INITIATION OF DELAYED HYDRIDE CRACKING IN Zr-2.5Nb

MICRO PRESSURE TUBES

by

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Abstract

Pressure tubes pick up hydrogen while they are in service within CANDU reactors. Sufficiently high hydrogen concentration can lead to hydride precipitation during reactor shutdown/repair at flaws, resulting in the potential for eventual rupture of the pressure tubes by a process called Delayed Hydride Cracking (DHC). The threshold stress intensity factor ($K_{TH}$) below which the cracks will not grow by delayed hydride cracking of Zr-2.5Nb micro pressure tubes (MPTs) has been determined using a load increasing mode (LIM) method at different temperatures. MPTs have been used to allow easy study of the impact of properties like texture and grain size on DHC. Previous studies on MPTs have focused on creep and effects of stress on hydride orientation; here the use of MPTs for DHC studies is confirmed for the first time.

Micro pressure tube samples were hydried to a target hydrogen content of 100 ppm using an electrolytic method. For DHC testing, 3 mm thick half ring samples were cut out from the tubes using Electrical Discharge Machining (EDM) with a notch at the center. A sharp notch with a root radius of 15 µm was introduced by broaching to facilitate crack initiation. The direct current potential drop method was used to monitor crack growth during the DHC tests. For the temperature range tested the threshold stress intensity factors for the micro pressure tube used were found to be 6.5-10.5 MPa.m$^{1/2}$ with the value increasing with increasing temperature. The average DHC velocities obtained for the three different test temperatures 180, 230 and 250°C were 2.64, 10.87 and 8.45 x 10$^{-8}$.
m/s, respectively. The DHC data obtained from the MPTs are comparable to the data published in the literature for full sized CANDU pressure tubes.
Acknowledgements

I would like to acknowledge and thank the following people who made the completion of this thesis possible:

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And, to my family and friends for providing all the support I needed.
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<thead>
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<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AECL</td>
<td>Atomic Energy of Canada Limited</td>
</tr>
<tr>
<td>CANDU</td>
<td>CANada Deuterium Uranium Reactor</td>
</tr>
<tr>
<td>MPT</td>
<td>Micro Pressure Tube</td>
</tr>
<tr>
<td>DHCv</td>
<td>Delayed Hydride Cracking Velocity, m/s</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TTT</td>
<td>Time-Temperature Transformation</td>
</tr>
<tr>
<td>TSSD</td>
<td>Terminal Solid Solubility of Dissolution</td>
</tr>
<tr>
<td>TSSP</td>
<td>Terminal Solid Solubility of Precipitation</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Stress intensity factor, MPa.m$^{1/2}$</td>
</tr>
<tr>
<td>$K_{IH}$</td>
<td>Threshold stress intensity factor, MPa.m$^{1/2}$</td>
</tr>
<tr>
<td>$K_{IC}$</td>
<td>Fracture toughness of the material, MPa.m$^{1/2}$</td>
</tr>
<tr>
<td>$\alpha_{Zr}$</td>
<td>high temperature hexagonal close-packed phase in zirconium</td>
</tr>
<tr>
<td>$\beta_{Zr}$</td>
<td>high temperature body-centered cubic phase in zirconium</td>
</tr>
<tr>
<td>$\beta_{Nb}$</td>
<td>low temperature body-centered phase near the niobium rich end of the Zr-Nb phase diagram</td>
</tr>
<tr>
<td>$\beta_{enr}$</td>
<td>low temperature body-centered phase enriched in Nb in the Zr-Nb phase diagram</td>
</tr>
<tr>
<td>$\omega$</td>
<td>low temperature metastable hexagonal phase in Zr-2.5Nb</td>
</tr>
<tr>
<td>$\delta$-hydride</td>
<td>low temperature face-centered cubic phase in Zr-H phase diagram</td>
</tr>
<tr>
<td>$\epsilon$-hydride</td>
<td>low temperature face-centered tetragonal phase near the hydrogen rich end of the Zr-H phase diagram</td>
</tr>
<tr>
<td>$\sigma_{th}$</td>
<td>Threshold stress, MPa</td>
</tr>
<tr>
<td>DCPD, PD</td>
<td>Direct Current Potential Drop</td>
</tr>
<tr>
<td>AE</td>
<td>Acoustic Emission</td>
</tr>
<tr>
<td>LIM</td>
<td>Load Increasing Mode</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>LDM</td>
<td>Load Decreasing Mode</td>
</tr>
<tr>
<td>$T_{\text{test}}$</td>
<td>Test temperature, °C</td>
</tr>
<tr>
<td>$a_{\text{avg}}$</td>
<td>Average crack length measured using Image analysis, mm</td>
</tr>
<tr>
<td>$B$</td>
<td>Thickness of the sample, mm</td>
</tr>
<tr>
<td>$W$</td>
<td>Width of the sample, mm</td>
</tr>
<tr>
<td>$D_H$</td>
<td>diffusion coefficient of hydrogen in $\alpha$-Zr</td>
</tr>
<tr>
<td>$C_H$</td>
<td>terminal solid solubility of hydrogen</td>
</tr>
<tr>
<td>$t_{\text{DHC}}$</td>
<td>time under load for DHC</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

The delayed hydride cracking (DHC) phenomenon has been the topic of extensive study since its identification in pressure tubes in the Pickering CANDU reactors in the mid-1970’s. DHC is a step-wise delayed failure’ process involving the diffusion of hydrogen to a high tensile stress region, formation of hydrides with an orientation normal to the applied tensile stress and the eventual fracture of these hydrides. The process has been identified as starting at areas of high residual stresses or in pre-existing crack fronts or notches which act as stress-raisers.

Under operating conditions hydrogen is present in solution in the zirconium alloy pressure tubes in CANDU reactors, not as hydrides, and hence cracking does not occur; however, when the temperature decreases during a shutdown, hydrides form and grow. They must reach a critical size before cracking occurs. At a blunt flaw a critical stress level must be reached to initiate a crack and at a sharp flaw, a critical stress intensity (K_I) must be reached before cracking starts. This threshold stress intensity factor, K_{IH}, for the initiation of cracks by the DHC process is thus an important parameter in characterizing and studying DHC.
A $K_{IH}$ of 10 MPa.m$^{1/2}$ or more is preferred in CANDU pressure tubes to give a large margin before cracking can occur. The value of $K_{IH}$ can be achieved by modifying the alloy composition, and by modifying the processing parameters (which affect texture and grain size). The work carried out in this thesis uses Micro Pressure Tubes (MPTs). MPTs are made with very similar microstructures and textures to those found in real pressure tubes, but using much less material. The effect of alloy composition or processing changes on microstructure, texture etc. and the subsequent effect on $K_{IH}$ and crack velocity can be studied more easily with MPTs than full size pressure tubes.

