Hydride Embrittlement Analysis on the End Cap Welded Zone and Heat Affected Zone of Zr-Nb alloy tube

2021. 10. 21.

Sangbum Kim, Youho Lee

Nuclear Fuel Materials and Safety Laboratory
Seoul National University
Contents

1. Introduction

2. Experiment and Discussion
   2.1. Optical Microscope
   2.2. BSE SEM
   2.3. Mechanical Test (Ring Compression Test)
   2.4. Vickers Hardness Test
   2.5. EBSD analysis

3. Conclusion
Introduction: Previous Study on the Hydride Embrittlement

**Materials**: Reactor-grade Zircaloy tube

<table>
<thead>
<tr>
<th>Element</th>
<th>Sn (%)</th>
<th>Fe (%)</th>
<th>Cr (%)</th>
<th>Ni (%)</th>
<th>O (%)</th>
<th>Hf</th>
<th>Zr</th>
<th>Nb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-4</td>
<td>1.2~1.7</td>
<td>0.18~0.24</td>
<td>0.07~0.13</td>
<td>-</td>
<td>0.12</td>
<td>&lt;100 ppm</td>
<td>bal.</td>
<td>-</td>
</tr>
<tr>
<td>Zr-Nb alloy</td>
<td>0~0.99</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
<td>40 ppm</td>
<td>bal.</td>
<td>0.98</td>
</tr>
</tbody>
</table>

**RCT test result**: **Abrupt Ductile-to-Brittle Transition**

![Schematic of DTB transition concept](image)

*Hydrogen concentration (wppm) and fuel Burn-up Effect (MWd/kgU) relations were obtained by FRAPCON 4.0 simulation.*
Introduction: Previous Study on the Hydride Embrittlement

- The DTB transition is known to occur when there is a sufficiently large number of hydrides for a crack to cross the hydrides and propagate in the matrix.

EBSD Analysis

Zircaloy-4: 1.86 \( \mu \text{m} \) (total GB length 8.89 mm)
Zr-Nb alloy: 0.89 \( \mu \text{m} \) (total GB length 18.1 mm)
Introduction: Previous Study on the Hydride Embrittlement

Hydride interconnectivity

- Zicaloy-4 (500 wppm)
- Zr-Nb alloy (500 wppm)

Zr-Nb alloy has better hydride inter-connectivity

Grain size effect on the GB density and Hydride interconnectivity

- Zr-Nb alloy with no annealing
- Zr-Nb alloy annealed at 500 °C for 3 h
Introduction: Research Motivations

Hydride embrittlement is closely related to the grain size of the cladding material.

Hydride embrittlement analysis on the end cap-cladding weld area


Introduction: End cap welding zone

- The welded area of nuclear fuel rods has high possibility of leakage during the operation.
- To prevent leakage of fissile material during the operation in a nuclear reactor, high integrity of a welding quality is required.

Introduction: Research Goals

1. To investigate the microstructure of the welding area (WZ and HAZ) of Zircaloy.
   * WZ: Welded Zone, HAZ: Heat Affected Zone

2. Hydride embrittlement analysis on the WZ and HAZ of Zr-Nb alloy tube.

3. To re-examine the welded area structural integrity in terms of SNF management.
Experiment & Discussion: Optical Microscope Analysis

- Hydrogen charging and specimen cutting
  - As received fuel rod
  - Charging H to claddings (400°C in furnace)
  - Half Cutting
  - Analysis (OM)

- Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)
  - a: End cap area
  - b: End cap-cladding welding area
  - c: Cladding tube area

✓ Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)
Experiment & Discussion: Optical Microscope Analysis

- Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)

a: End cap area
b: welding area
c: cladding tube area
Experiment & Discussion: Optical Microscope Analysis

- Morphology of Hydride precipitation (Averaged Hydrogen concentration: 815 wppm)

a: End cap area  
b: welding area  
c: cladding tube area

Zr-Nb alloy annealed at 500 °C for 3 h
• BSE SEM analysis

Through BSE SEM Macrographs of welded area, end cap area, HAZ, WZ, and tube area are roughly distinguishable.
Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen
Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen
Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen
Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen
Experiment & Discussion: EBSD analysis

