Ductile-to-Brittle Transition Temperatures for High-Burnup PWR Cladding Alloys

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Outline

- Introduction
- Materials and Experimental Methods
- Summary of Results
- Conclusions
- Future Priorities
Introduction: UFD ST R&D Objectives and NRC Concerns

Objectives of UFD Storage and Transportation (ST) R&D are to develop technical bases for demonstrating:

- Used fuel integrity for extended storage periods
- Fuel retrievability and transportation after long term storage
- Transportation of high-burnup (HBU, >45 GWD/MTU) fuel

NRC Spent Fuel Storage and Transportation (SFST)

- Concerned about HBU cladding embrittlement after 20-y storage
- Concerned about transporting HBU fuel below cladding ductile-to-brittle transition temperature (DBTT)
Introduction
Regulations and HBU Fuel Issues

**10 CFR 72: Criteria for Storage of Spent Nuclear Fuel**
- Protect against cladding degradation that leads to gross ruptures or...
- ISG-1, Rev. 2 (2007): gross rupture is a crack >1 mm in width

**10 CFR 71: Criteria for Transportation of Spent Nuclear Fuel**
- Ambient temperature: \(-29^\circ\text{C} \text{ to } 38^\circ\text{C}\) (use most unfavorable)

**NRC Interim Staff Guidance (ISG)–11, Revision 3 (2003)**
- Limits HBU cladding T to \(400^\circ\text{C}\) for drying-transfer, storage & transportation

**Embrittlement Concerns for HBU PWR Fuel Rod Cladding**
- Higher hydrogen content: may embrittle as-irradiated cladding
- Higher decay heat: may lead to higher drying-storage temperatures
- Higher internal gas pressure: leads to higher peak hoop stresses
- Higher peak hoop stress: may cause radial-hydride precipitation and embrittlement during vacuum drying, transfer, and storage
Loads on Fuel-Rod Cladding during Transport

- Normal transport conditions include vibration and shock
- Hypothetical accident conditions include severe impact loads
  - Axial stresses due to impact and bending
  - Hoop stresses ($\sigma_\theta$) due to gas-pressure and “pinch-type” loading (F)

Note: >500 partial pellet-pellet gaps due to “dishing”
Introduction: Data Needs and Argonne Experimental Program

Cladding Mechanical Properties and Failure Limits

- Available for HBU Zircaloy-4 (Zry-4) with circumferential hydrides
- Available for Zry-2 but data needed at high fast fluence (i.e., HBU)
- Data needs
  - Tensile properties of HBU M5® and ZIRLO™ cladding alloys
  - Failure limits for all cladding alloys following drying and storage
    - Radial hydrides can embrittle cladding in elastic deformation regime

Argonne Experimental Program

- Develop family of ductility curves following slow cooling from ≤400°C (ISG-11, Rev. 3 limit) and decreasing $\sigma_\theta$
- Determine DBTT for each set of peak drying-storage $T$ and $\sigma_\theta$
- Goal: determine ranges of peak $T$ and $\sigma_\theta$ for which DBTT ≤20°C
Introduction: Circumferential and Radial Hydrides in HBU Cladding

As-Irradiated

660 wppm H

After Drying-Storage

320 wppm H

650 wppm H

350 wppm H
Materials and Experimental Method

Note: Cladding materials are from fuel rods irradiated to HBU in commercial Pressurized Water Reactors (PWRs)
Materials: HBU Cladding Alloys in As-Irradiated Condition (Baseline) and after Simulated Drying-Storage (RHT) at 400°C

<table>
<thead>
<tr>
<th>Cladding Alloy</th>
<th>TMT</th>
<th>Burnup, GWd/MTU</th>
<th>H-Content, wppm</th>
<th>Peak RHT Stress, MPa</th>
<th>Drying Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5® RXA</td>
<td>63</td>
<td>68</td>
<td>72 ± 10</td>
<td>110</td>
<td>1</td>
</tr>
<tr>
<td>68</td>
<td>58 ± 15</td>
<td>90</td>
<td>76 ± 5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>70</td>
<td>94 ± 4</td>
<td>140</td>
<td>110</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>ZIRLO™ CWSRA</td>
<td>70</td>
<td>650 ± 190</td>
<td>425 ± 63</td>
<td>140</td>
<td>1</td>
</tr>
<tr>
<td>70</td>
<td>350 ± 80</td>
<td>110</td>
<td>90</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>68</td>
<td>530 ± 100</td>
<td>110</td>
<td>480 ± 131</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>68</td>
<td>300 ± 50</td>
<td>535 ± 50</td>
<td>0</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Zry-4 CWSRA</td>
<td>67</td>
<td>615 ± 82</td>
<td>520 ± 90</td>
<td>140</td>
<td>1</td>
</tr>
<tr>
<td>67</td>
<td>300 ± 15</td>
<td>110</td>
<td>640 ± 140</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>67</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Experimental Method: Simulation of Drying and Storage by Means of Radial Hydride Treatment (RHT)