Despite the large amount of research on DHC, there is some ambiguity as to the definition and method for determining the $K_{IH}$ which introduces difficulties in the study of DHC in pressure tubes; for example some authors measure $K_{IH}$ values from samples with machined notches, others from fatigue cracks. The small size of MPTs compared to full size pressure tubes also makes it difficult to carry out controlled cracking tests. Due to the complexity associated with small samples obtained from MPTs a modified experimental procedure for DHC has been developed as explained in the experimental section.

The objective of the work described in this thesis is to establish and validate an experimental technique for measuring $K_{IH}$ and DHC velocity using MPTs. It is anticipated that a proven method for the use of MPTs for DHC testing will enable a wide
range of studies investigating the impact of processing conditions on DHC and hence of the properties of full sized CANDU pressure tubes. For this work an electrolytic hydriding technique was developed to hydride the MPTs and a delayed hydride cracking thermomechanical loading rig was fabricated to carry out the cracking tests. The main objectives are given below:

- MPTs have been used to allow simplified and wide-ranging studies of the effect of process conditions on properties such as texture and grain size and hence on the performance of Zr-2.5Nb pressure tubes. To date studies using MPTs have focused on creep behavior and effects of stress on bulk hydride orientation. Here the aim is to evaluate the use of MPTs for DHC studies for the first time.

- To develop at Queen’s an electrolytic technique for hydriding MPT samples as well as a test rig to enable DHC tests on MPTs using the potential drop technique to monitor crack growth.

- To determine the threshold stress intensity factor and velocity associated with crack growth by DHC as a function of test temperature in an example microstructure.
Chapter 2
Literature Review

2.1 Introduction

The CANDU (CANada Deuterium Uranium) nuclear reactor is a successful nuclear power generating system. CANDU uses natural uranium (UO$_2$) as the fuel material with no enrichment; in natural uranium fuel, only 0.72% of the uranium atoms are fissionable. This is possible because the CANDU design attains a higher neutron economy than other reactors designs that use enriched uranium, i.e. fewer neutrons produced by the fission reactions are absorbed. Heavy water is used as both the moderator and the coolant (which has lower neutron absorption than light water). The overall structure of a CANDU reactor is shown in Figure 1. The heat produced by the fission reaction in the reactor core is transferred to the steam generators via the coolant. The primary coolant is kept under pressure to avoid steam forming in the core. Steam generator extracts heat from coolant; power is then generated via a conventional turbine attached to the steam generator.
Figure 1 CANDU nuclear reactor in a power plant\(^1\).

The core of the CANDU reactor contains the fuel channel shown in Figure 2. The core of the CANDU reactor is a large cylindrical vessel called the Calandria. Running through the Calandria from one end to the other are a set of concentric tubes; the calandria tubes with pressure tubes inside. The pressure tube themselves contain the uranium fuel bundles. The major fuel channel elements shown in Figure 2 are the calandria tubes, pressure tubes (forming the pressure boundary), fuel bundles and the spacers that maintain an annulus between the calandria tubes and the pressure tubes.

The Calandria contains the heavy water moderator, which is held at 80\(^\circ\)C. The moderator is separated from the coolant by the calandria tubes and the pressure tubes. The coolant
passes through the pressure tube and over the fuel with temperatures ranging from
~250°C at the inlet end to ~300°C at the outlet end, and a pressure of about 10-11 MPa.
This results in a hoop stress of about 130 MPa. The pressure tube environment is such
that the material from which is made thus needs to possess good corrosion properties in
the coolant water combined with good mechanical properties and low absorption of the
thermal neutrons. Zr-2.5Nb is used as the pressure tube material as it meets the required
properties for the pressure boundary.
Figure 2 CANDU fuel channel\textsuperscript{2}. 
2.2 Zirconium and its alloys in the nuclear industry:

Zirconium and its alloys are used extensively in nuclear reactor components such as the calandria tube, pressure tube and for fuel cladding due to its attractive properties including principally low absorption cross-section for thermal neutrons (0.185 barns)\(^3\), as well as good corrosion resistance at high temperatures and good mechanical properties. Some widely used alloys of zirconium currently in the nuclear industry are Zircaloy-2, Zircaloy-4, Zr-1Nb and Zr-2.5Nb; compositions are shown in Table 1. Pressure tubes in CANDU reactors were initially made of Zircaloy-2; however the requirement for high strength alloys and lower hydrogen ingress made Zr-2.5Nb the preferred material for pressure tubes. The mechanical properties of these alloys are compared in Table 2.
Table 1 Zirconium alloys used in the nuclear industry.

<table>
<thead>
<tr>
<th>Alloy Elements, wt%</th>
<th>Zircaloy-2 Sn</th>
<th>1.2-1.7</th>
<th>1.2-1.7</th>
<th>0.9-1.1</th>
<th>-</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>0.07-0.2</td>
<td>0.18-0.24</td>
<td>&lt;500ppm</td>
<td>&lt;650</td>
<td></td>
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<tr>
<td>Cr</td>
<td>0.05-0.15</td>
<td>0.07-0.13</td>
<td>-</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.03-0.08</td>
<td>-</td>
<td>&lt;200ppm</td>
<td>&lt;35</td>
<td></td>
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<tr>
<td>O, ppm</td>
<td>900-1300</td>
<td>900-1400</td>
<td>&lt;1000ppm</td>
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<tr>
<td>N, ppm</td>
<td>&lt;80</td>
<td>&lt;65</td>
<td>&lt;60ppm</td>
<td>&lt;65</td>
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<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
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<tr>
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<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;15ppm</td>
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<td>&lt;270</td>
<td>150-400</td>
<td>&lt;200ppm</td>
<td>&lt;125</td>
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<td>P, ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;10</td>
<td></td>
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<tr>
<td>Application</td>
<td>Fuel tube, Calandria</td>
<td>Fuel tube</td>
<td>Pressure tube</td>
<td>Fuel tube</td>
<td></td>
</tr>
</tbody>
</table>

-balznce Zr, with Al < 75ppm, B and Cd < 0.5ppm, Co and Mg < 20 ppm, and Hf < 50-150 ppm⁴.
2.2.1 Zr-2.5Nb pressure tubes:

Pressure tubes made of Zr-2.5Nb form the primary pressure boundary in the fuel channels in CANDU reactors. The Zr-Nb binary phase diagram is shown in Figure 3. Zirconium at temperatures above 862°C transforms from the low temperature stable hexagonal close packed α-structure to body centred β-phase. Alloying elements in Zr can be either α or β stabilizers. α-zirconium stabilizers include tin, aluminum and oxygen. β-stabilizers included niobium, iron, molybdenum, hydrogen and nickel. The combination of good strength and ductility in this alloy is achieved by a fine microstructure of elongated α-grains with 0.5% Nb and the β-phase containing 20% Nb at the grain boundaries.

