Trapping of Hydrogen at Irradiation Induced Defects

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Background

• Hydrogen is absorbed into zirconium alloys exposed to light water reactor environments as a part of the surface corrosion reaction.
• Hydrogen can diffuse significantly faster through zirconium alloys than oxygen
  – Does not necessarily build up as a surface film at its location of entry
• Its migration and segregation within a zirconium alloy component is often a life limiting concern
  – Effect on mechanical properties
  – Effect on dimensional stability
Background

- Hydrogen diffuses in response to
  - Solid solution concentration gradients
  - Thermal gradients
  - Stress gradients

\[ J_h = -D\nabla c_h - \frac{Dc_h Q^*}{RT^2} \nabla T - \frac{Dc_h \gamma}{RT} \nabla P \]

- With stress gradients producing the smallest driving force.

- Because the entry of hydrogen due to corrosion is slow in relation to its diffusion rate in zirconium, a solid solution steady state profile develops
  - \( C = C_0 \exp(Q^*/RT) \)
  - Higher solid solution concentration develops at the lower temperatures in the component
Background

- Hydrogen however has limited solid solution solubility in the zirconium hcp lattice
  - Above the solid solution solubility, hydrogen precipitates out of solid solution as a Zr hydride.
    - Under the diffusion conditions and cooling conditions of zirconium components in light water reactors, typically as the delta hydride (Zr$_2$H$_3$)
  - Once the solid solution concentrations of hydrogen in the cooler regions of the component reach solubility, the solid solution profile becomes “fixed” and additional hydrogen will tend to accumulate as hydride in the cooler regions of the component.
  - Factors that influence the solubility of hydrogen as an interstitial in the zirconium hcp lattice will have a large affect on the amount of hydrogen build up in the cooler regions of the component
    - Any hysteresis in the dissolution and precipitation solvus
    - Any functional dependence of the solvus on the hydride content of a region
  - Trapping of hydrogen at irradiation induced defects is another potentially important factor
Hypothesized Trapping Model

- Four hydrogen concentrations to consider.
  - $C_T$ is all the hydrogen in a region
    - What is measured in a LECO analysis
  - $C_L$ is the hydrogen dissolved as an interstitial in the hcp zirconium lattice
    - This is the hydrogen that can diffuse through the lattice
  - $C_\delta$ is the hydrogen concentration of a hydride
  - $C_p$ is the hydrogen concentration in a trap produced by irradiation
    - This is the new form of hydrogen to this model

$$C_T = C_L \left(1 - V_\delta - V_p\right) + C_\delta \ V_\delta + C_p \ V_p$$

- Excess hydrogen in the lattice above $C_L$ precipitates out as hydride in accordance with the solubility model
- A steady state equilibrium exists between $C_L$ and $C_p$
  - Described next
Hypothesized Trapping Model

- In the simple model used here a trap is considered an imperfect region in the Zircaloy crystal lattice where the free energy of a hydrogen atom is lower than in its normal interstitial site in the undisturbed Zircaloy lattice.

Net hydrogen flux between trap and lattice

\[ J = \kappa r_0 [C_L - C_P Z - \frac{C_L C_P}{ms} (1 - Z)], \]

\[ r_o = A_o \exp \left( -\frac{Q_L}{RT} \right), \]

\[ Z = Z_o \exp \left( -\frac{E_p}{RT} \right), \]

and \[ Z_o = \exp \left( \frac{S_p}{R} \right) \approx 1. \]

Assuming a steady state equilibrium exists between the hydrogen in the traps and the hydrogen in the hcp lattice.

- At a constant temperature, as the concentration of hydrogen dissolved in the lattice increases, the concentration of hydrogen in the trap increases.
- At a constant lattice hydrogen concentration, as the temperature increases, the concentration of hydrogen in the trap decreases.
Hypothesized Trapping Model

• The density of traps within the material depends on their rate of creation by the fast neutron flux and their rate of destruction by thermal annealing.
  
  – If $V$ is the volume fraction of the Zircaloy occupied by hydrogen traps,

  \[
  \frac{dV}{dt} = A\phi (1 - V) - bV \\
  b = b_0 \exp \left(-\frac{Q_b}{RT}\right)
  \]

  – Where $\phi$ is the fast neutron flux and the terms $A$ and $b$ are assumed to be independent of both the volume fraction $V$ and the time $t$.

• If flux and temperature are constant the volume fraction of traps is.

\[
V = V_\infty + (V_0 - V_\infty) \exp\left(-\left(A\phi + b\right)t\right).
\]

where $V_0$ is the initial unirradiated volume fraction of trap and $V_\infty$ the saturation volume fraction.

\[
V_\infty = \frac{A\phi}{A\phi + b}
\]
Ran In-Reactor ATR test to Check Model Concept

Diffusion couples
• Zircaloy-4 in the Recrystallized alpha annealed condition
• One half precharged above solubility at test temperature
• Other half not precharged

Hypothesis Result
• During exposure the hydrogen concentration of the original uncharged end will come into solid solution equilibrium with the original charged end.
  • Out-of-reactor will measure dissolution solvus at original uncharged end.
  • In-reactor as flux / fluence increases will measure more than dissolution solvus by the amount pulled into traps.
  • In-reactor as temperature increases will measure less hydrogen in traps

Exposure Environment

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Days</th>
<th>Fast Neutron Flux (E&gt;1MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>271°C - 279°C</td>
<td>403</td>
<td>Out-of-flux</td>
</tr>
<tr>
<td>314°C</td>
<td>282</td>
<td></td>
</tr>
<tr>
<td>354°C</td>
<td>105</td>
<td>Out-of-flux</td>
</tr>
</tbody>
</table>
Test Diffusion Couples

