Materials Evaluation and Corrosion Test Needs for a Direct-Fired sCO2 Oxy-Combustion Plant

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Hanwha Power Systems

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Korea Electric Power Corporation
Presentation Overview

• Oxy-Combustion Application
• Overview of Materials
• Existing Test Data & Oxy-Combustion Variables of Interest
• Materials of Interest
  • 400 – 500 °C
  • 650 – 750 °C
• Future Test Needs and Recommendations
Oxy-Combustion Plant Application

• sCO2 oxy-combustion cycles have potential for
  • High thermal and plant efficiencies
  • Reduced CO2 emissions

• KEPCO Research Institute leading project to develop an oxy-combustion gas turbine power plant
  • Minimize development risk with maximum turbine inlet conditions of 750 °C and 300 bara.
  • Hanwha Power Systems (turbomachinery)
  • Southwest Research Institute (ox-combustor)
  • Other academic Institutions in Korea and U.S.
What’s an Oxy-Combustion sCO₂ Cycle?

Closed Loop Composition is Affected by Air Separation, Combustion, and Cleanup

sCO₂ MATERIALS FOR OXY-COMBUSTION
Oxy-Combustor Material Needs

- Combustor pressure vessel at process temperature
- Injector, liner cooled by process but at higher temperatures, lower stress
- Two temperature ranges identified:
  - 400 – 500 °C
  - 650 – 750 °C
Why Focus on Corrosion?

- The **majority of metal alloys** will corrode.
- Corrosion affects **every industry**: Infrastructure, Utilities, Transportation, Production & Manufacturing, Government
- Engineering design usually increase corrosion issues.
- Corrosion is **expensive**: estimated between B$575 (3.1% GDP) to T$1.1 (6% GDP).
Materials Deterioration in sCO$_2$

- **Corrosion:**
  - Reaction of metals with oxygen.
  - Oxygen comes from: $\text{CO}_2 = 0.5 \text{O}_2 + \text{CO}$.
  - Growth of oxide film layer.

- **Carburization:**
  - Cr reacts with C → chromium carbide.
  - Carbon penetrate through grain boundary.
  - Carburization leads to spalliation of oxide films.
Materials of Interest

• 5 families of materials:
  • **MFSS**: martensitic stainless steels (10%-30% Cr) and ferritic stainless steels (12%-17% Cr with 0.15 – 0.63% C)
  • **ASS**: austenitic stainless steels (16 to 30% chromium and 2 to 20% nickel).
  • **Al SS**: alumina oxide austenitic stainless steels.
  • **CrNi**: chromium nickel alloys.
  • **AlNi**: alumina oxide nickel alloys.
## Experimental Methods Summary

<table>
<thead>
<tr>
<th>Method</th>
<th>Measure</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight measurement</td>
<td>Oxide film growth</td>
<td>• Easy</td>
<td>• No carburization/corrosion product differentiation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Cheap</td>
<td>• Spalliation and material loss affect measurement.</td>
</tr>
<tr>
<td>Micro hardness</td>
<td>Carburization</td>
<td>Easy</td>
<td>Coupled with SEM/EDS to confirm carburization</td>
</tr>
<tr>
<td>SEM/EDS</td>
<td>Oxide film morphology and composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile test</td>
<td>mechanical properties</td>
<td>Environmental effect on mechanical properties</td>
<td>Only after exposure</td>
</tr>
<tr>
<td>GENERAL</td>
<td></td>
<td></td>
<td>Lack of in-situ (HTHP problem)</td>
</tr>
</tbody>
</table>
Effect of Temperature

Temperature $\uparrow$ = worsen corrosion, increase carburization

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>660</th>
<th>650</th>
<th>700</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>900</th>
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</thead>
<tbody>
<tr>
<td>Type of alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Based on combination of mass gain, oxide thickness, presence of crack, carburization, etc...:

**Green**: acceptable

**Red**: avoid

Alumina alloys are not good at low temperature because the alumina oxide does not form fast enough.
Contamination of $\text{sCO}_2$ with $\text{O}_2$

- Contamination with $\text{O}_2$, water, and combination of both.
  - $\text{O}_2$: may be beneficial or detrimental.
  - Water: accelerates corrosion.
  - Combination: accelerates corrosion.