CANDU pressure tubes are produced by a standard fabrication route as shown in Figure 4. Quadruple-arc melted sponge zirconium and a master alloy of Zr-Nb were used for the ingot production of CANDU Zr-2.5Nb pressure tubes of the composition shown in Table 1. The ingots are then pre-heated to 1015°C (βZr phase) and press-forged into polygons followed by preheating to 800°C (αZr+βZr phase) and rotary forging into logs of approximately 210 mm in diameter. These logs are then machined into hollow billets, heated into the βZr phase field (1015°C), quenched or slow-cooled and then re-machined for extrusion. The as forged billets have a microstructure of hcp α-grains (≤ 1 wt% Nb) with a grain boundary network of metastable bcc β-phase containing about 20% Nb; while forged and β-quenched billet have fine Widmanstatten or martensitic structure with
a uniform distribution of Nb. As the forging is carried out in the $\beta$-phase field with a subsequent phase transformation, the forging produces a relatively random basal plane texture\textsuperscript{5}. The forged billet’s grain size affects the extruded billet microstructure, extrusion from forged and $\beta$-quenched billets having finer microstructures compared to extrusion from a forged billet.

It is principally the extrusion of the pressure tube in the $\alpha_{Zr}+\beta_{Zr}$ phase field at 815°C (Figure 3) that yields the preferred microstructure and texture of the CANDU pressure tubes. Extrusion at 815°C gives the pressure tube a microstructure with $\alpha_{Zr}$ grains flattened in the radial and elongated in the axial direction with a grain boundary network of $\beta_{Zr}$ containing 18-20% Nb\textsuperscript{6}. Thermal treatments like annealing could decompose this $\beta_{Zr}$ as discussed later in this section.
Figure 3 Zr-Nb equilibrium phase diagram\textsuperscript{7}.
Sponge Zr
+ alloy addition

Double or quadruple vacuum arc melt ingot

Forge at 1015°C and 815°C

Solution anneal at 1015°C and Water Quench

Extrude at 815°C
10.5:1 Extrusion Ratio

Cold-draw 20-30%
(normally about 27%)

Autoclave 400°C for 24h

Figure 4 CANDU fabrication route.8
### Table 2. Mechanical properties of Zr alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature</th>
<th>0.2% yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Percent elongation (TCE in %)</th>
<th>Fracture toughness</th>
<th>Creep strain rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>Room</td>
<td>80</td>
<td>220</td>
<td>45</td>
<td>–</td>
<td>At $\sigma = 88$MPa and 310°C</td>
</tr>
<tr>
<td></td>
<td>300°C</td>
<td>45</td>
<td>120</td>
<td>55</td>
<td>–</td>
<td>($\sim 1 \times 10^{-4}$ h$^{-1}$)</td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room</td>
<td>275</td>
<td>435</td>
<td>20 (18)</td>
<td>–</td>
<td>At 300°C, 110MPa</td>
</tr>
<tr>
<td>(Fully annealed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($\sim 2.4 \times 10^{-6}$ h$^{-1}$, cut-off-pile)</td>
</tr>
<tr>
<td></td>
<td>343°C</td>
<td>103</td>
<td>200</td>
<td>–</td>
<td>–</td>
<td>($\sim 3.6 \times 10^{-6}$ h$^{-1}$, in pile)</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>Room</td>
<td>410</td>
<td>480</td>
<td>20 (10)</td>
<td>–</td>
<td>At $\sigma = 88$MPa and 350°C</td>
</tr>
<tr>
<td>(Stress relieved)</td>
<td>Room</td>
<td>205</td>
<td>272</td>
<td>28</td>
<td>–</td>
<td>($\sim 1 \times 10^{-4}$ h$^{-1}$)</td>
</tr>
<tr>
<td>Zr+1Nb (annealed)</td>
<td>Room</td>
<td>300°C</td>
<td>270</td>
<td>33</td>
<td>–</td>
<td>$K_V = 55-45$MPa.m$^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>Room</td>
<td>127</td>
<td>145</td>
<td>33</td>
<td>–</td>
<td>$K_I = 60-75$</td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room</td>
<td>420</td>
<td>580</td>
<td>18</td>
<td>–</td>
<td>$K_{IC} = 16-17$MPa.m$^{1/2}$</td>
</tr>
<tr>
<td>(Cold worked)</td>
<td>Room</td>
<td>300°C</td>
<td>270</td>
<td>33</td>
<td>–</td>
<td>After $\sigma = 150$MPa and 350°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>325</td>
<td>460</td>
<td>14</td>
<td>–</td>
<td>($\sim 1 \times 10^{-4}$ h$^{-1}$)</td>
</tr>
</tbody>
</table>

The texture produced by the standard extrusion conditions has most of the $\alpha$-grains having basal plane normals oriented in the circumferential direction\(^9\). The exact texture is controlled by the extrusion pre-heat temperature, extrusion ratio and billet quench state. High pre-heat temperatures result in inhomogenous and coarse grains with a Widmanstatten microstructure; in contrast low pre heat temperatures give fine uniform $\alpha$-grains with higher yield strength, ductility and fracture toughness\(^10\). Figure 5 shows the transmission electron micrographs of the tubes after extrusion and cold working. After extrusion the tubes shows a microstructure with elongated $\alpha$ grains in the direction of extrusion and a grain boundary network of $\beta$ phase. Figure 6 shows the texture variation in the pressure tubes during processing. In small tubes used by Holt and Aldridge\(^5\), increasing $\alpha$-grain size increases the fraction of radial to tangential basal plane normals.

The smaller range of grain sizes or the lower strain rate for the large extrusions resulted
in the observed differences between the small and full sized pressure tubes. Increasing the pre-heat temperature was found to increase the proportion of basal plane normals in the axial direction and decrease the ratio of the number of basal plane normals in the radial to the transverse direction. Extrusion ratio was also found to affect the texture, with an increase in extrusion ratio the proportion of the basal plane normals decreases in the radial direction and increases in the axial and transverse direction.

![Micrographs](image)

(a) (b)

Figure 5 TEM micrographs showing extruded Zr-2.5Nb tubes (a) with elongated α grains in the direction of extrusion and a grain boundary network of β phase; (b) micrograph of cold drawn tube with elongated α grains many dislocation networks and grain boundary β phase.
In CANDU Zr-2.Nb pressure tubes, it is the extrusion step that is found to define the texture of the tubes; the subsequent cold drawing process which results in a 20-30% reduction in total area after extrusion does not appear to affect the texture but elongates the $\alpha$-grains\textsuperscript{11,12}. Figure 6 (b) shows the tube microstructure with elongated $\alpha$ grains with dislocation networks and grain boundary $\beta$ phase. Cold drawing of the pressure tubes is
followed by stress-relieving at 400°C for 24 hours. Stress-relieving does not affect the texture but may affect the microstructure of the tube. During the annealing process Zr-2.5Nb undergo β decomposition to transition phases such as α andω, before forming the equilibrium phases. The Time-Temperature Transformation diagram for this temperature range is shown in Figure 7\textsuperscript{13}.

