>
<th>Ticusil</th>
<th>Copper ABA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu$</td>
<td>$\sigma$</td>
<td>$\mu$</td>
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<tr>
<td>CVD SiC</td>
<td>3205.8</td>
<td>185.5</td>
<td>3395</td>
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<tr>
<td>Braze</td>
<td>58.8</td>
<td>0.4</td>
<td>55.35</td>
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<tr>
<td>Molybdenum</td>
<td>324.4</td>
<td>8.5</td>
<td>316.2</td>
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# Energy Dispersive Spectroscopy (EDS) Analysis of SiC – Braze Interface

## Reaction Layer at Braze/SiC Interface

<table>
<thead>
<tr>
<th>Point Marker</th>
<th>Si</th>
<th>Ti</th>
<th>Cu</th>
<th>Mo</th>
<th>Ag</th>
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<td>3</td>
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<td>4</td>
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<td>8</td>
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<td>51.096</td>
<td>9.52</td>
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<td>24.578</td>
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</table>

*20 kV 5kX 5 µm*
Metallic Interlayer Approach Used to Absorb Residual Stresses

- SiC – Cusil ABA – Metal system exhibits good wetting and strong bonding
- Residual stresses are still a major concern
- Ductile interlayer approach is looked at to absorb thermal induced residual stresses
- Ceramic strain energy calculations are used to support ductile interlayer approach
Effect of Ductile Braze Layers on Residual Stresses

Ceramic Strain Energy Calculations

- Finite Element Method (FEM) used to calculate ceramic strain energy
- Analytical results accurate to within 1% of FEM – verified experimentally
- Eq. 1 can represent rectangular joints when interface area is approximated by a suitable \( r \)

\[ U_{e,c} = \frac{\sigma_{yI} r^3}{E_c} \{0.03\Pi_I + 0.11\varphi + 0.49\} \]

where \( \Pi_I = \frac{(\alpha_m - \alpha_c)\Delta T E_I}{\sigma_{yI}} \)

and \( \varphi = \left(\frac{\alpha_m - \alpha_I}{\alpha_c - \alpha_I}\right)^m \)

Calculated Values

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>Strain Energy mJ</th>
<th>Braze Temp. °C</th>
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<tbody>
<tr>
<td>Copper ABA</td>
<td>16.85</td>
<td>1044</td>
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<tr>
<td>Cusil ABA</td>
<td>15.69</td>
<td>825</td>
</tr>
<tr>
<td>Ticusil</td>
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<td>910</td>
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<tr>
<td>Nickel</td>
<td>5.43</td>
<td>825</td>
</tr>
<tr>
<td>Copper</td>
<td>1.22</td>
<td>825</td>
</tr>
</tbody>
</table>

\( \alpha_m = \) CTE for Molybdenum
\( \alpha_c = \) CTE for SiC
\( \alpha_I = \) CTE for interlayer
\( E_c = \) Elastic Modulus for SiC
\( E_I = \) Elastic Modulus for Interlayer
\( \sigma_{yI} = \) Yield Strength of Interlayer
\( \Delta T = \) Braze Temp. – Room Temp.
\( r = \) radius of interface area

Formation of Brittle Phases Using Nickel Interlayers

- Cracking in SiC Due to Brittle Phase Formation
- Cracking in Brittle Phase

Diagram showing layers:
- SiC
- Nickel
- Cusil ABA
- Nickel
- Kovar
Microstructure of W-Cu-SiC Brazed Joint

- Excellent wetting and bonding at all interfaces
- Copper interlayer has eliminated any residual stress cracking within the SiC substrate
- Copper acts as a possible diffusion barrier preventing unwanted silicide formation
Knoop Microhardness Profiles for SiC-Cu-W Joints

<table>
<thead>
<tr>
<th>Material</th>
<th>CVD SiC</th>
<th>Hexoloy-SA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ</td>
<td>σ</td>
</tr>
<tr>
<td>SiC</td>
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<tr>
<td>Cusil ABA</td>
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<tr>
<td>Copper</td>
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<tr>
<td>Cusil ABA</td>
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</tr>
<tr>
<td>HD-18</td>
<td>384.6</td>
<td>22.0</td>
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</table>
Microstructure of Mo-Cu-SiC Brazed Joint

- Excellent wetting and bonding at all interfaces
- Copper interlayer has eliminated any residual stress crack within the SiC substrate
- Possible silicide formation at SiC/braze interface
Energy Dispersive Spectroscopy (EDS) Analysis of SiC – Braze Interface

**Titanium Silicide**

<table>
<thead>
<tr>
<th>Point Marker</th>
<th>Ti</th>
<th>Cu</th>
<th>Mo</th>
<th>Ag</th>
<th>Si</th>
</tr>
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<td>0.312</td>
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<td>57.545</td>
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<td>45.855</td>
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<tr>
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<tr>
<td>5</td>
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<td>10.015</td>
<td>0.018</td>
<td>10.442</td>
<td>32.151</td>
</tr>
</tbody>
</table>
Single Lap Offset (SLO) Shear Testing

- **Testing Conditions**
  - Crosshead speed: 0.5mm/min
  - Air
  - RT, 500°C, 700°C

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

- Cusil ABA offered excellent wetting of the SiC and Metal substrates
- Brazing SiC to Molybdenum or Tungsten introduced residual stresses and caused cracking in the α-SiC substrate despite relatively small CTE mismatch.
- The use of nickel interlayers in a SiC system produced extensive diffusion of the nickel forming a possible nickel silicide
- Copper interlayers proved to be capable of absorbing residual stresses introduced from brazing and acted as a diffusion barrier preventing unwanted silicide and carbide formation
- Initial mechanical testing shows that Mo-SiC joints brazed with a copper interlayer are capable of high strength – failure typically occurred within the ceramic
Acknowledgements

• One of the authors (Bryan C.) would like to thank LERCIP Program at NASA Glenn Research Center for summer research support and the University of Wisconsin-Stout for providing the necessary funding to present this research.