Active Metal Brazing and Adhesive Bonding of Titanium to C/C Composites for Heat Rejection System

M. Singh, Tarah Shpargel, and Jennifer Cerny
QSS Group, Inc.
NASA Glenn Research Center
Cleveland, OH 44135

Gregory N. Morscher
Ohio Aerospace Institute
NASA Glenn Research Center
Cleveland, OH 44135

Robust assembly and integration technologies are critically needed for the manufacturing of heat rejection system (HRS) components for current and future space exploration missions. Active metal brazing and adhesive bonding technologies are being assessed for the bonding of titanium to high conductivity Carbon-Carbon composite sub components in various shapes and sizes. Currently a number of different silver and copper based active metal brazes and adhesive compositions are being evaluated. The joint microstructures were examined using optical microscopy, and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). Several mechanical tests have been employed to ascertain the effectiveness of different brazing and adhesive approaches in tension and in shear that are both simple and representative of the actual system and relatively straightforward in analysis. The results of these mechanical tests along with the fractographic analysis will be discussed. In addition, advantages, technical issues and concerns in using different bonding approaches will also be presented.
Active Metal Brazing and Adhesive Bonding of Titanium to C/C Composites for Heat Rejection System

M. Singh, Tarah Shpargel, and Jennifer Cerny
QSS Group, Inc.
NASA Glenn Research Center
Cleveland, OH 44135

Gregory N. Morscher
Ohio Aerospace Institute
NASA Glenn Research Center
Cleveland, OH 44135
Outline

• Need for Joining and Integration Technologies
• Challenges in Bonding of Metal-Composite System
  • Thermal Expansion
  • Joint Design and Testing
• Active Metal Brazing of Titanium to C/C Composites
  • Microstructural Analysis of Brazed Joints
  • Mechanical Behavior
• Adhesive Bonding of Titanium to C/C Composites
  • Adhesive Selection and Joint Microstructure
  • Mechanical Behavior

• Summary and Conclusions
Thermal Management Technologies are Critical for Space Exploration Systems
Heat Rejection System: Materials and Technologies

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

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

- Titanium

- Bonding/Assembly
  - Active Metal Brazing
  - Adhesives

- Thermal Control Coatings and Treatments

- Mechanical Attachments

- Heat Pipes and Related Technologies
  - Testing and Analysis
  - Lifetime Testing
  - Property Database
  - Performance database
Assembly and Integration Technologies are Key to Manufacturing of Heat Rejection System

Advanced C/C Composite Radiators

Assembly of Composites with Titanium Tubes
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.
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
Active Metal Brazing of Titanium Tubes and Plates to C/C Composites
Active Metal Brazing

- Ti tubes and plates brazed to P120 CVI C/C composite (Goodrich)
- 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 (~ 300 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 Tubes and C-C Composites using TiCuSil Paste

Compositions (atm\%):
1) 92\%Ti, 7\%Cu, 1\%Ag
2) 70\%Ti, 30\%Cu
3) 42\%Ti, 54\%Cu, 4\%Ag
4) 4\%Cu, 96\%Ag
5) 33\%Ti, 63\%Cu, 4\%Ag
6) 84\%Ti, 13\%Cu, 3\%Ag
7) 100\%C
Microstructure of Brazed Ti and C-C Composites using CuSil ABA Paste

Composition:
1) 100%C
2) 1%Ti, 3%Cu, 96%Ag
3) 1%Ti, 95%Cu, 4%Ag
4) 15%Ti, 80%Cu, 4%Ag
5) 43%Ti, 54%Cu, 3%Ag
6) 99%Ti, 1%Ag
Microstructure of Joint Interface in Ti and C-C Composites Brazed using CuSin ABA Foil

Composition:

1) 98% Ti, 1% Cu, 0.5% Ag, 0.5% Sn
2) 61% Ti, 36% Cu, 2% Ag, 2% Sn
3) 37% Ti, 59% Cu, 2% Ag, 2% Sn
4) 28% Ti, 47% Cu, 25% Ag
5) 3% Ti, 84% Cu, 13% Ag
6) 1% Ti, 3% Cu, 96% Ag
7) 100% C
Mechanical Testing of Brazed/Soldered Joints