![Figure 7 TTT diagram of Zr-19 wt. % Nb cooled from 850°C\textsuperscript{13}.](image)

The metastable hexagonal ω phase forms by aging of quenched β\textsubscript{Zr} phase or directly by β quenching, which then transforms to the stable α zirconium phase and body centred β\textsubscript{Nb} phase. The transformation from metastable β\textsubscript{Zr} is given by Aldridge and Cheadle\textsuperscript{14} is as follows,

\[ \beta_{Zr} \rightarrow \omega + \beta_{enr} \]
\[ \beta_{enr} \rightarrow \omega + \beta_{Nb} \text{ or } \beta_{Zr} \rightarrow \alpha_{Zr} + \beta_{Nb} \]
\( \omega \rightarrow \alpha + \beta_{\text{Nb}} \)

This transformation of \( \alpha_{\text{Zr}} \) and \( \beta_{\text{Nb}} \) is a strongly time dependent one and the amount increases with increasing time\(^{13} \). Typically the kinetics is such that the transformation has only started to occur when the pressure tube is first placed in the reactor.

### 2.3 Hydrides in Zr-2.5Nb alloy pressure tubes:

At temperatures above 500°C, Zr and its alloys can accept hydrogen up to 450 ppm in solid solution. The solubility of hydrogen in solution follows an Arrhenius relationship with temperature. With a decrease in temperature the solubility decreases at a higher rate and will precipitate as brittle hydrides when the local terminal solubility at that particular temperature is exceeded. The hcp \( \alpha \) zirconium has low solubility for hydrogen, reaching as low as 0.05 ppm at room temperature\(^{15} \).

The CANDU pressure tube fabrication route is such that the tubes have a hydrogen concentration of less than 10 ppm\(^{4} \) (<25 ppm until 1994 and <5 ppm in recent years). However the Zr-alloys used in nuclear reactors absorb hydrogen from the coolant during the reactor service according to the following reaction\(^{15} \),

\[
\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \quad \text{(Equation 1)}
\]
Some of the hydrogen released from the heavy water from the above corrosion reaction enters the pressure tubes. The amount of hydrogen diffusing into the Zr because of the reaction is usually less than 2-10% of that produced, but does result in an increase in hydrogen concentration with the life of the tube.

The solubility of hydrogen at 300°C can be 65 ppm and at room temperature it goes down to as low as 0.05 ppm\textsuperscript{16,17}. As already noted, when the concentration of hydrogen exceeds this solubility limit, which is called the terminal solid solubility for precipitation (TSSP) at the temperature under consideration, hydrides form and can result in hydride embrittlement\textsuperscript{16,18,19}. The hydrides can be seen by optical light microscope or Scanning or Transmission Electron Microscopy (TEM). They are observed as elongated platelets. The presence of hydrides generally affects the mechanical properties of the parent material decreasing the fracture toughness, impact strength and tensile ductility at slow strain rates. The exact effects of the hydrides depend on their morphology and orientation with respect to the stress axis. Thus the mechanism of hydride formation and its orientation relative to the stress axis in Delayed Hydride Cracking (DHC, a slow cracking phenomenon discussed in detail later) has become the focus of many researchers for a few decades since its identification.
In Zirconium alloys the hydrides formed may have one of the following three structures:\(^\text{20}\)

(i) $\gamma$-hydride; ZrH; fct, $a = 0.4596 \text{ nm}; c = 0.4969 \text{ nm}$

(ii) $\delta$-hydride; ZrH\(_{1.66}\); fcc, $a = 0.4778 \text{ nm}$

(iii) $\varepsilon$-hydride; ZrH\(_{2}\); fct, $a = 0.4980 \text{ nm}; c = 0.4445 \text{ nm}$

The Zr-H phase diagram is shown in Figure 8; the stable phases are $\delta$ and the $\varepsilon$ hydrides. Northwood and Gilbert\(^\text{21}\) have earlier shown that, fcc $\delta$-hydride is the predominant hydride in zirconium alloy materials.
Figure 8 Zr-H phase diagram with different hydride phases\textsuperscript{21}.

To assess the service life of pressure tubes, knowledge of the TSS of hydrogen is required. A large hysteresis is observed, with the temperature required for the hydrides to precipitate and dissolve being different in Zr-2.5Nb\textsuperscript{18, 22, 23}. Fong and Spooner\textsuperscript{23} studied the hydride dissolution and precipitation in Zr-2.5Nb alloys using Small Angle Neutron Scattering (SANS) from room temperature to 600 K containing 0.06 and 0.27 at% hydrogen. The SANS results allowed information about the concentration and shape of the hydrides to be obtained (Figure 9). For example, ice quenching of the samples produced needle-shaped hydrides oriented in the axial direction, while furnace cooling
resulted in plate-shaped hydrides with their normals oriented towards the radial direction. The Terminal Solid Solubility for Dissolution (TSSD) temperatures for 0.06 and 0.27 at% hydrogen was found to be 463 and 523 K, respectively.

![Figure 9 SANS intensity increasing with hydrogen concentration](image)

Figure 9 SANS intensity increasing with hydrogen concentration²³
Figure 10 (a) Young’s modulus versus temperature showing TSS hysteresis on a Zr-2.5Nb with 86 μg/g hydrogen\textsuperscript{18}; (b) graph demonstrating simplified TSS hysteresis response in Zr-2.5Nb.
Other techniques that have been used to study the phenomena include Differential Scanning Calorimetry (DSC)\textsuperscript{24} and Dynamic Elastic Modulus (DEM)\textsuperscript{18}. Change in dynamic elastic modulus measurements have been used to express TSS as a function of temperature and the hysteresis between the TSS of hydride dissolution and precipitation has been studied by Puls et al \textsuperscript{18}. The sharp knees observed in Figure 10 (a) of DEM versus temperature are associated with hydride Dissolution while heating and Precipitation during cooling. This particular temperature at the knee can be used to obtain the TSS hysteresis boundary, i.e. to determine TSSD and TSSP. Modulus measurements clearly indicated the amount of hydrogen in solution depends on whether the hydrides precipitate or dissolve at the given temperature. It is also found that the thermal history of the samples has a strong effect on TSSP but little on TSSD; in turn the hysteresis also depends on the thermal history of the sample. Thus two bounding solubility curves can be defined-TSSP1, based on the precipitation of new hydrides and TSSP2, based on precipitation associated with hydride growth or the precipitation at previously formed hydrides. The TSS values obtained by dynamic elastic modulus measurements are given in Table 3.

