Effect of Irradiation on Terminal Solid Solubility of Hydrogen in Zr-2.5Nb

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18th International Symposium on Zirconium in the Nuclear Industry
May 15-19, 2016, Hilton Head, South Carolina
Introduction

• The mechanical properties of zirconium alloys are adversely affected by hydrogen.

• Delayed Hydride Cracking (DHC) can occur if the hydrogen concentration exceeds the terminal solid solubility (TSS) of hydrogen, and sufficient tensile stress is applied.

• The apparent TSS is affected by irradiation and the state of the $\beta$-phase in Zr-2.5Nb.
Introduction

• In Zircaloy, neutron irradiation was found to increase the solubility of hydrogen.*
  • Associated with trapping of hydrogen atoms in irradiation-induced defects.

• Limited data are available showing the effect of irradiation in Zr-2.5Nb.

• Objective: To investigate the effect of irradiation on hydride dissolution temperatures in Zr-2.5Nb using Differential Scanning Calorimetry (DSC).

Experiment - Unirradiated Specimens

• A ring of 27% cold worked pressure tube (Tube A) material was electrolytically hydrided in 1%H$_2$SO$_4$ for 72 hours at 70°C.
• The ring was cut into 1 cm x 2 cm x 0.4 cm sections that were annealed at different times and temperatures to obtain [H] values in the range 40-160 µg/g.
• The hydride layer was removed from the sections and then they were heat treated at 400°C for 72 hours.
  • Consistent with the heat treatment for specimens irradiated in the OSIRIS reactor.
• 2 small pieces were cut from each section for DSC analysis.
Experiment - Irradiated Specimens

- OSIRIS Reactor
  - Curved compact tension specimens from Tube A were heat treated at 400°C for 72 hours.
  - Irradiated (NaK coolant) at 250°C in a cosine flux profile with a maximum flux of $1.8 \times 10^{18} \text{n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at the centre.
  - Fluence ranged from $0.5 - 1.7 \times 10^{25} \text{n} \cdot \text{m}^{-2}$.
  - Specimens absorbed hydrogen (20-150 µg/g) from unknown source during test.
  - 3-4 DSC specimens cut from each sample.

- Halden Reactor
  - Corrosion coupons (3 cm x 1 cm x 0.1 cm) machined from Tube B were subjected to 400°C for 24 hours in steam to form an oxide layer.
  - Exposed in a heavy-water loop at 325°C (out-flux and in-flux: $3 - 5 \times 10^{17} \text{n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) with pH = 10.7.
  - Fluence ~ $1.9 \times 10^{25} \text{n} \cdot \text{m}^{-2}$; $[\text{H}_{\text{eq}}]$ ~ 10 µg/g.
  - 2 DSC specimens cut from each sample.
Experiment - DSC

500°C anneal for 1 hour

4 DSC runs
ramp/cool rate: 10°C/min

Temperature (°C)

0  100  200  300  400  500  600

Time (minutes)
Results - Example of Unirradiated and Irradiated Specimens

![Graph showing TSSD temperature vs. DSC Run # for unirradiated and irradiated specimens.]

- Unirradiated - H737-01-RN (44 ppm H)
- Irradiated - ER-I3-44-LN (48 ppm H, fluence = 2.64)

DSC Run # (Note: Runs 5-8 are after a 1 hour anneal at 500°C)
Results - Irradiated Specimens

- Tube A, before anneal
- Tube B, before anneal
- Tube A, after anneal
- Tube B, after anneal

H Concentration (µg/g) vs. Average TSSD Temperature (°C)
Effect of Irradiation on Zr-2.5Nb

- Formation of dislocation loops and increase in dislocation density.
  - a-type dislocation structure increases rapidly at low fluence, at higher fluences there is a small increase in density.
  - c-type dislocation structure evolves at a slow rate over long periods of irradiation.
- Changes to the state of the β-phase
  - Competing processes:
    - Temperature decomposing the β-phase leading to increased Nb in solution in the remaining β-phase.
    - Flux reconstituting the β-phase.
Effect of Irradiation on Integral Breadth

Effect of Annealing (500°C for 1 Hour) on Integral Breadth of Irradiated Specimens
Competing Effects on β-Phase

%Nb in the β-phase

Condition

Initial | No flux 280°C | No flux 335°C | Flux 280°C | Flux 335°C
Effect of Irradiation on the $\beta$-Phase

Effect of Annealing (500°C for 1 Hour) on the β-Phase in Irradiated Specimen from Tube A

- 2 component β-phase component formed after annealing.
- Untransformed β-phase (β1).
- Decomposed β-phase filaments (β2).
Effect of Irradiation and State of $\beta$-Phase on TSSD

- Irradiation decreases the temperature at which hydrides completely dissolve in Zr-2.5Nb.
  - Hydrogen trapped by irradiation induced defects ($a$-component and $c$-component dislocations and loops);
  - More hydrogen partitions to the flux-reconstituted $\beta$-phase, which has a higher solubility for hydrogen than $\alpha$-Zr.

- The flux effect on the $\beta$-phase can be estimated from:
  - How %Nb in the $\beta$-phase changes with fluence (slide 14);
  - Assuming the 500$^\circ$C heat treatment decomposes the $\beta$-phase (i.e., 70%Nb);
  - How TSSD temperature changes in unirradiated material following similar heat treatment. (D. Khatamian, J. Alloys Cmpds, 356-357, 2003, p. 22.)
ΔTSSD for Irradiated Specimens

![Graph showing ΔTSSD for different fluences (1x10^{25} n/m^2)].

- **Average Measured ΔTSSD**
- **Average Calculated ΔTSSD from %Nb Change**

Fluence values: 0.52, 0.61, 1.9, 2.64, 10.8, 17.4
Summary

• Irradiation reduced TSSD temperatures for Zr-2.5Nb.
  • Similar effect observed in Zircaloy (A. McMinn et al., P. Vizcaino et al.).
• Thermal annealing for 1 hour at 500°C increased TSSD temperatures.
  • values approached those of unirradiated specimens.
• Estimates of β-phase contributions explain only part of the shift in TSSD temperatures for irradiated specimens,
• A significant contribution is attributed to hydrogen trapped in irradiation-induced defects.
  • Consistent with observations on Zircaloy.
Acknowledgements

• OSIRIS
• OECD Halden Reactor Project
• CNL hot cell facility
• CNL HVEMS facility