**Tube Tensile Test**
- C/C composite
- Ti Tube
- Rigid Block
- 12.7 mm
- Applied Load

**Butt Strap Tensile Test**
- Ti
- C/C
- ~9 mm
- 25.4 mm

**Factors to consider:**
- Braze composition, Processing variables
- Bonded area, Location of failure
- Architecture effects
Tube Tensile Test Data for Brazed Joints

- TiCuSil Foil: 41.1
- TiCuSil Paste: 34.2
- Cusil-ABA Foil: 18.7
- Cusil-ABA Paste: 49.7
- Cusin-1ABA Foil: 13.5
- Incusil Foil: 8.2

Best spreading and largest bonded area
Butt Strap Tensile (BST) Test Data

No thermal-induced cracks in C/C

Thermal-induced cracks in C/C

<table>
<thead>
<tr>
<th>Material</th>
<th>Shear Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCuSil ABA Foil</td>
<td>0.90</td>
</tr>
<tr>
<td>TiCuSil ABA Paste</td>
<td>0.80</td>
</tr>
<tr>
<td>CuSil ABA Foil</td>
<td>0.49</td>
</tr>
<tr>
<td>CuSil ABA Paste</td>
<td>1.51</td>
</tr>
<tr>
<td>S Bond Solder</td>
<td></td>
</tr>
<tr>
<td>C/C to C/C w/CuSilABA Paste</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>8.21</td>
</tr>
</tbody>
</table>
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.

\[ \Delta \alpha = \alpha (\text{Ti}) - \alpha (\text{C/C}) \]

\[ \Delta T = T \text{ (liquidus ~ processing)} - 25\degree C \]

<table>
<thead>
<tr>
<th>Joint Material</th>
<th>Proc. Temp., C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-Bond</td>
<td>~ 300</td>
</tr>
<tr>
<td>CuSil ABA</td>
<td>830</td>
</tr>
<tr>
<td>TiCuSil</td>
<td>910</td>
</tr>
</tbody>
</table>
Adhesive Bonding of Titanium to C/C Composites
## Typical Properties of Commercial Adhesives