- EBSD analysis of the hydrided Specimen
Experiment & Discussion: EBSD analysis

- EBSD analysis of the hydrided Specimen
Zr-Hydride interface orientation analysis: Misfit strain ($\chi$) calculation

$$\Delta G_{strain} = \frac{6 \mu \eta \gamma}{\eta (\gamma - 1) + 1}$$

$$\Delta G = -V \Delta G_{chem} + A \Delta G_{surface} + V - S \Delta G_{GB}$$

HCP $\{0 0 0 1\}$

FCC $\{1 1 1\}$

Experiment & Discussion: EBSD analysis

• Zr-Hydride interface orientation analysis: Misfit strain ($\chi$) calculation

Averaged Misfit strain ($\bar{\chi}$) = 0.059531

Experiment & Discussion: EBSD analysis

1: Cap - HAZ
2: HAZ-WZ
3: WZ-HAZ
4: Tube
5: Tube

\[ \bar{\chi} \approx 0.0595 \sim 0.0633 \]
Experiment & Discussion: Hardness test (Vickers)

- Micro Vickers Hardness Result of As-Received Specimen

Vickers Hardness test with 0.3kgf, 15 seconds

Hardness value is the highest at the Welding Zone.
Experiment & Discussion: Thermodynamic model

- Hardness-Shear modulus relations

\[ H_V \approx 3 \cdot \sigma_y \]

\[ H = \frac{2\sigma_y}{3} \left\{ 1 + \ln \left[ \frac{E}{3(1-\nu)\sigma_y} \right] \right\} \]

\[ E = 2G(1+\nu) = 3K(1-2\nu) \]

oShear modulus, G
End cap : 30.1 GPa / Welding Zone : 42.7 GPa / Tube : 36.4 GPa

- Hydride nucleation Gibbs free energy equation [1]

\[ \Delta G = -V \Delta G_{chem} + A \Delta G_{surface} + V \Delta G_{GB} - S \Delta G_{GB} \]

\[ \chi = \frac{6 \eta \gamma^2}{\eta (\gamma-1) + 1} \]

Chemical free energy per unit volume
the interphase energy btw nucleus and matrix
the GB energy between the parent grains
misfit strain
\[ \eta = (1 + \nu)/3(1 - \nu) \]
\[ \gamma \]
the ratio of the bulk modulus of the precipitate to that of the matrix

Experiment & Discussion: Thermodynamic model

- Shear modulus - $\Delta G$ strain curve

\[ \Delta G_{\text{strain}} = \frac{6 \mu \eta \gamma^2}{\eta(\gamma - 1) + 1} \]

- WZ (G=42.7 GPa)
  - $\Delta G$ strain: 5.81 ~ 6.56 [$x10^8$ J/m$^3$]

- Cladding tube (G=36.4 GPa)
  - $\Delta G$ strain: 4.95 ~ 5.59 [$x10^8$ J/m$^3$]

- Hydride precipitation at the WZ is more difficult than at the cladding tube.
Conclusion and Path forward

1. In the end cap to tube welding, WZ and HAZ are within the 1 mm length area.

2. Microstructure mapping via EBSD on the end cap to cladding welding area is completed.

3. WZ and HAZ seems to have hydride embrittlement resistance.
   - Hardness of WZ is the highest among other area in the fuel rod.
   - Martensite phase in the WZ and HAZ, increases the stiffness of the material
   - shear modulus increase in the WZ and HAZ
   - G strain energy of WZ is much higher than cladding tube (using thermodynamic model)
Acknowledgements

This work was financially supported by

the Institute for Korea Spent Nuclear Fuel (iKSNF) and National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT, MSIT) (2021M2E1A1085226).

Also, materials and experimental devices were partially supported by the KEPCO Nuclear Fuel (KEPCO NF) and Dr. Joo-Hee Kang, the Korea Institute of Materials Science (KIMS).
Thank you