\[ \Delta p(T) = \left[ \frac{T+273}{296} \right] \Delta p(23^\circ C) + 0.057 \text{ MPa} \]

\[ \sigma_\theta(T) = \left( \frac{R_{mi}}{h_m} \right) \Delta p(T) \]

Radial Hydride Treatment

5°C/h

Temperature (°C)

Time (Hours)
Experimental Method: Ring Compression Test (RCT)

Controlled displacement rates
5 mm/s typical
1.7-mm maximum displacement

Orientation:
12 o’clock = applied load

Elastic $\sigma_\theta (3, 9) \approx 60\% \sigma_\theta (6, 12)$

Controlled temperature

Maximum permanent displacement $\approx 10\%$ for uncracked rings
Summary of Results

Susceptibility to Radial-Hydride Precipitation
- Low for HBU Zry-4 cladding
- Moderate for HBU ZIRLO™
- High for HBU M5®

Susceptibility to Radial-Hydride-Induced Embrittlement
- Low for HBU Zry-4
- Moderate for HBU M5®
- High for HBU ZIRLO™

DBTT Values for HBU Cladding Alloys
- Peak drying-storage hoop stress at 400°C: 140 MPa → 110 MPa → 90 MPa → 0 MPa
- DBTT for HBU M5® after slow cooling: 80°C → 70°C → <20°C → <20°C
- DBTT for HBU ZIRLO™ after slow cooling: 185°C → 125°C → 20°C → <20°C
- DBTT for HBU Zry-4 after slow cooling: 55°C → <20°C → >90°C
  - Embrittled by circumferential hydrides: 615±82 wppm  520±90 wppm  640±140 wppm
  - HBU Zry-4 with 300±15 wppm was highly ductile at 20°C
RCT Ductility vs. Test Temperature for HBU M5®

- **90 MPa at 400°C**
- **110 MPa at 400°C**
- **140 MPa at 400°C**

**High-Burnup M5®**

- **As-Irradiated**
- **76±5 wppm H**
- **58±15 wppm H (90 MPa)**
- **72±10 wppm H (110 MPa)**
- **94±4 wppm H (140 MPa)**

**Ductile**

**Brittle**
Hydrides in Baseline and RHT (400° C, 140/110 MPa) HBU M5®

Baseline HBU M5®: 76±5 wppm H
RCT Ductility vs. Test Temperature for HBU ZIRLO™

- 530±70 wppm H
- 535±50 wppm H
- 530±115 wppm H
- 385±80 wppm H
- 650±190 wppm H

**High-Burnup ZIRLO™**

- 110 MPa at 400°C
- 140 MPa at 400°C
- 80 MPa at 400°C
- 90 MPa at 400°C

Ductile and Brittle phases are indicated on the graph.
Baseline HBU ZIRLO™: 530 ± 70 wppm H
RCT Ductility & DBTT for RHT (400°C) HBU Zry-4

- As-Irradiated
- Brittle
- Ductile

**High-Burnup Zircaloy-4**

Offset Strain (%)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>300±15 wppm H</th>
<th>640±140 wppm H</th>
<th>520±90 wppm H</th>
<th>615±82 wppm H</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 MPa at 400°C</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>140 MPa at 400°C</td>
<td>3</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

**Brittle**

**Ductile**
Hydrides in Baseline and RHT (400°C, 140/110 MPa) HBU Zry-4

Baseline HBU Zry-4: 640 ± 140 wppm H
Conclusions

Susceptibility to Radial-Hydride Precipitation
- Low for HBU Zry-4
- Moderate for HBU ZIRLO™
- High for HBU M5® (recrystallized-annealed microstructure & low H content)

Susceptibility to Radial-Hydride-Induced Embrittlement
- Low for HBU Zry-4
  However, circumferential hydrides with >800 wppm will embrittle HBU Zry-4
- Moderate for HBU M5® due to sparse distribution of radial hydrides
- High for HBU ZIRLO™ due to denser distribution of continuous radial-circumferential hydrides