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Company</th>
<th>Base</th>
<th>Filler</th>
<th>Thermal Conductivity $W/m \cdot K$</th>
<th>Maximum Rated Temperature ($°F$)</th>
<th>$°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramabond 865</td>
<td>Aremco</td>
<td>ceramic</td>
<td>Aluminum Nitride</td>
<td>170 **</td>
<td>3000</td>
<td>1922</td>
</tr>
<tr>
<td>Pyro-duct 597</td>
<td>Aremco</td>
<td>inorganic system</td>
<td>silver</td>
<td>9.1</td>
<td>1200</td>
<td>922</td>
</tr>
<tr>
<td>Aremco-Bond 805</td>
<td>Aremco</td>
<td>epoxy</td>
<td>aluminum</td>
<td>1.8</td>
<td>572</td>
<td>573</td>
</tr>
<tr>
<td>Staytik 501/101</td>
<td>Cookson</td>
<td>thermoplastic</td>
<td>silver</td>
<td>3-3.5</td>
<td>575 *</td>
<td>575</td>
</tr>
<tr>
<td>Resbond 931C</td>
<td>Cotronics</td>
<td>99% pure graphite</td>
<td>graphite</td>
<td>8.65</td>
<td>5400</td>
<td>3255</td>
</tr>
<tr>
<td>Resbond 950</td>
<td>Cotronics</td>
<td>ceramic bonded graphite</td>
<td>graphite</td>
<td>5.78</td>
<td>2500</td>
<td>1644</td>
</tr>
<tr>
<td>Resbond 903HP</td>
<td>Cotronics</td>
<td>ceramic</td>
<td>alumina</td>
<td>5.78</td>
<td>3250</td>
<td>2061</td>
</tr>
<tr>
<td>Resbond 906</td>
<td>Cotronics</td>
<td>ceramic</td>
<td>magnesia</td>
<td>5.78</td>
<td>3000</td>
<td>1922</td>
</tr>
<tr>
<td>Duralco 124</td>
<td>Cotronics</td>
<td>epoxy</td>
<td>silver</td>
<td>7.2</td>
<td>650</td>
<td>616</td>
</tr>
<tr>
<td>Duralco 133</td>
<td>Cotronics</td>
<td>epoxy</td>
<td>aluminum</td>
<td>5.78</td>
<td>600</td>
<td>589</td>
</tr>
<tr>
<td>122-39</td>
<td>Creative Materials</td>
<td>epoxy</td>
<td>Aluminum Nitride</td>
<td>108 **</td>
<td>450 ****</td>
<td>505</td>
</tr>
<tr>
<td>102-32</td>
<td>Creative Materials</td>
<td>silicone</td>
<td>Silver</td>
<td>12.1</td>
<td>500 ****</td>
<td>533</td>
</tr>
<tr>
<td>GC</td>
<td>Dylon</td>
<td>100% carbonaceous</td>
<td>graphite</td>
<td>unknown</td>
<td>5000</td>
<td>3033</td>
</tr>
<tr>
<td>EP45-HTAN</td>
<td>Masterbond</td>
<td>epoxy</td>
<td>Aluminum Nitride</td>
<td>3.6</td>
<td>500 ****</td>
<td>533</td>
</tr>
<tr>
<td>SS-26</td>
<td>Silicone Solutions</td>
<td>silicone</td>
<td>Silver</td>
<td>unknown (high)</td>
<td>500 **</td>
<td>533</td>
</tr>
<tr>
<td>SS-35</td>
<td>Silicone Solutions</td>
<td>silicone</td>
<td>alumina</td>
<td>0.63</td>
<td>500 *</td>
<td>533</td>
</tr>
<tr>
<td>Tra-Bond 813J01</td>
<td>Tra-Con</td>
<td>silicone</td>
<td>Undisclosed</td>
<td>1.1</td>
<td>500 *</td>
<td>533</td>
</tr>
<tr>
<td>FM 680</td>
<td>CTYEK</td>
<td>polyimide</td>
<td>Undisclosed</td>
<td>unknown (low)</td>
<td>700</td>
<td>644</td>
</tr>
</tbody>
</table>

*Listed as 575 to 700°F (575 to 644 K)

**Theoretical, based on the thermal conductivity and % of filler.

***Maybe capable of higher temp, only tested to 500. Silicone stiffens but keeps adhesion above 500.

****Rated by manufacturer to this temperature and "above". Actual high temperature capability limit is untested.
Adhesive Testing and Evaluation (Schematic)

Make three ½" x ½" samples of each adhesive for microscopy: as cured, heat treated @ 325°C (600K) for 24 hours, and liquid nitrogen (-196°C/77K) for 15 minutes.

Poor performance considerations:
These are extreme thermal conditions, if results are poor, can back down high temp to 530K and quench slowly to low temp.

Evaluate microstructure for bond quality, voids, etc.
Poor performance considerations:
Poor Ti bond may be amended by etching/abrating Ti surface. Primers can be used on C/C surface. Vacuum may be needed to remove air incorporated by mechanical mixing.

Screen and order top (20) adhesives based on literature review
Substrates: P120 (pitch based + CVI carbon) C/C from BFG and CP grade 2 Ti plates, as received without and surface treatment.

