Fracture of Gamma and Delta Hydrides during Delayed Hydride Cracking

19th International Symposium on Zirconium in the Nuclear Industry

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May 2019
**Limiting Conditions for DHC**

- Delayed Hydride Cracking (DHC) is a mechanism responsible for extension of flaws in pressure tubes and fuel cladding
  - Nucleation, growth, fracture of hydrides
  - Chemical potential
  - Leak-before-break

**Limiting conditions**
- $[\text{H}]$, solubility limits
- Stress intensity ($K_{\text{IH}}$)
- Temperature
- Temperature history

Mechanism: $[\text{H}]$ in bulk and at crack tip depends on temperature history [34]

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Hydrides

• Bulk hydrides and DHC hydrides do not necessarily form under the same conditions

• X-Ray Diffraction (XRD) of fracture surfaces can reveal how DHC hydride morphology changes with test temperature
  • Focus on DHC hydrides rather than bulk hydrides

• $\delta$ core - $\gamma$ shell hydride morphology [20,21,24]
Experimental

- Material: Zr-2.5Nb plate (similar to pressure tube)
- Cantilever beam specimens (3.2 mm width)
- Axial cracking in transverse plane
- $K=17$ MPa√m (constant load)
- Test temperatures from 25 °C to 270 °C
  - Heat-up tests on quenched material
  - $T_1$ ranges from -30 °C to 220 °C
- Over 200 tests performed
- DSC on quenched material
Cool-down DHC Data

- Cool-down data (below T6) follows Arrhenius behaviour
- No effect of [H] below T6
**Quenched ‘Conundrum’**

- Slow cooling to a $T_{test}$ leads to similar DHCV as quenching and then heating to the same $T_{test}$
- Slow cooling and then heating to the same $T_{test}$ leads to slower DHC rates
- No history effect at room temperature
Quenching and DSC

- Quenching is an ‘extreme’ temperature history
  - Affects bulk hydride morphology
- Shifts the apparent solubility measured by DSC
  - Similar to removing radiation damage
  - Shift decreases as test temperature increases
- More hydrogen in solution generally means higher DHCV
All DHC Data

- Various hydrogen concentrations
- Accuracy of schematic diagram
- Determine conditions under which DHC will not occur
Stopping DHC by Heating

- Good agreement with previous work (irradiated Zircaloy-2)
- Quenching increases required temperature difference (empty symbols in box)
- Can be used to inform reactor manoeuvering strategies
  - Confirm with irradiated Zr-2.5Nb data

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DHC Modelling

- Prediction 1 is the Diffusion First Model [10]
  - Accurately predicts \( T_5 \) to \( T_6 \) region
- Prediction 2 is the Precipitation First Model [33]
- Both models under-predict at low temperatures


Poor DHC Model Predictions at Low Temperature

- Hydrogen in solution is very low at room temperature – less than 5 ppm [18]
  - Very little hydrogen available to diffuse to crack tip
  - Diffusion is slow at room temperature
- Trend in temperature maneuver plot changes around 200 °C
- DHC models either directly or indirectly assume the DHC hydride phase does not change with temperature
  - Ambler et al. assumed DHC hydride is always δ [11]
  - In-situ room temperature TEM shows γ at room temperature [29]
  - δ and γ have different stoichiometry, crystal structure, and morphology

DHC Hydride Phase on Fracture Surfaces

- XRD spectra from DHC fracture surfaces
  - Room temp
- Top: test temperature of 240 °C
- Bottom: test temperature of 25 °C
- Small fraction of signal from bulk hydrides
- No change after 1 year at RT
- Consistent with γ hydride stability at low temperature
DHC Hydride Phase on Fracture Surfaces

- Fractured DHC hydride phase changes with test temperature
  - $\delta$ prevalent at high temperatures, $\gamma$ prevalent at low temperatures
- Presence of $\gamma$ should be considered in future DHC models
- No apparent effect of temperature history on fractured hydrides
Conclusions

- DHC data can be used to provide empirical guidelines and inform reactor temperature maneuvers to reduce DHC susceptibility.
- Quenched results reveal a ‘conundrum’
  - Slow cooling to $T_{test}$ leads to similar DHCV as quenching then heating to $T_{test}$
  - Slow cooling then heating leads to slower DHC rates at the same $T_{test}$
  - Not explained/predicted by current DHC models
- Observed DSC shifts provide a partial qualitative explanation for the quenched ‘conundrum’
- $\gamma$ hydride is dominant on DHC fracture surfaces below about 125 °C while $\delta$ is dominant above 225 °C
  - Implications for fuel storage
- The presence of $\gamma$ hydride on DHC fracture surfaces may explain why DHC model predictions are poor below 150 °C
  - DHC models should include DHC hydride phase temperature dependence
- Follow-up with irradiated material
Questions?
\( n_c(T_e) = DFMW \left[ C(b) - C_p(T_e) \frac{\gamma(a)}{\gamma(b)} \exp \left( \frac{\mu^e(a) - \mu^e(b)}{RT_t} \right) \right] \)