As said above, the $\delta$-hydride is the predominant hydride phase formed in Zr-2.5Nb pressure tube alloys\textsuperscript{21}. There is a 17\% volume change associated with the transformation of alpha zirconium to delta hydride\textsuperscript{25}. Internal stresses developed during the transformation of alpha zirconium to delta hydride and the plastic work (hence
work (hence dislocations) due to the precipitation or dissolution of hydrides are responsible for the hysteresis of hydrogen solubility behavior in zirconium alloys\textsuperscript{25,26,27}.

Table 3\textsuperscript{26} TSSP and TSSD results from DEM.

<table>
<thead>
<tr>
<th>H + D/2 \textsuperscript{a} (µg/g)</th>
<th>TSSD (°C)</th>
<th>TSSP1 (°C)</th>
<th>T\textsubscript{max} (°C)</th>
<th>TSSP2 (°C)</th>
<th>T\textsubscript{max} (°C)</th>
<th>Sample no.</th>
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<td>99</td>
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<td>126.5</td>
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</tbody>
</table>

\textsuperscript{a} Uncertainty (two standard deviations) = 10%.
\textsuperscript{b} Ni-plated and gaseously hydrided at 250°C.

In Zr-2.5Nb alloys the addition of the β-stabilizers like Nb or Ni, decreases the maximum hydrogen pick up in these alloys\textsuperscript{28}. As the solubility of niobium in zirconium decreases
with temperature and a niobium rich phase precipitates, this eventually decreases the solubility of hydrogen in the $\beta + \delta$ region of the Zr-2.5Nb-H$_2$ system.

### 2.3.1 Hydride morphology and orientation:

Under reactor conditions when the terminal solid solubility is exceeded the hydrides precipitate in the form of needles or platelets. The hydrides tend to precipitate as platelets rather than needles with increasing hydrogen concentration and decreasing cooling rate$^{17}$. The hydrides will tend to precipitate in the grain boundary region in order to lower the total internal energy of the system. Hydride morphology studies have shown that the embrittlement effect can be reduced by changing the hydrides morphology from platelet to globular$^{29}$. This study on the impact of properties of unirradiated Zr-2.5Nb tubes quenched or furnace cooled also helps to understand the effect of hydride size on embrittlement. The deleterious effects of hydride formation increases significantly with the size of the hydrides, smaller hydrides formed by quenching results in better overall properties than larger hydrides.

### 2.3.2 Stress reorientation of hydrides:

The hydride embrittlement effect mostly depends on the orientation of the hydride platelets with respect to the stress axis. The two different orientations of hydrides in
pressure tubes are circumferential and radial orientations as shown in Figure 11. In CANDU pressure tubes, the microstructure of the cold worked and stress relieved Zr–2.5 wt% Nb alloy pressure tube material is such that under unstressed condition, only circumferentially oriented hydrides form\textsuperscript{9,30}. Figure 12 shows the hydride orientation in Zr-2.5Nb pressure tube materials hydrided electrolytically in the radial-circumferential plane of the tube\textsuperscript{31}. Hydrides reorient along the radial direction with their normals parallel to the applied tensile stress. The ease of stress reorientation increases with the amount of cold work done, or an increase in solution temperature and decreases with decreasing grain size; also the time under stress does not appear to significantly influence the amount of reorientation\textsuperscript{15}. Under an applied tensile hoop stress any radial hydrides behave in a brittle manner by providing an easy crack path. Circumferential hydrides have negligible effect on the mechanical properties under operating conditions unlike the radial hydrides assisting in fracture of the tubes. However, as noted the circumferentially oriented hydrides reorient in the radial directions under stressed condition since, by doing so, they effectively relieve the applied stress. There is a critical stress for this reorientation process called threshold stress for reorientation ($\sigma_{th}$), below which no reorientation of hydrides will occur.
The degree of embrittlement due to hydride reorientation is observed to be strongly influenced by the orientation of the hydride platelets and a certain minimum volume of reoriented hydride phase is required to cause a significant effect on the properties of the material.
reoriented hydride phase is required to cause a significant effect on the properties of the material\textsuperscript{32,33}. The threshold stress ($\sigma_{th}$), below which no reorientation occurs, is observed to increase with material strength and decrease with solution annealing temperature. This critical stress appears to depend on both microstructure and texture\textsuperscript{34}. It has been found that $\sigma_{th}$ is around 200 MPa in the axial direction for Zr-2.5Nb pressure tubes\textsuperscript{35,36,37}. Stress reorientation of hydrides is a reversible process i.e. if the material is heated to dissolve the hydrides and then cooled under zero stress, the hydrides will mostly return to their original, microstructure determined orientations. The degree of reorientation is found to increase with level of reorientation stress, for a given temperature and hydrogen concentration. The magnitude of the threshold stress required for reorientation decreases with increase in reorientation temperature.

For example, Marshall\textsuperscript{30} noted that the stress-orientation of the hydrides appeared to be a characteristic of the fabrication history in Zircaloy materials. The susceptibility to reorientation depends on the type of reduction, here hot-reduction or cold-reduction during fabrication were considered. The author showed that the degree of stress reorientation was much higher for hot-reduced tubes than the cold-reduced tubes regardless of the thickness reduction during fabrication. This suggestion helped to control the amount of reorientation by minimizing the working temperature of the pressure tubes.
Marshall also observed that the ease of stress reorientation is high in the direction of the material where the major fabrication strain is compressive rather than tensile. Thus stress-reorientation is higher in the radial and circumferential direction for the reduced tubes while for expanded tubes it is higher in the longitudinal and radial directions; and also in the case of rolled plates, in the thickness direction. By controlling the fabrication procedure, stress reorientation can be reduced. Texture effects however were not observed clearly by the author. Reorientation of hydrides in pressure tube alloys is influenced by many factors like crystallographic texture\textsuperscript{38,39,40,41}, prior strain\textsuperscript{30}, grain structure\textsuperscript{34} and applied stress\textsuperscript{15,17,42}.

2.3.3 Memory effect:

There seems to be a memory effect associated with the precipitation of hydrides in Zr-2.5Nb alloys. That is the hydrides that are present in the material before a thermal treatment to above the solution temperature influence the size, distribution and morphology of the re-precipitated hydrides on subsequent cooling\textsuperscript{43}.

Much of the work carried out in the literature on stress reorientation did not account for the memory effect. The degree of stress reorientation increases with increasing cold work, with decreasing grain size and is insensitive to the quantity of basal plane normals in the direction of stress\textsuperscript{44}. Parry\textsuperscript{35} found that reorientation is insensitive to the time under
stress but increased with increasing solution temperature and also does not vary consistently with initial hydrogen concentration.

The stress reorientation of hydrides leads to a crack growth mechanism in pressure tubes with time, when the hydrogen in solution increases. This forms the basic cause of delayed hydride cracking (DHC).

