Zirconium Cladding

Why?

- Physical Properties
- Corrosion Resistance
- Radiation Effects

In the early 1950’s the Navy was looking for a material with:

- low $\sigma_a$
- high corrosion resistance
- high strength

Disadvantages of Zr in early 1950's;

- poor ductility
- poor corrosion resistance
- high cost
- difficult fabrication

1943 - Zr produced by iodide process

- $\approx 1400 \$$/kg
- $\approx 0.05$ kg in entire country
- $\sigma_a = 105$ barns

1948 - cost 280 to 500 $$/kg

- production rate $\approx 40$ kg/y
- $\sigma_a = 0.4$ barns (removed Hf impurity, 1.5 to 2.5% in most Zr ores)

1953 - cost 30 to 70 $$/kg

- 125,000 kg/y
- $\sigma_a = 0.18$ barns

( first Mark I STR core - Zr)
( second Mark II STR core - Zr alloy)
Table 1
Neutron Economy of Various Metals Compared to Zr

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Ultimate Strength @ 300 °C (MPa)</th>
<th>Macroscopic Thermal Neutron Xsection, cm⁻¹</th>
<th>Relative Neutron Absorption for Given Design Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>900</td>
<td>0.010</td>
<td>1</td>
</tr>
<tr>
<td>Be</td>
<td>350</td>
<td>0.001</td>
<td>0.5</td>
</tr>
<tr>
<td>Mg</td>
<td>90</td>
<td>0.005</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>90</td>
<td>0.014</td>
<td>14</td>
</tr>
<tr>
<td>Fe</td>
<td>1100</td>
<td>0.170</td>
<td>14</td>
</tr>
<tr>
<td>Ni</td>
<td>1100</td>
<td>0.310</td>
<td>25</td>
</tr>
<tr>
<td>Ti</td>
<td>1000</td>
<td>0.260</td>
<td>28</td>
</tr>
</tbody>
</table>

Physical Properties

Phase transformations; Phase Diagram
α - up to 865 °C - hcp
β - 865 to 1845 °C - bcc

Mechanical properties:

- Can increase the strength by cold working but the recrystallization temperature is ≈ 400 to 500 °C
- Oxygen-Strengthens and embrittles Zr
- Hydrogen-(hydrides) reduces ductility
<table>
<thead>
<tr>
<th>Property</th>
<th>Al</th>
<th>Zr</th>
<th>Zircaloy-2</th>
<th>347SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cc</td>
<td>2.71</td>
<td>6.5</td>
<td>6.55</td>
<td>7.98</td>
</tr>
<tr>
<td>Melting T, °C</td>
<td>660</td>
<td>1845</td>
<td>=1830</td>
<td>=1399</td>
</tr>
<tr>
<td>Trans. T, °C</td>
<td>-</td>
<td>862</td>
<td>=1000</td>
<td>-</td>
</tr>
<tr>
<td>Recryst. T, °C</td>
<td>150-290</td>
<td>450-550</td>
<td>550-600</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha \times 10^{-4}/^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-100°C</td>
<td>23.5</td>
<td>6.38</td>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>25-200</td>
<td>24.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-300</td>
<td>25.6</td>
<td>7.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-500</td>
<td>9.46</td>
<td></td>
<td></td>
<td>18.0</td>
</tr>
<tr>
<td>25-700</td>
<td>6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k-cal/cm-s-°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>0.53</td>
<td>0.050</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0.049</td>
<td>0.034</td>
<td>0.038</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>0.042</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>538</td>
<td></td>
<td></td>
<td></td>
<td>0.051</td>
</tr>
<tr>
<td>Thermal n Xsection-b</td>
<td>0.22</td>
<td>0.18</td>
<td>&gt;0.18</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>Ultimate Strength-psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>13,000</td>
<td>34,800</td>
<td>68,600</td>
<td>90,000</td>
</tr>
<tr>
<td>100</td>
<td>9,700</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>6,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2,500</td>
<td>18,000</td>
<td>12,000</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1,300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>8,000</td>
<td>22,000</td>
<td>65,000</td>
<td></td>
</tr>
<tr>
<td>Yield Strength-psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>5,000</td>
<td>9,900</td>
<td>44,800</td>
<td>35,000</td>
</tr>
<tr>
<td>100</td>
<td>4,100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>3,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1,500</td>
<td>6,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>800</td>
<td>4,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>5,000</td>
<td>10,500</td>
<td>31,000</td>
<td></td>
</tr>
<tr>
<td>Elongation-%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>45</td>
<td>47</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>100</td>
<td>57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>90</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>93</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>48</td>
<td>36</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>
Corrosion