Contamination of sCO$_2$ with H$_2$O

- Contamination with water accelerates corrosion.
- Impact of water on weight change in sCO$_2$ at 8 MPa, 40°C.

S. Sim, et al., Corrosion, 2, 2014
Coating

- Thermal barrier coating (TBC) for corrosion protection:
  - Diffusion bond coatings (Pt diffusion or simple or Pt-modified aluminide) with commercially vapor-deposited yttria-stabilized zirconia (YSZ) top coatings.
  - High velocity oxygen fuel (HVOF) sprayed MCrAlYHfSi bond coatings with air-plasma sprayed YSZ top coatings.

- Data only at higher temperature (1150°C): failure after 2260 1 hr cycles.
- CO₂ and/or air contamination reduces the time to failure.
- Intrinsic damages: oxide growth, internal stresses leading to cracking and failure.
- Extrinsic damages: erosion, local damages due to impact or particles melting, diffusing, and hardening the top coat leading to potential failure.
### Chosen Materials – 400-500°C Combustor Inlet & Pressure Vessel

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>UNS</th>
<th>Standard Specification</th>
<th>Notes</th>
<th>Max Temperature Limit [°C] (BPV Code Section)</th>
<th>Allowable Stress at 500°C [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr91</td>
<td>K90901</td>
<td>ASTM A387 Grade 91 Class 2</td>
<td>Reference. Most commonly tested MFSS.</td>
<td>649 (VIII-2)</td>
<td>204</td>
</tr>
<tr>
<td>800H</td>
<td>N08800</td>
<td>ASTM B407</td>
<td></td>
<td>816 (VIII-2)</td>
<td>138</td>
</tr>
<tr>
<td>310</td>
<td>S31000</td>
<td>ASTM A965</td>
<td></td>
<td>816 (VIII-2)</td>
<td>116</td>
</tr>
<tr>
<td>347H/347HF G</td>
<td>S34709</td>
<td>ASTM A965</td>
<td></td>
<td>816 (VIII-2)</td>
<td>125</td>
</tr>
</tbody>
</table>
## Alternative Materials – 400-500°C Combustor Inlet & Pressure Vessel

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>UNS</th>
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<th>Max Temperature Limit [°C] (BPV Code Section)</th>
<th>Allowable Stress at 500°C [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>625</td>
<td>N06625</td>
<td>ASTM B443</td>
<td>593 (I) or 649 (VIII-1)</td>
<td>192</td>
</tr>
<tr>
<td>HK40</td>
<td>J94204</td>
<td>ASTM A351</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HK50</td>
<td>J94224</td>
<td>ASTM A297</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>310HCbN/HR3C</td>
<td>S31042</td>
<td>ASTM A959</td>
<td>732 (I)</td>
<td>117-158</td>
</tr>
<tr>
<td>NF709</td>
<td>S31025</td>
<td>ASTM A213</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HR120</td>
<td>N08120</td>
<td>ASTM B515</td>
<td>899 (VIII-1)</td>
<td>113-153</td>
</tr>
</tbody>
</table>
## Chosen Materials – 650-750°C Combustor Exit & Liner