2.4 Hydrogen induced delayed hydride cracking:

Delayed hydride cracking, (DHC) is a sub-critical crack growth mechanism involving the formation of brittle hydrides at the crack tip followed by the failure of the hydride. This results in crack extension and then growth of new hydrides at the new crack tip. The crack can extend again and eventually lead to rupture if the crack is not identified before the critical crack length is reached. Knowledge of the length of the initial crack size under which DHC can occur, the critical crack length for rupture and the velocity of the DHC, are all required to understand the process.

In zirconium alloys the hydrogen in solution will preferentially diffuse to the tensile stress field of the crack tip and hence can precipitate as hydrides even if the average hydrogen concentration is below TSSP. This hydrogen diffusion depends on thermal gradients as well as the stress state. When the hydrides reach a critical size and a critical
stress intensity at the crack tip, the hydrides fracture and the crack propagates, extending through the hydrides by approximately the length of the hydride and is then arrested in the matrix. The process can repeat hence the cracking occurs in steps, with each step of crack propagation leading to crack extension leaving striations on the resultant fracture surface. Crack growth is delayed by the time required for the hydrogen to reach the crack tip and form hydrides, and by the time for the hydride to grow to reach the critical size. Hence the name ‘delayed hydride cracking’. Since the hydrogen diffusion depends on the stress state and the stress state near a crack tip in turn is a function of the yield stress of the zirconium material; there is an expectation that the driving force for DHC is higher for materials with a high yield stress. Hydrogen diffusion will also depend on the availability of hydrogen in the material and the ease with which it can diffuse to the crack tip; it is a thermally activated process. Hence the crack growth rate (crack velocity) is also a thermally activated process. The dependence of the crack velocity on the stress intensity factor is shown schematically in Figure 13. It can be seen from the figure that the crack velocity is negligible below a threshold stress intensity factor, $K_{IH}$, even if there is a large amount of hydrogen diffused at the crack tip, since the crack grows only when the critical stress intensity is reached. Above this stress intensity there is no change in crack velocity until it reaches another threshold, the fracture toughness of the zirconium material $K_{IC}$. After $K_{IC}$ the crack growth is abrupt corresponding to unstable fracture. The crack velocity decreases with decrease in temperature as seen in Figure 14. The mechanism is highly important in determining the life of pressure tubes in
CANDU reactors due to the increasing hydrogen concentration with time as discussed in Section 2.3.

Figure 13 Schematic relationship between crack velocity versus stress intensity factor shown by DHC phenomenon\textsuperscript{48}. 
Figure 14 DHC velocity versus temperature\textsuperscript{45}

2.4.1 Theory of delayed hydride cracking velocity:

The process of delayed hydride cracking is shown in a simple schematic sketch in Figure 15. The hydrogen content in the pressure tube material increases with time due to the corrosion reaction in Equation 1 and hydrogen diffuses to the crack tip. The hydride nucleating at the crack tip will usually precipitate perpendicular to the tensile stress direction\textsuperscript{47}, i.e., in the radial direction, when the stress is applied in the circumferential direction of the tube (shown in the figure below) and described in Section 2.3.2.

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Theoretical models of delayed hydride cracking based on crack tip stress states and the above outline of the process have been developed by a number of authors like Dutton et al.\cite{Dutton}, Simpson and Puls\cite{Simpson}. The model by Dutton et al. assumes a cylindrical geometry of crack length (a) as shown in Figure 16. Due to the volume change in hydride precipitation from the $\alpha$-zirconium matrix, the hydrides precipitate favorably in a region of radius $l'$ as in the figure, which gives rise to a thermodynamic driving force for hydrogen located far away in the matrix to diffuse and precipitate at the crack tip.
Figure 16 Crack geometry used by Dutton et al.\textsuperscript{48}

The DHC velocity obtained depends on the diffusion coefficient and the solubility limits of hydrogen. The crack velocity expression as given by the model is,

\[ V = D_H C_H F \]  \hspace{1cm} (Equation 2)

where \( V \) is the crack velocity,

\( D_H \), the hydrogen diffusion coefficient,

\( C_H \), the terminal solid solubility, and

\( F \) is a function of hydriding morphology and diffusion geometry.
Dutton identified two regimes of crack propagation, stage I and II. Stage I is highly stress dependent and is controlled by the hydrides growing in the elastic gradient of the crack tip, while stage II is controlled by hydrides growing in the plastic zone at the crack tip and has a weak stress dependency. This model does not account for the TSS hysteresis of hydride formation.

Puls\textsuperscript{26} incorporated this hysteresis and updated the model of hydride growth to account for DHC. A recent model which accounts for the hysteresis of the solvus and focuses on the temperature gradient from the crack tip to the bulk is given by Puls\textsuperscript{26} and Sagat et al.\textsuperscript{49}. It has been observed experimentally and demonstrated using the model that above a certain temperature the crack cannot grow and the DHC cannot occur. This temperature above which DHC cannot occur is defined as DHC arrest temperature. When the testing temperature is approached from lower temperatures, Ambler\textsuperscript{50} found the arrest temperature to be \( \sim 200^\circ\text{C} \). When approached from above, so long as the material has sufficient hydrogen in solution, the arrest temperature is found to be around \( \sim 320^\circ\text{C} \).\textsuperscript{51,52}

\textbf{2.4.2 DHC crack initiation criteria:}

The criteria for crack initiation due to DHC in Zr alloys has been studied by many authors based on a critical stress value\textsuperscript{53,54,55,56}. The recent papers by Shi and Puls\textsuperscript{57} have
established quantitative models for the existence of threshold stress intensity ($K_{\text{TH}}$) and a critical hydride size for fracture to occur. According to Shi and Puls, when the local stress inside the hydride exceeds a particular stress needed for hydride fracture, a crack initiates,

$$\sigma_{\text{local}} > \sigma^h_f$$  \hspace{1cm} (Equation 3)

and further simplifying this local stress as the effective stress ($\sigma_{\text{eff}}$) on the hydride due to the applied stress plus the stress due to the formation of hydride ($\sigma^h$), the equation becomes,

$$\sigma_{\text{eff}}^* + \sigma^h > \sigma^h_f$$  \hspace{1cm} (Equation 4)

Here $\sigma^h_f$ is assumed to have a specific value and to be a material property of the hydride.

By analyzing these stresses a quantitative equation based on the threshold stress intensity factor $K_{\text{TH}}$ can be determined for the initiation of crack, given below for a mono-hydride-platelet model;
\[
(K_{ii})^2 = \frac{E^2 \varepsilon_i t}{8\pi(1 - \nu^2)\left(1 - \frac{\sigma_f}{\sigma_y}\right)}
\]

(Equation 5)

where \(t\) is the thickness of the hydride platelet, \(\nu\) is the Poisson’s ratio, \(\varepsilon\) is the stress free normal strain and \(\sigma_y\) is the yield strength of the zirconium matrix. From the Equation 5 it can be seen that the \(K_{ii}\) depends on the yield stress of the matrix material. Decrease in the material yield strength \(\sigma_y\) increases \(K_{ii}\), as will any other changes such as an increase in temperature, which affect the yield strength. The other term in the equation that strongly affects the \(K_{ii}\) is the thickness of the hydride. With increase in the hydride platelet thickness \(K_{ii}\) increases, and the crack initiation becomes difficult.