Drying-Storage Conditions for which DBTT ≤20°C
- HBU M5® and ZIRLO™: peak hoop stress (σ_θ) ≤90 MPa
- HBU Zry-4: peak σ_θ ≤110 MPa and hydrogen content <570 wppm

What is Fraction of HBU Fuel Rods with Peak σ_θ ≤90 MPa?
- Insufficient database to answer question (see next slide)
End-of-Life Internal Gas Pressure for HBU PWR Fuel Rods
- Hundreds of thousands of PWR rods irradiated to >45 GWd/MTU
- EPRI-published data points (2007): 25
- Fuels Subcommittee expanded database (2013): 25 → 60
- Ongoing effort to expand database to >100 HBU PWR fuel rods

Best-Estimate Cladding and Plenum Temperatures
- Feedback from cask vendors
- Feedback from other tasks within UFD program

Range of Hydride Distributions across Cladding Wall
- Depends on operating conditions
- Difficult to find open-literature data beyond what Argonne has published
- Fuel vendors have restricted datasets; work with EPRI to establish data trends

Mechanical Properties of HBU M5® and ZIRLO™
- Very little data in open literature
- Fuel vendors have extensive datasets; work with EPRI to establish data trends
FY2014 Priorities

Support Planning & Implementation of Industry HBU DEMO Project
- Effects of “rewetting” and multiple drying cycles

Help Establish Technical Bases for Extended Storage and Transportation of UNF, Especially HBU Fuel
- Effects of lower peak cladding temperature (e.g., 350°C)
  - Solubility limits: 200 wppm at 400°C → 120 wppm at 350°C
  - Less hydrogen available for precipitation as radial hydrides
- Effects of multiple drying cycles at >90 MPa hoop stress and 350°C
- Mechanical properties and failure limits


Backup Slides
As-Irradiated Fuel and Cladding
HBU (68 GWd/MTU) Fuel Pellets and Pellet-Pellet Interfaces

Fuel Cross Section near Pellet Mid-plane

Fuel Cross Section near Pellet-Pellet Interface
Hydride Distribution in HBU Fuel Rod Cladding

- 15×15 Zry-4
  - 300 ± 15 wppm
  - Lower dT/dr

- 17×17 ZIRLO™
  - 530 ± 70 wppm
  - 200 μm
  - Higher dT/dr

- 545 ± 80 wppm

- 320 ± 30 wppm
Hydride Distribution in HBU Fuel Rod Cladding with High Hydrogen Content

17×17 ZIRLO™
660±150 wppm H
840 wppm max local H
Higher dT/dr

15×15 Zry-4
640±140 wppm H
850 wppm max local H
Lower dT/dr
As-Irradiated (Baseline) HBU Cladding and HBU Cladding after Simulated Drying-Storage
<table>
<thead>
<tr>
<th>Cladding Alloy</th>
<th>H-Content, wppm</th>
<th>Peak RHT Stress, MPa</th>
<th>Effective Radial-Hydride Length, % of Clad. Wall</th>
<th>DBTT, °C</th>
<th>Sponsor</th>
</tr>
</thead>
<tbody>
<tr>
<td>RXA M5®</td>
<td>94±4 72±10 58±15 76±5</td>
<td>140 110 90 0</td>
<td>72±10 61±10 31±13 ≈0</td>
<td>80 70 &lt;20 &lt;20</td>
<td>DOE DOE DOE DOE</td>
</tr>
<tr>
<td>CWSRA ZIRLO™</td>
<td>650±190 425±63 350±80 530±100 480±131 535±50 530±70</td>
<td>140 110 110 (24-h hold) 90 90 (3-cycle) 80 0</td>
<td>67±11 27±10 33±13 19±9 20±9 9±3 ≈0</td>
<td>185 &lt;150 125 20 20 &lt;20 &lt;20</td>
<td>NRC NRC NRC DOE DOE DOE DOE</td>
</tr>
<tr>
<td>CWSRA Zry-4</td>
<td>615±82 520±90 640±140 300±15</td>
<td>140 (3-h hold) 110 (8-h hold) 0 0</td>
<td>16±4 9±5 0 0</td>
<td>55 &lt;20 &gt;90 &lt;20</td>
<td>NRC NRC DOE DOE</td>
</tr>
</tbody>
</table>
Results for HBU M5®

Baseline Studies for As-irradiated M5®

- 8-µm oxide-layer ($\delta_{ox}$), 0.56-mm $h_m$, 9.51-mm $D_{mo}$
- $C_H = 76 \pm 5$ wppm, some radial hydrides, RHCF $\approx 0$
- High ductility (no cracking through 1.7 mm displacement)