Microstructure Good Results:
Down-select to top adhesives

Testing:
Thermal Conductivity
Mechanical - tensile and shear using ASTM C297 sandwich tensile and butt strap shear at first RT then HT

Additional testing and evaluation:
Life cycle/aging with thermal cycling
Radiation
Microscopy

Make samples for testing using sample mount for uniformity:
1" circle sandwiches: (1) for thermal conductivity, (5) for tensile test
Butt Strap shear test – (5) each for RT and HT testing: (1) ½ x 1" BFG C/C bonded to (2) ½ x 3" Ti plates, ¼" overlap

Down-select to top (3) adhesives
Currently working on Completed
Microstructure of Adhesive Bonded Ti-C/C Composite Specimens

**As Cured**
- Master Bond EP45HTAN, aluminum nitride filled epoxy rated to 533K. 100x
  - ok
- Aremco Resbond 805, aluminum filled epoxy rated to 573K. 100x
  - ok
- Tra-Con Tra-Bond 813J01, fibrous alumina and silicon filled silicone rated to 500F. 200x
  - ok

**Liquid Nitrogen, 15 minutes**
- Master Bond EP45HTAN, aluminum nitride filled epoxy rated to 533K. 100x
  - ok
- Aremco Resbond 805, aluminum filled epoxy rated to 573K. 100x
  - ok
- Tra-Con Tra-Bond 813J01, fibrous alumina and silicon filled silicone rated to 500F. 200x
  - ok

**Heat Treated 600K with untreated titanium**
- Master Bond EP45HTAN, aluminum nitride filled epoxy rated to 533K. 100x
  - Failure at Ti
- Aremco Resbond 805, aluminum filled epoxy rated to 573K. 100x
  - Failure at Ti
- Tra-Con Tra-Bond 813J01, fibrous alumina and silicon filled silicone rated to 500F. 200x
  - Failure at Ti

**Heat Treated 530K with roughened titanium**
- Master Bond EP45HTAN, aluminum nitride filled epoxy rated to 533K. 100x
  - ok
- Aremco Resbond 805, aluminum filled epoxy rated to 573K. 100x
  - ok
- Tra-Con Tra-Bond 813J01, fibrous alumina and silicon filled silicone rated to 500F. 200x
  - Failure at Ti
Mechanical Testing of Adhesive Joints

• **Butt- Strap Tensile Test**
  – 12.7 mm wide by 25.4 mm long C/C composite bonded to two 12.7 mm wide Ti pieces
  – Tested at RT:
    • as-produced
    • after a liquid nitrogen (15 min) treatment
    • after 530 K (24 hr) heat treatment
• **Ti bonded to P120 CVI C/C (Goodrich)**
• **Three Adhesives Tested:**
  – Aremco-Resbond 805
  – Tra-Con- Tra-Bond 813J01
  – Masterbond- EP45HTAN
• **Future tests will include additional adhesives and testing at elevated temperatures**
Shear Strength of Adhesive Joints

- Aremco 805
- EP45HTAN
- Trabond 813J01

Shear Strength, MPa

As-produced | LN2 Treated | Heat Treated
Fracture Surfaces of BST Shear Specimens

- Aremco-Bond 805 and Tra-bond 813J01 adhesives
- RT tested as-produced, Liq N2 treated and heat-treated (24 hr @ 530 K)

Aremco-Bond 805
- Very strong (failed in C/C) for as-processed and LN2 treated
- Weak after heat treatment (change in fracture surface)

Tra-Bond 813J01
- Moderate strength as-produced (no C/C failure)
- Slight increase in strength with heat-treatment (better adhesion?)
Summary and Conclusions

- Brazing and adhesive bonding technologies are critically needed for the fabrication of heat rejection system components.
- Braze/Solder effectiveness is dictated by several issues: wetting, spreading, bonding, and thermal mismatch.
- Thermal expansion mismatch between C-C/Braze/Titanium and interlaminar properties of C/C composites play a key role in mechanical behavior of joint.
  - CuSil ABA paste was most successful even though not the lowest temperature braze.
  - S-Bond Solder had best shear strengths due to low processing temperature.
- EP45HTAN epoxy has retained highest shear strengths through thermal cycling.
- A combination of tensile, shear, and subcomponent testing of joints coupled with fracture mechanics based design and analysis is needed to generate useful engineering design data.