High-Temperature Corrosion of Diffusion Bonded Ni-Based Superalloys in CO₂

The 5th International Supercritical CO₂ Power Cycles Symposium, San Antonio, TX, March 28-31, 2016

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Supercritical CO₂ Power Cycles

**Indirect sCO₂ Cycle**

- **Main Compressor**
- **Recycle Compressor**
- **sCO₂ Turbine**
- **Heater**
- **Low Temperature Recuperator**
- **High Temperature Recuperator**

**Direct sCO₂ Cycle**

- **Pressurized Oxy-combustion**
- **sCO₂ Turbine**
- **Primary Heat Exchanger**
- **Generator**

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<table>
<thead>
<tr>
<th>Cycle/Component</th>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (C)</td>
<td>P (MPa)</td>
</tr>
<tr>
<td>Indirect</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater</td>
<td>450-535</td>
<td>1-10</td>
</tr>
<tr>
<td>Turbine</td>
<td>650-750</td>
<td>20-30</td>
</tr>
<tr>
<td>HX</td>
<td>550-650</td>
<td>8-10</td>
</tr>
<tr>
<td>Direct</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustor</td>
<td>750</td>
<td>20-30</td>
</tr>
<tr>
<td>Turbine</td>
<td>1150</td>
<td>20-30</td>
</tr>
<tr>
<td>HX</td>
<td>800</td>
<td>3-8</td>
</tr>
</tbody>
</table>

Essentially pure CO₂

CO₂ with combustion products including H₂O, O₂, and SO₂
Compact Heat Exchangers

• Higher efficiency
  – Due to much shorter heat diffusion lengths in fluid

• Smaller size
  – Use of less materials (expensive superalloys)
  – Takes less space

• Modular design
  – Expandable to large power plants
Microlamination-

1. Pattern microscale flow paths into laminae using a variety of methods (etching, micromachining, laser cutting, EDM, others)

2. Bond these laminae using a variety of methods (diffusion bonding, laser welding, brazing, others). For sCO$_2$, diffusion bonding and brazing are the most robust approaches


Oregon State University
### Nominal chemical composition (weight %) of materials used in this study (Haynes 230 and Haynes 282)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>W</th>
<th>Ti</th>
<th>Mo</th>
<th>Fe</th>
<th>Co</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>H230</td>
<td>57</td>
<td>22</td>
<td>14</td>
<td>--</td>
<td>2</td>
<td>3*</td>
<td>5*</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.10</td>
<td>0.015*</td>
</tr>
<tr>
<td>H282</td>
<td>57</td>
<td>19.5</td>
<td>--</td>
<td>2.1</td>
<td>8.5</td>
<td>1.5*</td>
<td>10</td>
<td>0.3*</td>
<td>0.15*</td>
<td>1.5</td>
<td>0.06</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* = maximum

- **Haynes 230**: Solid-solution strengthened, Cold rolled and 1232 °C solution annealed sheet
- **Haynes 282**: Precipitation strengthened, 1149 °C solution annealed sheet
Diffusion Bonding

• Sheets were water-jet cut into shims
• 100 shims were bonded together in each stack
• All shims were reverse current etched and cleaned with acetone
• Some stacks used shims plated with electroless nickel, 2 - 4 µm thick
• Some shims contained pin-fin microfeatures identical to those used in a heat exchanger
• All shims were thoroughly cleaned by hand and in an ultrasonic acetone bath for 15 minutes immediately before bonding
Diffusion Bonding

- Shim stacks were held in a fixture during bonding and pressure was applied only after the temperature ramped up to the desired value.
- The hot press vacuum was maintained at approximately $5 \times 10^{-6}$ torr (0.0007 Pa).
- 1150°C for 8 hours at 12.7 MPa.
- After bonding, each stack was machined to produce 6 tensile specimens using wire EDM and a CNC lathe.
- After bonding, H230 experienced approximately 4.1% strain (2.5% predicted by model).
- H282 without Ni plating did not bond well.
Wednesday – March 30th
8:50 am
Session: Heat Exchangers III
Salon A

Diffusion Bonding of H230 Ni-superalloy for application in microchannel heat exchangers
M. Kapoor, Ö. Doğan, K. Rozman, J. Hawk, A. Wilson, T. L’Estrange, V. Narayanan

The 5th International Symposium - Supercritical CO2 Power Cycles
March 28-31, 2016, San Antonio, Texas

March 30th 2016
Diffusion Bonding

- Diffusion bonding is the “weak link” in the fabrication process.
- Sharp edges in the architecture lead to locations of high stress concentration in the mechanical design simulations.
- **We need information on**
  - The parameters for diffusion bonding ($T, P, t$) for these superalloys.
  - The strength of the diffusion bond.
  - Whether the high stress concentration predicted by the mechanical design simulations is indeed a problem or not.
  - Corrosion behavior of diffusion bonded regions in sCO$_2$. 
Oxidation tests

Gas: 1 bar CO₂ (99.999% purity)
Gas flow rate: 0.032 kg/h
Temperature: 700°C
Duration: 500 h
24 h purging with CO₂ before heating

Characterization
Mass Change
XRD
SEM
Unlike in sH₂O, there is no evidence of increased oxidation rates at high pressure in sCO₂

Thursday – March 31st
9:00 am
Session: Materials I
Salon C
Oxidation Results

Mass changes as a result of the CO₂ exposure at 700°C for 500 h. Averages and standard deviations are from three coupons for each condition.