The experimental \(K_{ii}\) data observed seems to be significantly higher than that of the model prediction (Figure 17). This is proposed to be mainly because the model does not account for the multiple-hydrides present in reality. So the improvements subsequently needed included the effect of multi-layered hydrides as the hydrides precipitated in radial-axial planes, and the effect of the incomplete hydride coverage ratio, \(f\); i.e. the area fraction of hydride present in front of the crack tip. With these the equation becomes,

\[
K_{ii} = fK_{ii}^* + (1 - f)K_{IC}^{Zr}
\]

Equation 6
where $K_{IC}^{Zr}$ is the threshold stress intensity factor for the pressure tube alloys without hydrides and $K_{III}^{Zr}$ is the $K_{III}$ from the mono-hydride threshold equation above.

![Graph showing $K_{III}$ vs T(K)](image)

**Figure 17** Comparison of theoretical $K_{III}$ and experimental data\textsuperscript{57}.

### 2.4.3 Hydrogen concentration and factors influencing DHC:

DHC occurs only when the hydrogen in solution exceeds the solubility limit (TSSP) at the particular temperature. The average hydrogen concentration increases when hydrogen is absorbed in the alloy from the coolant during the service of the pressure tube.
2.4.3.1 Temperature effects on DHC

DHC is temperature dependent since the three processes involved, i.e. hydrogen diffusion, hydride formation and fracture of the hydrides, all depend on the temperature. Many authors have noted two particular temperature effects for DHC in Zr-2.5Nb pressure tubes. Firstly, different DHC behaviour is found to depend upon the direction of approach to the test temperature i.e. by heating or cooling. When cooling from the solvus (TSSD), the DHC velocity follows an Arrhenius relationship with the test temperature$^{58}$. When heated to the test temperature the DHC velocity shows the same relationship as in the cooling case up to a temperature, $T_{DAT}$ (‘Direction of Approach” temperature) and then decreases with further increase in temperature. The $T_{DAT}$ temperature found by Ambler et al. is around 150°C for pressure tube alloys$^{50}$.

Early authors$^{51}$ observed a temperature limit for fracture initiation, above which the crack does not grow. The crack arrest happens irrespective of whether there is enough hydrogen in solution as mentioned in Section 2.4.1. This temperature is sometimes identified as $T_{CAT}$ (‘Crack Arrest Temperature’). It has been found that the $T_{CAT}$ for 110ppm of hydrogen in Zr-2.5Nb alloys is around 320°C. There is not much literature regarding the mechanism by which cracking stops.

2.4.3.2 Yield strength and Microstructure:

Higher yield strength of the zirconium alloy seems to increase the DHC velocity (DHCV). CANDU pressure tubes made of Zr-2.5Nb alloys with semi-continuous β-phase
and higher yield strength are found to have higher DHCV than the Russian RBMK Zr-2.5Nb pressure tubes with fully discontinuous β-phase and lower yield strength\(^5^9\).

Y.S. Kim et al.\(^5^9\) suggested that the higher diffusion and hydrogen concentration governs the DHCV as proposed by the DHC model proposed in the equation given below\(^6^0\), rather than the hydrogen diffusion and solubility as explained by Dutton et al\(^4^8\). They also found that the CANDU pressure tubes had narrower striation spacing than the RBMK tubes, as the yield stress is lower.

Kim’s DHC model is given by,

\[
V = kD_H\frac{\Delta C}{\Delta X} = kD_H\frac{\Delta C(\sigma_{ys})^2}{(K_{ih})^2}
\]  

(Equation 7)

as \(\Delta X = k_s(K_{ih} / \sigma_{ys})^2\)

where \(V\) is the DHCV, \(D_H\) is the hydrogen diffusion, \(\Delta C\) is the supersaturated hydrogen concentration, and \(k, k_s\) are constants. Here \(\Delta X\), is the critical zone size in the plastic zone where hydride grows to the critical size to fracture. Therefore the activation energy for the DHCV \(Q_{DHCV}\) is the sum of the activation energy for hydrogen diffusion \(Q_H\) and activation energy for the formation of the hydrogen concentration gradient at the crack tip \(Q_{ss}\), given by,
\[ Q_{DHCV} = Q_H + Q_{SS} \]  \hspace{1cm} \text{(Equation 8)}

A hydride fractures when it reaches the \( \Delta X \) size representing the striation spacing observed after DHC. Thus the activation energy for hydrogen concentration gradient is obtained from the temperature dependency of the striation spacing which is dependent on the yield strength, \( K_{\mu} \) and \( \Delta C \). That indicated with higher yield strength the DHCV tends to increase with temperature.

As already noted, the microstructure of Zr-2.5Nb consists of \( \alpha \)-Zr matrix with continuous grain boundaries of \( \beta \)-Zr phase Figure 18(a). The \( \beta \)-Zr film of grain boundaries consists of 20\% Nb and it has been shown that the diffusion coefficient of hydrogen in \( \beta \)-Zr is two orders of magnitude higher than in \( \alpha \)-Zr \textsuperscript{61}. This greatly enhances the diffusion of hydrogen through a short-circuiting effect and hence the DHCV in as received Zr-2.5Nb materials with continuous \( \beta \)-Zr. With suitable heat treatment, the \( \beta \)-Zr phase becomes discontinuous, so the diffusion of hydrogen can be reduced resulting in lower values of DHCV than as-received Zr-2.5Nb material with no further heat treatments (Figure 18-b). This indicates the importance of the thermal history of the Zr on the DHCV determined.
Figure 18 Dark-field TEM micrographs showing the continuous (a) and the discontinuous (b) beta phase in as-received and heat-treated Zr-2.5Nb pressure tube specimens respectively\textsuperscript{61,62}.

Any step that causes a change in $\beta$ morphology, such as a stress relieving, will affect DHC since the DHC depends on the hydrogen diffusion. As noted the $\beta$-Zr is unstable and decomposes with heat treatment as shown below\textsuperscript{62&63}.

\[
\beta_{Zr} \rightarrow \omega + \beta_r \quad - - - - - T < 450^\circ C
\]
\text{or}
\[
\beta_{Zr} \rightarrow \alpha + \beta_{Nb} + \beta_r \rightarrow \alpha + \beta_{Nb} \quad - - - - - T > 450^\circ C
\]

(Equation 9)
Any decomposition of $\beta$-Zr phase will also likely affect the hydride precipitation and so the DHCV. Thus for any DHC study we should have a clear understanding of the thermal history of the sample.

