Zircaloy-4 for Low-Temperature Use with Hydrogen and Neutron Exposure

Lauren Garrison
Chinthaka Silva

Mo-99 Topical Meeting 2018
ORNL supports SHINE with materials research for the target solution vessel and support pipes

Conditions of the Target Solution Vessel:
- Neutron irradiation
- Hydrogen exposure
- Water exposure
- Uranyl sulfate solution corrosion
- Temperature <100°C
- Low pressure

Initially, several materials were surveyed:
- Stainless steels
- Zr2.5Nb
- Zircaloy-4
Zircaloy-4 Investigation

- Zircaloy-4 has a long history in the nuclear industry, but typically is used as cladding, ~200-400°C

- Considerations for SHINE target solution vessel:
  - Neutron irradiation
  - <100 °C
  - Hydrogen, water, uranium solution
  - Welding

- Additional data is needed to confidently use this material for the unique application and to satisfy the NRC for licensing of the facility
Preparation of Material

Zircaloy-4 material

Machined bars for welding tests

C. M. Silva, C. D. Bryan. “Evaluation of Zircaloy-4 as the structural material for the Target Solution Vessel and support lines of SHINE — Sample preparation for the third-round neutron irradiation” FY17 Report. ORNL/TM-2017/482
Tungsten Inert Gas Welding

- Welding tests performed at Major Tool & Machine Inc.
- ORNL developed a weld quality analysis procedure
Post-weld heat treatment - Motivation

- **Base metal** total elongation is $\sim 22-29\%$

- **After TIG welding**, no post-weld heat treatment, total elongation is **similar to base metal for asymmetric samples** (one tab was in the weld and one tab reached the base metal)

- **After TIG welding**, no post-weld heat treatment, total elongation is $\sim 10-13\%$ for symmetric weld samples

C. M. Silva, C. D. Bryan. "Evaluation of Zircaloy-4 as the structural material for the Target Solution Vessel and support lines of SHINE — Sample preparation for the third-round neutron irradiation" FY17 Report. ORNL/TM-2017/482
Zircaloy-4 Phases

Alpha phase Zircaloy-4 (HCP)  
Beta phase Zircaloy-4 (BCC)  
Melted Zircaloy-4

Temperature (°C)

0 500 1000 1500 2000

https://www.atimetals.com/Products/Documents/datasheets/zirconium/alloy/Zr_nuke_waste_disposal_v1.pdf#search=zircaloy-4
Zircaloy-4 Phases

- How weld affects phases and properties
  - Ultimate tensile strength decreases
  - Yield strength increases
  - Total elongation decreases significantly

C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)
Zircaloy-4 Phases

- Annealing affects corrosion and mechanical properties

C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)

- Forms significant beta phase
- 20-80% increased corrosion in 350°C water or 750°C steam
- Tensile total elongation reduced
• Annealing affects corrosion and mechanical properties

Annealing below ~800°C
• Stays in alpha phase
• No change to corrosion rate
• Tensile properties can be improved

C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)
Heat treatment parameters for Zry-4, weld-6 samples. **Holding time 1h.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target temperature (°C)</th>
<th>Ramping</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-1</td>
<td>500</td>
<td>500 °C in 4.5 hours</td>
<td>Furnace cooling</td>
</tr>
<tr>
<td>6-2</td>
<td>600</td>
<td>600 °C in 5.0 hours</td>
<td>Furnace cooling</td>
</tr>
<tr>
<td>6-3</td>
<td>700</td>
<td>700 °C in 7.0 hours</td>
<td>Furnace cooling</td>
</tr>
<tr>
<td>6-4</td>
<td>750</td>
<td>750 °C in 7.0 hours</td>
<td>Furnace cooling</td>
</tr>
<tr>
<td>6-5</td>
<td>800</td>
<td>800 °C in 7.0 hours</td>
<td>Furnace cooling</td>
</tr>
</tbody>
</table>
## Post Weld Heat Treatment

Heat treatment parameters for Zry-4, weld-6 samples. **Holding time 1h.**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Cut location</th>
<th>PWHT temp. (°C)</th>
<th>Layer from surface</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Yield stress (MPa)</th>
<th>Total elongation* (%)</th>
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<tbody>
<tr>
<td>ZFA01</td>
<td>SW</td>
<td>500</td>
<td>1</td>
<td>571</td>
<td>442</td>
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<td>ZFA02</td>
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<td>468</td>
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<tr>
<td>ZFA03</td>
<td>SW</td>
<td></td>
<td>3</td>
<td>586</td>
<td>468</td>
<td>19.3</td>
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<tr>
<td><strong>Average</strong></td>
<td>SW</td>
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<td></td>
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<td>459</td>
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<tr>
<td>ZFB01</td>
<td>SW</td>
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<td>601</td>
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<td>17.2</td>
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<td>SW</td>
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<tr>
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<td>15.6</td>
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<tr>
<td><strong>Average</strong></td>
<td>SW</td>
<td></td>
<td></td>
<td>595</td>
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<td>583</td>
<td>481</td>
<td>19.7</td>
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<td><strong>Average</strong></td>
<td>SW</td>
<td></td>
<td></td>
<td>584</td>
<td>479</td>
<td>21</td>
</tr>
</tbody>
</table>

