Sandia Brazing Research and Modeling Capabilities*

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Brazing is widely used to join metals and ceramics to each other for a variety of high reliability components

- headers
- connectors
- feedthroughs
- thermal batteries
- high voltage tubes
- electromechanical devices
- storage containers

**New active brazing alloys simplify hermetic joining issues**

**Basis:** Oxide-forming additives to filler metal (e.g., V, Ti, Zr, Hf) promote direct wetting and adhesion to the ceramic materials (Al₂O₃, Si₃N₄, cermet, …)

**Payoff:** Eliminate complex Mo-Mn metallize / Ni-plate & related processing for conventional alloys

**Issue:** Complex reactions between active braze elements and ceramic/metal base materials need to be understood to control and optimize process

![TEM Image](image1.png)

TiO, Ti₂O & Cu₃Ti₅O reaction products

![TEM Image](image2.png)

SECA SOFC Seal Meeting
July 8-9, 2003
Braze flow visualization and dissolution reactions are important components in understanding the braze process.

Recent Accomplishments
- Conference paper / presentations (IBSC’03; CSM Materials Science Seminar; C6 ASCI Solidification Working Group)
- S&T of Welding & Joining journal paper
- In-Situ Visualization of Braze Flow patent

<table>
<thead>
<tr>
<th>Specimen Temperature (ºC)</th>
<th>Terminal Solidus (wt. % Ni)</th>
<th>EMPA Ni Content (wt. %)</th>
<th>Joint Thickness (µm)</th>
<th>Resident Time Above 1085ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1095</td>
<td>3</td>
<td>6</td>
<td>175</td>
<td>0.5</td>
</tr>
<tr>
<td>1120</td>
<td>12</td>
<td>14</td>
<td>195</td>
<td>1.5</td>
</tr>
<tr>
<td>1145</td>
<td>18</td>
<td>20</td>
<td>210</td>
<td>3</td>
</tr>
<tr>
<td>1140 (H2Frn)</td>
<td>18</td>
<td>10</td>
<td>190</td>
<td>660</td>
</tr>
</tbody>
</table>

Note: At 1145ºC, C_{liquidus} ~ 10 wt. % Ni
Active brazing technology is bridging a wide range of needs because of the fundamental knowledge being developed.

Alumina ceramic / braze interface reactions vary significantly with active element.

Fracture strengths for 94 & 99.8% alumina brazed with Ti & V-bearing Au-Ni filler metals exhibit dependency on glassy phase and more stable TiO\textsubscript{x} reaction product.
A multidisciplinary approach to characterizing the different brazing reactions and properties is necessary for success.

Determining effects of reaction products & microstructures on properties (hermeticity & strength) as a function of active element (thermodynamics / kinetics), base material (adhesion / dissolution), brazing conditions (temperature, time, atmosphere, heating cycle & gradients, orientation), surface preparation (ceramic air-firing).
Ability to correlate braze interface reactions with desired properties will yield more producible & reliable joints

BSE image shows continuous HfO$_2$ reaction layer at ceramic interface

Trace From Kovar Through Ag - 3.4Hf Braze Alloy into Alumina (Trace 3)
Sample Brazed 990°C/10 min., dry H$_2$

BSE image shows continuous HfO$_2$ reaction layer at ceramic interface

- Single crystal sapphire & polycrystalline alumina brazed with Ag-2Zr
- 94% alumina brazed with Ag-2Zr is hermetic, fails in the bulk ceramic and has 130 MPa tensile strength

Ag-3.4Hf ceramic braze joints also demonstrate similar excellent properties (hermetic & 125 MPa)

Recent Accomplishments
- Implementation of active brazing in production
- Conference paper / presentations (ASM Materials Solutions 2002; AWS IBSC’03; ACerS 2003)
- Metallurgical Transactions A paper (in publication)
- Coating System for Direct Ceramic Brazing patents
Diffusion bonding offers an alternative joining process

Ceramic-metal and metal-metal joints are possible

a) Hard ceramic and comparatively soft metal surfaces come in contact (T, t, P)
b) Metal surface yields under high local stresses
c) Deformation continues mainly in the metal, leading to interface diffusion & void shrinkage
d) Metallurgical bond is formed

FEA Brazing Model Development & Validation

Thermal Responses

Fixtured Assembly

Stress & Failure Predictions

Fluid Flow Responses

Engineering Sciences Center Simulations

Design & Production
FEA Thermal Modeling of Furnace Brazing

- Nonlinear, 3-D transient thermal finite element code
- Ability to mesh very fine details (large node and surface radiation enclosure)

Typical Model Inputs
- materials density
- thermal conductivity
- specific heat
- emissivity
- thermal boundary conditions

Simulations processed on massively parallel teraflop compute server

- convective heating by hydrogen gas is assumed negligible
- heating driven by radiation from furnace elements & conduction from Mo shelves to work piece
Example: Two-Step, Cu + 50Au-50Cu Braze Assembly Process Characterization

FEA Thermal Model

Braze Fixture

- housing weight
- ceramic ring
- backup ring
- fixture alignment
- frame
- Cu 1st Braze
- backup ring

Oven - 1/2 section

- backup ring weight
- pins
- small flange
- Au-Cu 2nd Braze
- housing
- large flange
- base
- housing frame
- backup ring
- ceramic ring
- backup ring

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Process Space Simulations

Process Space:
• Thermal boundary conditions:
  – 1st ramp rate (10, 40°C/min)
  – 1st hold time (5, 25 min)
  – 1st hold temp (930, 960°C)
  – 2nd ramp rate (10, 40°C/min)
  – peak temp (1000, 1030°C)
  – time @ peak temp (0, 10 min)
  – cooling rate (10, 40°C/min)
• Number of shelves (4, 7)
• Number of fixtures/shelf (2, 5)
• Shelf type (solid, perforated)
• Fixture material (Mo, Kovar®)
• Emissivity (low, high)

Data acquired:
• Peak brazing temperature
• Time braze is melted
• Temperature uniformity
• Determine optimization parameters in process space versus experimental “point solutions”

Trends at Peak Temperature:
• Top and bottom shelves are hottest (trim heater settings)
• Middle shelf most uniform
• Center unit of five on each shelf is coolest (~ 5°C lower)
• 10 min. hold at set temp. gives uniform heating, but increases time above melting
• Brazeing temperature is uniform within individual units

Two-level fractional factorial design for 12 factors in 16 unique trials
Example: DoE$_{x}$ Screening Sensitivities for Thermal Characterization of Brazing Process

Factor sensitivities to the brazing conditions on the central shelf

--- main effect factor significance