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>UNS</th>
<th>Standard Specs</th>
<th>Max Temperature Limit [°C] (BPV Code Section)</th>
<th>Allowable Stress at 500°C [MPa]</th>
<th>Yield Strength at 750-760°C [MPa]</th>
<th>Creep Rupture Strength at 750°C [MPa] (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>740H</td>
<td>N07740</td>
<td>ASTM B983</td>
<td>800 (I)</td>
<td>84.1</td>
<td>596</td>
<td>200 (10k)</td>
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<tr>
<td>282</td>
<td>N07208</td>
<td>ASTM B637-12</td>
<td>800 (est.)</td>
<td>105 (est.)</td>
<td>612</td>
<td>186 (10k)</td>
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<tr>
<td>230</td>
<td>N06230</td>
<td>ASTM B572-06</td>
<td>982 (VIII-1)</td>
<td>50.8</td>
<td>323</td>
<td>91-98 (10k)</td>
</tr>
</tbody>
</table>
## Alternative Materials – 650-750°C Combustor Exit & Liner

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>UNS</th>
<th>Standard Specs</th>
<th>Max Temperature Limit [°C] (BPV Code Section)</th>
<th>Allowable Stress at 500°C [MPa]</th>
<th>Yield Strength at 750-760°C [MPa]</th>
<th>Creep Rupture Strength at 750°C [MPa] (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waspaloy</td>
<td>N07001</td>
<td>ASTM B637</td>
<td>-</td>
<td>706</td>
<td>770</td>
<td>290 (1k)</td>
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<tr>
<td>Udimet 720</td>
<td>N07720</td>
<td>n/a</td>
<td>-</td>
<td>770</td>
<td>938</td>
<td>480 (1k)</td>
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<tr>
<td>Rene 41</td>
<td>N07041</td>
<td>SAE AS7469B</td>
<td>-</td>
<td>938</td>
<td>276</td>
<td>276 (1k)</td>
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<tr>
<td>617</td>
<td>N06617</td>
<td>ASTM B167</td>
<td>982 (VIII-1)</td>
<td>50.4</td>
<td>872</td>
<td>140 (1k)</td>
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<tr>
<td>MA 754</td>
<td>N07754</td>
<td>n/a</td>
<td>-</td>
<td>275</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>N06002</td>
<td>ASTM B572-06</td>
<td>482 (VII-2)</td>
<td>-</td>
<td>218</td>
<td>107 (1k)</td>
</tr>
</tbody>
</table>
Proposed Materials: Existing Data in sCO₂, constant pressure.

- Data adjust to mass gain in \( \mu g/(cm^2 \cdot hr) \) because not all tests are the same duration.
- Increase in mass gain with increase in temperature at 20 MPa.

References:
Cao, G., et al., Corrosion Science, 60, 2012
Jelinek, J.J., et al., NACE Paper C2012-1428
Pint, B.A., et al., NACE Paper C2016-7747
Proposed Materials: Existing Data in sCO₂, constant temperature.

- No visible trend of mass gain with increase in pressure at 750°C.
- High temperature materials had lower mass gain than low temperature materials.

References:
Pint, B.A., et al., NACE Paper C2016-7747
Test Plan – Variables of Interest

- **Temperature**: low (combustor inlet) and high (high temperature)
- **Pressure**: high pressure based on design
- **Contamination** \((O_2, H_2O)\): \(CO_2, H_2O, \text{ and } O_2\) mixture matching predicted composition at combustor inlet (low temperature) and exit (high temperature).
- **Welding**: potential negative impact on the corrosion behavior of chromium-containing alloys
Test Plan – Variables of Interest

• **Stress corrosion cracking**: corrosion combined with stress can lead to early mechanical failure.

• **Galvanic corrosion**: corrosion may worsen when dissimilar materials are in contact.

• **Coating**: testing bare and coating materials vapor deposited YSZ, and air-plasma sprayed YSZ.
Test Plan

- The recommended tests in O₂/H₂O/CO₂ are:
  - **High Temp Weight Gain with Tensile Test**
  - **High Temp C-Ring/U bend**
  - **Low Temp Weight Gain with Tensile Test**
  - **High Temp Welding**
  - **Low Temp C-Ring/U bend**
  - Micro hardness

- Statistic: 5 specimens for each test.
- Combine all low temperature and all high temperature.