600°C slightly lower elongation

800°C slightly higher elongation

*TE values are overestimated here from raw data
## Post Weld Heat Treatment

Heat treatment parameters for Zry-4, weld-7 samples. 800 °C, varied holding times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer from surface</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Yield stress (MPa)</th>
<th>Total elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZGA01, 800°C, 12h</td>
<td>1st of 4</td>
<td>588</td>
<td>487</td>
<td>18.1</td>
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<tr>
<td>ZGA02, 800°C, 12h</td>
<td>2nd of 4</td>
<td>582</td>
<td>489</td>
<td>16.6</td>
</tr>
<tr>
<td>ZGA03, 800°C, 12h</td>
<td>3rd of 4</td>
<td>584</td>
<td>476</td>
<td>17.2</td>
</tr>
<tr>
<td>ZGA04, 800°C, 12h</td>
<td>4th of 4</td>
<td>572</td>
<td>474</td>
<td>17.0</td>
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<tr>
<td>Avg.</td>
<td></td>
<td>582</td>
<td>482</td>
<td>17.2</td>
</tr>
<tr>
<td>ZGB01, 800°C, 24h</td>
<td>1st of 4</td>
<td>581</td>
<td>368</td>
<td>23.6</td>
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<tr>
<td>ZGB02, 800°C, 24h</td>
<td>2nd of 4</td>
<td>495</td>
<td>428</td>
<td>9.1</td>
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<tr>
<td>ZGB03, 800°C, 24h</td>
<td>3rd of 4</td>
<td>553</td>
<td>485</td>
<td>12.9</td>
</tr>
<tr>
<td>ZGB04, 800°C, 24h</td>
<td>4th of 4</td>
<td>466</td>
<td>425</td>
<td>8.7</td>
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<tr>
<td>Avg.</td>
<td></td>
<td>524</td>
<td>427</td>
<td>13.6</td>
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<tr>
<td>ZGC01, 800°C, 48h</td>
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<td>346</td>
<td>17.8</td>
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<td>ZGC02, 800°C, 48h</td>
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<td>366</td>
<td>358</td>
<td>10.9</td>
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<tr>
<td>ZGC03, 800°C, 48h</td>
<td>3rd of 4</td>
<td>352</td>
<td>350</td>
<td>13.7</td>
</tr>
<tr>
<td>ZGC04, 800°C, 48h</td>
<td>4th of 4</td>
<td>495</td>
<td>434</td>
<td>13.4</td>
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<tr>
<td>Avg.</td>
<td></td>
<td>391</td>
<td>372</td>
<td>14.0</td>
</tr>
</tbody>
</table>

*TE values are overestimated here from raw data

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Large grain growth likely caused spread in tensile data for long hold 800°C treatments

- ZGB2, 9.1% elongation

Typical grain structure

Large grain boundary-free area corresponded to fracture location

- Long holds at 800°C cause large grain growth and scatter in tensile elongation
- Similar recoveries were measured for test temperatures below 800°C
- Future post weld heat treatments will be below 800°C
Hydrogen in Zircaloy-4

- The most significant source of H in reactors is from water corrosion

\[ \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \]

- Radiolysis of water can also be a source
Zircaloy-4 has less H absorption than Zircaloy-2

- **Zircaloy-2 (Grade R60802)**
  - Zr
  - 1.5%Sn
  - 0.15%Fe
  - 0.1%Cr
  - **0.05%Ni**
  Responsible for significant H absorption

- **Zircaloy-4**
  - Zr
  - 1.5%Sn
  - 0.2%Fe
  - 0.1%Cr

https://www.atimetals.com/Products/Documents/datasheets/zirconium/alloy/Zr_nuke_waste_disposal_v1.pdf#search=zircaloy-4

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Hydrogen effect on mechanical properties

- Hydrogen absorption in Zircaloy is expected to reduce the ductility.
- Historical data for Zircaloy-2 shows severe effect above ~100 ppm H.
- This must be tested for Zircaloy-4 under low temperature neutron irradiation.