HBU M5® Results after Simulated Drying/Storage

- 140 MPa @ 400°C: $C_H = 94 \pm 4$ wppm, RHCF = 72±10%, DBTT $\approx 80°C$
  - Dissolution at 329°C; precipitation at 283°C ($\sigma_\theta = 116$ MPa)
- 110 MPa @ 400°C: $C_H = 72 \pm 10$ wppm, RHCF = 61±10%, DBTT $\approx 70°C$
  - Dissolution at 307°C; precipitation at 261°C ($\sigma_\theta = 87$ MPa)
- 90 MPa @ 400°C: $C_H = 58 \pm 15$ wppm, RHCF = 31±13%, DBTT <20°C
  - Dissolution at 291°C; precipitation at 245°C ($\sigma_\theta = 69$ MPa)
Hydrides in As-Irradiated HBU M5® at Same Elevation: Baseline Results

Radial Hydrides
Hydrides in Baseline and RHT (400° C, 140/110 MPa) HBU M5®

Baseline HBU M5®: 76±5 wppm H
Hydrides in Baseline and RHT
(400° C, 90 MPa) HBU M5®

Baseline M5®: 76 ± 5 wppm H
Results for HBU ZIRLO™

Baseline Results for HBU ZIRLO™
- 47-µm $\delta_{ox}$, 0.54 mm $h_m$, 9.44-mm $D_{mo}$
- 530±70 wppm $C_H$, local radial hydrides ($RHCF \approx 0\%$)
- 136±7 wppm H within inner 63% of cladding wall
- RCT ductility results ($DBTT < 20°C$): 7% → 11% for 20°C → 150°C

HBU ZIRLO™ Results after Simulated Drying/Storage
- 140 MPa @ 400°C & 650±190 wppm H:
  RHCF = 67±17%, $DBTT \approx 185°C$
- 110 MPa @ 400°C & 350-425 wppm H:
  RHCF = 30±12%, $DBTT \approx 125°C$ (no change for 24-h vs. 1-h hold time)
- 90 MPa @ 400°C & 530±100 wppm H:
  RHCF = 19±9%, $DBTT = 20°C$ (no change for 3-cycle drying)
- 80 MPa @ 400°C & 535±50 wppm H:
  RHCF = 9±3%, $DBTT < 20°C$
Hydrides in As-Irradiated HBU ZIRLO™ at Same Axial Elevation: Baseline Results

Radial Hydride
Hydrides in Baseline and RHT (400°C, 140/110 MPa) HBU ZIRLO™

Baseline HBU ZIRLO™:
530 ± 70 wppm H
Hydrides in Baseline and RHT (400°C, 80/90 MPa) HBU ZIRLO™

Baseline HBU ZIRLO™:
530 ± 70 wppm H
Effects of Multiple (3) Drying Cycles on Radial Hydride Precipitation in HBU ZIRLO™

**Single-Cycle Drying**

36% Maximum RHCF

**Multiple-Cycle Drying**

36% Maximum RHCF
Results for HBU Zry-4

Baseline Results for HBU Zry-4

- 95-µm $\delta_{ox}$, 0.69 mm $h_m$, 10.56-mm $D_{mo}$
- 640±140 wppm $C_H$, no radial hydrides ($RHCF = 0$)
- 246±29 wppm H within inner 63% of cladding wall
- Embrittlement at 20-90°C: high density of circumferential hydrides (>800 wppm H locally)
- HBU Zry-4 with 300±15 wppm $C_H$ exhibited high ductility at RT

HBU Zry-4 Results after Simulated Drying/Storage

- 140 MPa @ 400°C and 615±82 wppm H: $RHCF = 16±4\%$, $DBTT \approx 55°C$
- 110 MPa @ 400°C and 520±90 wppm H: $RHCF = 9±5\%$, $DBTT < 20°C$
Hydrides in As-Irradiated HBU Zry-4 at Same Axial Elevation

Low $C_H (<500$ wppm)
Ductile at RT

High $C_H (>800$ wppm)
Brittle at RT
Hydrides in Baseline and RHT (400°C, 140/110 MPa) HBU Zry-4

Baseline HBU Zry-4: 640±140 wppm H
Effects of Hydrogen Content on HBU Zry-4 (As-Irradiated) Ductility at RT

Load (kN) vs. Displacement (mm)

- HB Zry-4 with 640±140 wppm H
- HB Zry-4 with 300±15 wppm H

500 μm

1 of 2 Major Cracks
70% of Wall