Pure Zr exhibits fairly good resistance to corrosion by water at elevated temperatures, but the material can develop some weight gain.

Figure on Mechanism
Figure on Flaking

- At 316°C, VHP Zr does not reach breakaway in 200 days
- At 360°C, VHP Zr does reach breakaway in less than 7 days

Figure 15-8

Effect of Impurities

Table IV

Small amounts of Sn, Ta, and Nb can counter impurities.

<table>
<thead>
<tr>
<th>Zircaloy (USA)</th>
<th>Bad Neutronics (Canada)</th>
<th>Higher Strength (USSR)</th>
</tr>
</thead>
</table>

Figures 15-6 and 15-7
• Even the rates @ 316 and 399°C (5 to 15 x 10^{-4} cm / y) are small compared to a 1 mm cladding thickness (Figure 15-8)

### Composition of Commercial Zr Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zr</th>
<th>Sn</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zir -II</td>
<td>98.2</td>
<td>1.5</td>
<td>0.12</td>
<td>0.10</td>
<td>0.05</td>
<td>--</td>
<td>0.13</td>
</tr>
<tr>
<td>Zir -IV</td>
<td>98.2</td>
<td>1.3</td>
<td>0.22</td>
<td>0.10</td>
<td>--</td>
<td>--</td>
<td>0.13</td>
</tr>
<tr>
<td>Zr -1Nb</td>
<td>99</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.0</td>
<td>---</td>
</tr>
<tr>
<td>Zr -2.5Nb</td>
<td>97.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2.5</td>
<td>---</td>
</tr>
<tr>
<td>Zr -3 Nb -1Sn</td>
<td>96</td>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2.8</td>
<td>---</td>
</tr>
</tbody>
</table>

Pressurized Water Reactors (PWR's)

The coolant contains a highly reducing environment:

- Hydroxide - LiOH
- Hydrogen to keep oxygen level to < 0.05 ppm (Figure)
- Boric acid (0 to 2500 ppm) for control shim

Irradiation can accelerate corrosion by a factor of 8 to 10 (Figure)

(11 μ in 41,000 EFPH's, 8 x 10^{21} n cm^{-2})
Boiling Water Reactors (BWR’s)

- Can not control oxygen by adding hydrogen because it will just boil away;

  * Oxygen levels
    - 0.3 ppm in water
    - 20 ppm in steam

- Irradiation reduces the temperature sensitivity to oxygen level

Note: the reason we use Zr-4 (in PWR’s) instead of Zr-2, is because Zir - IV has about one half the H₂ pickup compared to Zr-2 (Ni picks up H₂)

Zr - Nb Alloys

Zr - 1Nb  (Figure 5)

- No apparent advantage at short times and at low temperatures

- USSR icebreaker - LENIN

Zr - 2.5 Nb (Figure 6)

Great Deal of Work reported!

1.) Zircaloy is not affected by oxygen alone but oxygen and neutron flux is more of a problem in Zr - Nb alloys.
2.) Zr - Nb is affected by increased oxygen levels, but the n flux lowers the temperature effect.

