Zirconium Alloys with Small Amounts of Iron and Copper or Nickel Show Improved Corrosion Resistance in Superheated Steam

Effect of metallurgical condition on corrosion of Zr-1.1 Cu-0.7 Fe (AE-13) in deoxygenated steam at 540°C and 600 psi.

Effect of metallurgical condition on corrosion of Zr-3 Ni-0.5 Fe (AE-10) in deoxygenated steam at 540°C and 600 psi.

The problem:
To improve the corrosion resistance of zirconium alloys to superheated steam at temperatures higher than 500°C.

Zirconium alloys serve as fuel cladding for water cooled nuclear-fueled reactors and have potential as fuel cladding for superheated-steam nuclear-fueled reactors as well as in autoclaves operating at modest pressures. However, commercial zirconium alloys experience severe corrosion when exposed to superheated steam. For example, Zircaloy 2 and Zircaloy 3 samples show corrosion weight gain rates of 265 to 4600 mg/sq dm/day (mdd) in deaerated steam at 540°C and 600 psi.

The solution:
Heat treat various compositions of zirconium alloys.

Composition of Heat Treated Zirconium Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE 10</td>
<td>0.6</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>AE 11</td>
<td>0.6</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>AE 12</td>
<td>0.5</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>AE 13</td>
<td>1.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>AE 15</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>AE 16</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

Heat Treatments Studied

<table>
<thead>
<tr>
<th>Code</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Hot roll + cold roll (reduction &lt;20%)</td>
</tr>
<tr>
<td>H</td>
<td>Hot roll</td>
</tr>
<tr>
<td>QH</td>
<td>Hot roll + quench from 900°C</td>
</tr>
<tr>
<td>AH</td>
<td>Hot roll + quench from 900°C + age at 700°C for 1 hr*</td>
</tr>
</tbody>
</table>

(continued overleaf)
RH Hot roll + quench from 900°C + cold roll (reduction <20%)
RHA Hot roll + quench from 900°C + cold roll (reduction <20%) + age at 700°C for 1 hr*

*Air-cooled in capsule from aging temperature.

Zirconium alloys have exhibited weight gain rates as low as 4 mg/dm²/day in deaerated steam at 540°C and 600 psi. Results for two of the better alloys are shown.

The following trends are observed:
1. Material having a higher total alloy content in the range studied exhibits a lower corrosion rate.
2. Corrosion rate is sensitive to metallurgical condition. Quenched material has a lower corrosion rate for short periods, but the structure is not stable. No long range improvement was accomplished by further heat treatment of hot rolled samples.
3. Flow of steam up to 300 ft/sec at 650°C and 600 psi does not affect corrosion rate. Corrosion rate is relatively insensitive to pressure in the range of 1 ton to 600 psi.
4. The presence of 30 ppm of oxygen or a mixture of 30 ppm of oxygen and 3.75 ppm of hydrogen in the steam at 650°C and 600 psi does not affect corrosion rate.
5. Absorption of corrosion-product hydrogen after long exposure is relatively insensitive to metallurgical condition and alloy composition.
6. Absorption of corrosion-product hydrogen decreases markedly as exposure temperatures is raised from 540°C to 650°C.
7. Metal embrittlement due to oxygen absorption becomes an increasingly serious problem as temperature is raised.
8. No correlation was observed between oxygen absorption and corrosion rate.
9. Sharp edges are vulnerable to film edge cracking and consequent loss of corrosion product. Component design should take this behavior into consideration.

Notes:
1. Corrosion resistance tests are performed at flow rates of <0.5 ft/min, 540°C or 650°C, and 600 psi under deaerated conditions, or are performed at 300 ft/sec, 650°C, and 600 psi under deaerated or under aerated (oxygen or a mixture of oxygen and hydrogen added to the steam) conditions.
2. Corrosion is determined in terms of rate of weight gain.
3. Hydrogen absorption is determined by vacuum extraction at 1200°C.
4. Oxygen absorption is determined by heating the alloy in a graphite crucible and titrating the resultant carbon dioxide.
5. Other heat treatments studied include the combination of hot roll, cold roll and reduction, and quenching treatments in various sequences.
6. Additional details are contained in: Corrosion, vol. 21, no. 4, p. 113-124 (1965) April.
7. Inquiries concerning this innovation may be directed to:

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Patent status:
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