<table>
<thead>
<tr>
<th></th>
<th>Average mass change (mg/cm²)</th>
<th>Standard deviation (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H230</td>
<td>0.077</td>
<td>0.012</td>
</tr>
<tr>
<td>H230-DB</td>
<td>0.115</td>
<td>0.013</td>
</tr>
<tr>
<td>H230-DB-Ni</td>
<td>0.112</td>
<td>0.005</td>
</tr>
<tr>
<td>H282</td>
<td>0.038</td>
<td>0.022</td>
</tr>
<tr>
<td>H282-DB-Ni</td>
<td>0.236</td>
<td>0.008</td>
</tr>
</tbody>
</table>

H230: Minor mass change increase
H282: More significant mass change increase
XRD signal from both oxide scale and underlying alloy
Chromia oxide scales form on both alloys
H230 contains W and Mo rich M₆C carbides
H282 contains γ’ precipitates, Ni₃(Al,Ti), but was not detected by XRD
SEM on the surface of oxidized samples

Cr$_2$O$_3$ grains 5-10 µm
Cr$_2$O$_3$ grains 5-10 µm
Cr$_2$O$_3$ grains 1-5 µm

H230-DB-Ni  
H230-DB  
H282-DB-Ni

Dense, fine-grained, oxide scales  
No observed differences in H230 between bond and non-bond areas  
Some contrast differences in H282 in and near bond areas

Secondary Electron Images
Slight Ni enrichment and Cr depletion were detected using x-ray elemental mapping on the bond regions of the H230-DB-Ni. The other elements did not show a detectable variation.

Ni plating was 2-4 µm (4-8 µm total for each bond), so bond area reflects diffusion zone.
SEM on the surface of oxidized samples – H282-DB-Ni

Elemental X-ray maps acquired on one of the bond regions of the H282-DB-Ni coupon after the 500 h CO$_2$ exposure at 700°C.

Enrichment of Ni, Al, Mo, Co in the bond region

Lower Cr in bond region
SEM on the cross-sections of oxidized samples

H230-DB-Ni

(a) Cr-oxide scale

5 μm

H230-DB

(b) γ′-free zone
γ′ zone

5 μm

H282-DB-Ni

(c) γ′-free zone
γ′ zone

5 μm

(d) Internal Al- and Si-oxides
Mn-rich Cr-oxide scale

5 μm

(e) M₆C

5 μm

(f) Internal Al-oxides

5 μm

No significant difference between bond regions and away from bond regions

More internal oxidation in H282, resulting from higher Al and Ti levels

γ′ loss in H282 below the internal oxidation layer

Back-Scattered Electron Images
SEM on the cross-sections of oxidized samples – H230-DB-Ni

X-ray maps of select elements for H230-DB-Ni far from the DB interface. W and Si were acquired in WDS mode and all other elements were collected in EDS mode.
SEM on the cross-sections of oxidized samples – H282-DB-Ni

X-ray (EDS) maps of select elements for H282-DB-Ni far from the DB interface
Summary

- As determined after a 500 h exposure to CO₂ at 700°C, diffusion bonding was not detrimental to the oxidation resistance of the H230. The diffusion bond regions of H230 did not exhibit an accelerated oxidation.

- Diffusion bonding of H282 resulted in increased mass gains during oxidation. However, a chromia scale was still formed, and overall oxidation rates were still low.
Materials Degradation in Supercritical CO$_2$ Power Cycles
Materials Science and Technology (MS&T) Conference

October 23-27, 2016
Salt Lake City, Utah

Abstracts are due on March 31, 2016
and can be submitted on ProgramMaster:
http://www.programmaster.org/PM/PM.nsf/Home?OpenForm&ParentUNID=F9FD0D2AAFA2D29285257D86004BE7A3
### Supercritical \( \text{CO}_2 \) Power Cycles

<table>
<thead>
<tr>
<th>Properties of sCO2 Cycles</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>No phase change (Brayton Cycle)</td>
<td>Higher efficiency</td>
</tr>
<tr>
<td>Recompression near liquid densities</td>
<td>Higher efficiency</td>
</tr>
<tr>
<td>High heat recuperation</td>
<td>Higher efficiency, Large HX footprint</td>
</tr>
<tr>
<td>Compact turbo machinery</td>
<td>Lower capital cost</td>
</tr>
<tr>
<td>Simple configurations</td>
<td>Lower capital cost</td>
</tr>
<tr>
<td>Dry/reduced water cooling</td>
<td>Lower environmental impact</td>
</tr>
<tr>
<td>Storage ready ( \text{CO}_2 ) in direct cycles</td>
<td>Lower environmental impact</td>
</tr>
</tbody>
</table>

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**S. A. Wright**, "OVERVIEW OF SUPERCRITICAL \( \text{CO}_2 \) POWER CYCLE DEVELOPMENT AT SANDIA NATIONAL LABORATORIES," in 2011 University Turbine Systems Research Workshop, Columbus, Ohio, 2011.