Fig. 10. Effect of Hydrogen on Elongation of Zircaloy-2.

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Hydrogen Charging

- Controlled hydrogen charging is accomplished with heating TiH$_2$ powder in a sealed vacuum tube with Zircaloy-4 samples present
- Samples with different ppm amounts are being produced now for inclusion in the neutron irradiation capsules

\[\text{TiH}_2(s) \rightarrow \text{Ti}(s) + \text{H}_2(g) \quad \text{[1]}\]

\[(1-x/2) \text{H}_2(g) + \text{Zr} \rightarrow \text{ZrH}_{2-x}(s) \quad \text{[2]}\]
Neutron Irradiation of Zircaloy-4

- Samples are being prepared for neutron irradiation in HFIR at temperatures of 60 and 100°C and fluences of $1\times10^{20}$ and $1\times10^{21}$ n/cm$^2$ (E>0.1 MeV)

Testing plan for irradiated samples
- Tensile tests at room temperature
- Microhardness
- Microstructure
Sub-size specimens for in-reactor irradiation

- Cannot fit in HFIR irradiation capsules
- Would have very high activity level after irradiation
- Cannot be used.

- Size and dose are significantly reduced with SS-3 samples
- End tabs used for microhardness measurements and microstructure characterization.

For certain applications, even smaller tensile samples can be used for neutron irradiated tests.
Overview of IMET

- Six interconnected steel-lined examination cells containing 30 m² of workspace.
- Cells 1~3 focusing on mechanical testing
- Low alpha contamination facility (<70 dpm / 100 cm²).
- Irradiation capsule disassembly, mechanical testing (tensile, fracture testing, microhardness), density measurement, SEM, general characterization (optical, video documentation).

In-cell JEOL 6010LA and fractograph from irradiated tensile specimen
LAMDA: Low Activation Materials Development and Analysis

- **Overview**
  - Facility designated for the study of radiological materials by advanced characterization methods and instruments.
  - 4327 Sq. Ft of clean lab space and 2732 Sq. Ft of radiological contamination area
  - ~9000 specimens: fuels, metals, ceramics, graphite

- **Specimen acceptance criteria**
  - 100,000 dpm/100cm² beta/gamma
  - 2,000 dpm/100cm² alpha
  - 100 mR/hr @ 30cm

- **Core capabilities**
  - Microstructure characterization
  - Thermal/physical property
  - Mechanical testing
  - Machining irradiated materials
  - Various specialized instruments
Mechanical property testing instruments

- **Test Resource 160 series torsion test machine**
  - 125Nm torsion system
  - Adjustable speed to 8 rpm

- **Tinius Olsen Impact 104**
  - Pendulum impact tester; Charpy or Izod configuration
  - 30J capacity
  - Testing temperatures from -196 to 400°C

- **Creep test stands**
  - 1kN load capacity; Air environment
  - Temperature from -196 to 500°C

- **Buehler Wilson VH3100 microhardness tester (10 to 1000g load, programmable)**

- **Mituyoyo Vickers Microhardness (10 to 2500g load, programmable)**

- **Agilent Technologies G200 Nano Indentation system**

- **Sonic velocity measurement system**
  - Measure Young’s and shear moduli with the sonic velocity methodology according to ASTM C769 and C1419
Microscopes: TEM, FIBs, and SEM

FIB with cryo-stage: Good for sensitive materials (i.e., prevent hydriding of Zr alloys)

FEI Quanta 3D 200i Dual Beam

Shielded FIB: Control panel outside of 50 mm-thick lead envelope. Allows high-dose samples to be milled under ALARA conditions

FEI Quanta 3D 200i Dual Beam

High-Brightness FEG Electron Source
- 0.96 nm resolution

Available Detectors:
- Secondary electrons (ETD and in-column)
- Backscattered electrons (ETD & concentric)
- STEM
- Secondary ions

High-Brightness FEG Electron Source
- <1.7 nm resolution

Available Detectors:
- Secondary electrons (ETD and In-Lens)
- Retractable annular Backscattered electron detector
- Extended wavelength cathodoluminescence (CL) detector

FEI Versa 3D Hi-Vac Dual Beam

- JEOL JEM 2100F Transmission Electron Microscope (FEG, TEM/STEM, EDS, EELS)
- FEI Talos F200X Transmission Electron Microscope (X-FEG, TEM/STEM, super-X EDS)
- XRADIA X-ray Tomography
- Positron Annihilation Spectroscopy

FEI Quanta 3D 200i Dual Beam

FEI Quanta 3D 200i Dual Beam

FEI Versa 3D Hi-Vac Dual Beam

Tescan MIRA3 GMH
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Questions?

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