3.) In a deoxygenated environment, Zr - 2.5Nb has far superior properties compared to Zircaloy in the long run (Figure 7)

Conclusions

1.) Corrosion and hydride resistance of Zr - IV is more than adequate

2.) Zr - Nb offers no real benefit over Zircaloy for normal (1-2 years) runs.

3.) For long exposures, Zr - Nb has a better corrosion resistance (in high n fluence)

See "Corrosion in Nuclear Systems"
by
Professor J. Blanchard

Video Tape (50 mins.)

Engineering Library

TV-0423-35
Corrosion in Nuclear Reactors

**Internal Corrosion:**
- Hydriding
- Stress Corrosion Cracking (SCC)

**External Corrosion**

<table>
<thead>
<tr>
<th>T °C</th>
<th>Out of Pile Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg dm²·d⁻¹</td>
</tr>
<tr>
<td>310</td>
<td>0.006</td>
</tr>
<tr>
<td>360</td>
<td>0.3</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
</tr>
<tr>
<td>510</td>
<td>20</td>
</tr>
</tbody>
</table>

-- Zr alloys typically absorb about 40% of the hydrogen liberated by oxidation.

-- Zircalloy-4 was developed to reduce the absorbed hydrogen.

-- The absorption of hydrogen was reduced by a factor of 3.

**Irradiation Effects**

- During irradiation, H₂O (D₂O) is decomposed to H₂ + O₂ (D₂ + O₂)
• In a BWR, liquid phase contains 0.05 to 0.2 ppm O2, and vapor phase contains 5 to 20 ppm O2.
• In PWR's, a hydrogen over pressure is used to suppress the evolution of O2.

• In BWR's, irradiation increases corrosion rates by a factor of \( \approx 100 \) @ 240°C, \( \approx 10 \) @ 300°C, and \( \approx 1 \) @ 400 °C.

• Irradiation also decreases the difference of absorption rates in Zr-2 and Zr-4.

• Even the highest BWR corrosion rates @ 325 °C leads to only 35 microns thickness lost per 5 years.

-------------------------------------------

• **Nodular Corrosion**

• General corrosion of Zr alloys leads to thin black protective layers (ZrO2).

• These alloys also form localized, lens-shaped, white oxides (especially in BWR's).

• Nodules generally grow much faster than "uniform" films.

• The extent of coverage depends on material, water chemistry, temperature, etc.

Crud-Induced Localized Corrosion (CILC)
CILC is found in 12-15% of operating BWR's containing GE fuel.

- It tends to occur in BWR's with brass condensers and determines filter demineralizer condensate water cleanup systems.

- CILC is also more common in (U,Gd) O2 fuels.
  - (U,Gd) O2 rods are referred to as burnable poisons. Gd has a high absorption cross-section.
    \[ \sum_{a}^{\text{thermal}} (\text{Gd}) = 1400 / \text{cm} \]

- Two types of crud formed in BWR's
  1.) Low density, loosely adherent crud (Fe2O3) with excellent thermal conductivity.
  2.) High density, tightly adherent crud (CuO) scale with poor thermal conductivity.

- CILC involves scale-type crud containing >50% Cu cations.

- Local pits (3 mm to 6 mm diameter) are found in failure regions.

Contributing Factors

Environment:
• CILC requires Cu content to be sufficient.

• Cu does 3 things:
  1.) Promotes scale formation.
  2.) Deposits between nodules.
  3.) Deposits in layers with oxides, forming steam pockets, which cause the temperature to rise, which causes enhanced corrosion + pitting

**Duty Cycle**

• CILC is more likely in (U,Gd)O₂ because low initial power allows nodules to form, higher power later leads to CILC.

**Materials**

• Zircaloy's are particularly susceptible to CILC.

• Heat treatment of the cladding can increase the resistance to nodule formation.
Design Curves For Zr-702

- Creep Rate
- 2/3 Yield
- 1/4 Ultimate
- 2/3 Rupture

Temperature °F vs. Stress ksi graph.