An Archive Section Created for Each Diffusion Couple

Post holes for assembly into ATR holders

Non-Precharged Side

Precharged Side

Met sample

<table>
<thead>
<tr>
<th>Hydrogen 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen 2</td>
</tr>
<tr>
<td>Hydrogen 3</td>
</tr>
<tr>
<td>Hydrogen 4</td>
</tr>
<tr>
<td>Hydrogen 5</td>
</tr>
<tr>
<td>Hydrogen 6</td>
</tr>
</tbody>
</table>

Met sample

<table>
<thead>
<tr>
<th>Hydrogen R1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen R2</td>
</tr>
<tr>
<td>Hydrogen R3</td>
</tr>
<tr>
<td>Hydrogen R4</td>
</tr>
<tr>
<td>Hydrogen R5</td>
</tr>
<tr>
<td>Hydrogen R6</td>
</tr>
</tbody>
</table>
Test

Hydrogen Pickup Controls
Uncharged and Uniformly Precharged
An Archive Section Created for Each Pickup Control
## Results

**Corrosion Weight Gain (mg/dm²)**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Days</th>
<th>Out-of-Flux</th>
<th>$1 \times 10^{11}$</th>
<th>$6 \times 10^{12}$</th>
<th>$1.1-1.4 \times 10^{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pre-film / Total</td>
<td>Pre-film / Total</td>
<td>Pre-film / Total</td>
<td>Pre-film / Total</td>
</tr>
<tr>
<td>314°C</td>
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<td>105</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### 590°F High Flux

**Non-Precharged Side**

**Precharged Side**

![Images of corrosion samples](Image)

590°F High Flux

520°F High Flux

520°F Low Flux

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25.4 μm
Results
Hydrogen Concentration Measured by LECO

Results of Standards Run With Specimens

Chronological Time of Analysis

Average 48.6 ppm
Sigma 3.7 ppm

Average 110.9 ppm
Sigma 3.8 ppm

Hydrogen Pick-up From Uncharged Control Samples (ppm)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Days</th>
<th>Out-of-Flux</th>
<th>$1 \times 10^{11}$</th>
<th>$6 \times 10^{12}$</th>
<th>$1.1-1.4 \times 10^{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>271°C - 279°C</td>
<td>403</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>314°C</td>
<td>282</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>354°C</td>
<td>105</td>
<td>6</td>
<td></td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>
Results

Examples of Results from Diffusion Couples

271 C Autoclave Exposure Example

271 C High Flux Exposure Example

271 C Mid Flux Exposure Example

314 C High Flux Exposure Example
## Results

### Summary of Results

<table>
<thead>
<tr>
<th>Location</th>
<th>Measured $C_E$ (ppm)*</th>
<th>Measured Pickup (ppm)**</th>
<th>Measured Diffusion (ppm)***</th>
<th>Solubility (ppm)****</th>
<th>Measured Trapping (ppm)*****</th>
</tr>
</thead>
<tbody>
<tr>
<td>271C Autoclave</td>
<td>64</td>
<td>7</td>
<td>57</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>279C Low Flux</td>
<td>84</td>
<td>7</td>
<td>77</td>
<td>60</td>
<td>17</td>
</tr>
<tr>
<td>278C Mid Flux</td>
<td>83</td>
<td>7</td>
<td>76</td>
<td>59</td>
<td>17</td>
</tr>
<tr>
<td>275C High Flux</td>
<td>103</td>
<td>14</td>
<td>89</td>
<td>57</td>
<td>32</td>
</tr>
<tr>
<td>314C High Flux</td>
<td>125</td>
<td>5</td>
<td>120</td>
<td>89</td>
<td>31</td>
</tr>
<tr>
<td>354C out of flux</td>
<td>142</td>
<td>6</td>
<td>136</td>
<td>138</td>
<td>--2</td>
</tr>
<tr>
<td>354C High Flux</td>
<td>184</td>
<td>50</td>
<td>134</td>
<td>138</td>
<td>-4</td>
</tr>
</tbody>
</table>

* Average of post test sample H1 and H2 data in Table 5.
** Hydrogen Pickup Data From Uncharged Control
*** Column 3 subtracted from Column 2
**** Dissolution Solvus from Reference [12] in paper
***** Column 5 subtracted from Column 4
Literature Data

“Irradiation Effect on Dissolution Solvus”

Irradiation effect on Dissolution solvus from McMinn, Darby, Schofield Paper (ASTM STP 1354)

- Material irradiated between 250°C to 300°C to fluences of 5.5 to 55 x 10^{20} neutrons / cm^2
- See about a 10 to 20 ppm effect on the reported dissolution solvus at 250 to 300°C

Irradiation effect on Dissolution solvus from Vizcaino Paper (ASTM STP 1529)

- Material irradiated between 250°C to 300°C to fluences of 70 to 100 x 10^{20} neutron/cm^2
- See about a 30 to 60 ppm effect on the reported solvus at 250 to 300°C

Measured effect is not inconsistent with “Irradiated Solvus” measurements through calorimetry. The comparison may also be indicating increased trapping occurs at C component loops formed at higher fluence.
Conclusions

• Trapping of hydrogen at irradiation induced defects in the metal is occurring.
• The amount of trapping occurring is a function of the irradiation conditions (temperature, flux and/or fluence).
• The amount of hydrogen being trapped will change as the irradiation conditions change.
• To accurately account for the effect of trapping of hydrogen at irradiation induced defects, more than an “irradiation effect” on the hydride solvus needs to be considered.
• The overall effect of including trapping of hydrogen at irradiation induced defects in hydrogen migration models will be to make hydrogen migration less dependent on thermal gradients within a component than predicted by current models considering only the hydride solvus. The effects will be greater under lower temperature and lower thermal gradient irradiation conditions.