2.4.3.3 Texture effects:

Recent studies by Y.S. Kim et al.\textsuperscript{64,65} on Zr-2.5Nb pressure tubes observed that the DHCV is two times higher in the axial direction than in the radial direction of the same cracking plane. This anisotropic DHCV was explained by the faster rate of hydrogen diffusion in the $\beta$-Zr grain boundaries in the axial direction in the temperature range of testing (150-250$^\circ$C). The threshold stress intensity factor $K_{\text{IH}}$ was also higher in the radial direction than the axial direction. The results are given in Figure 19 and Figure 20. S.S. Kim et al. also had similar results in their studies\textsuperscript{66,67}. Levi and Sagat\textsuperscript{68} confirmed this through their experiments on CANDU pressure tubes with either a heat treatment at 400$^\circ$C for 1000 h or annealing at 650$^\circ$C for 9 h. Their results are shown in Figure 21. Here the crack growth rate in the axial (T-L) and the radial direction (T-R or T-ST) was very similar the due to the fact that the initial non-uniform distribution of $\beta$-Zr became uniform after heat treatment.
Figure 19 DHCV with the orientation, fc-furnace cooled; wq-water quenched, thermal cycle and no thermal cycle representing heat treatment where the test temperature approached by cooling and by a heating without a cooling respectively\(^{64}\)

Figure 20 Threshold stress intensity factor for the onset of DHC with the orientation by load decreasing mode\(^{64}\)
Figure 21 DHC velocity varying with the orientation in a) Zr-2.5Nb tube annealed at 400°C for 1000h and b) Zr-2.5Nb tube annealed at 650°C for 9h$^{64}$ & $^{68}$. 
It has been proposed that DHC can be constrained if the crystallographic texture can be arranged such that the basal plane normals of the $\alpha$-grains are normal to the direction of the stress applied$^{69}$. CANDU pressure tubes are such that the fabrication process results in 60% of the basal plane normals in the circumferential direction and the rest mostly in the radial direction. Therefore, the cracking is easier in the plane perpendicular to the circumferential direction, i.e., in the radial or the axial direction on the axial-radial plane.

The fabrication route effect on DHC was studied by Singh et al.$^{70}$ They compared cold-worked and stress-relieved (CWSR) CANDU and Indian pressure tubes with quenched and aged (Q&A) Russian RBMK pressure tubes. The DHCV observed for Q&A pressure tubes appeared to be 2-3 times lower than that of the CWSR tubes (Figure 22). They attributed the difference in DHCV to the higher yield strength of the CWSR tubes and higher hydrogen diffusion rate, even though they found similar activation energies in all materials.
2.5 DHC test procedure:

Most of the studies to date on DHC have used cantilever beam (CB)\textsuperscript{66,71}, compact toughness (CT)\textsuperscript{72,73}, and arc shaped CT specimens\textsuperscript{39,74} to study both the crack initiation and growth rate. The DHC tests are carried out with notches in the specimen either at constant load or at constant stress intensity factor, $K_I$. The specimen contains the maximum amount of hydrogen available in solution at the test temperature. To achieve this, the specimens are heated to a peak temperature at least $10^\circ$C higher than the terminal solid solubility for dissolution (TSSD) temperature for the corresponding hydrogen concentration required for the study\textsuperscript{64}. The sample is kept at the peak temperature for one hour. Then the sample is cooled down to the test temperature and held for 30 minutes.
before applying the load. The thermal cycle typically used for DHC tests in the literature is shown in Figure 23.

Fatigue pre-cracking is sometimes used to attain a sharp crack tip to facilitate DHC initiation\textsuperscript{70}, although machined (‘broached’) sharp notches (root radius of 15\(\mu\)m) are also used\textsuperscript{74}. Once a DHC crack is formed the DHC crack was allowed to extend up to a reasonable distance, the sample is cooled down to room temperature. The DHC crack growth velocity is determined after pulling the sample apart into two halves and examined in the microscope. The DHC crack length has been estimated by two methods; the crack area divided by the specimen thickness gives the average crack length using Image Analysis software\textsuperscript{64,72} or the crack length average for a nine point equidistant interval measurement across the surface of the crack\textsuperscript{31}. The crack growth itself is monitored either by the direct current potential drop (DCPD) method\textsuperscript{31,58} or an acoustic emission (AE) technique\textsuperscript{49,64,70,75} (methods are discussed in more detail below).

To determine the threshold stress intensity factor (\(K_{\text{IH}}\)) two different methods have been used, either load increasing mode (LIM)\textsuperscript{74,76} or load decreasing mode (LDM)\textsuperscript{64,76}. In LIM, the load is increased in steps until crack growth is seen within 24 hours of the load being applied. Here the \(K_{\text{IH}}\) is defined as the maximum load at which the crack growth starts. In the case of LDM, the load is decreased from a higher \(K_I\) until the crack growth stops (i.e. none observed over 24 hours). Here the threshold stress intensity factor is the
minimum load applied at which the crack growth is arrested. In either case the observation of ‘zero’ crack growth depends somewhat on the sensitivity of the observation method used (e.g. noise level in the DCPD system).

![Schematic thermal cycle for a DHC test](image)

**Figure 23 Schematic thermal cycle for a DHC test**

### 2.6 Crack monitoring techniques:

Fracture studies of the DHC surfaces are required to determine many details of the crack initiation and crack propagation and hence to determine the fracture behavior of the pressure tube materials. However, monitoring the crack growth in situ can provide considerable extra information to assist in interpreting the fracture surfaces observed. There are two popular crack detection systems that have been used in the study of DHC, they are the acoustic emission (AE) and direct current potential drop (DCPD) techniques.
The acoustic emission principle is based on the release of elastic strain energy during fracture. The AE method works by recording minute mechanical vibrations caused by localized cracking in the material. These mechanical vibrations are converted to an electrical signal by a piezoelectric transducer, allowing monitoring and recording. Qualitative AE measurements can be used for crack initiation studies, but for DHC velocity measurements a quantitative AE measurement is needed. While the quantitative AE measurement are found to be somewhat unreliable due to the fact that the AE signals depend on the measuring conditions such as the type of transducers, the position of transducers, contact of transducers with material, distance of AE sources, and the shape and properties of the specimen.

The direct current potential drop (DCPD) method has been used for many crack monitoring studies, and has been successful in determining the DHC crack growth rates at high temperatures. The DCPD technique has the main advantage of having a simple set up and a relatively simple correlation between crack size and the observed potential drop signal. The principle behind the DCPD technique is that when a constant current is flowing through a cracked specimen, the electrical field in the cracked specimen is a function of the specimen geometry, and in particular on the crack size. There will be a change in voltage through the specimen when the crack grows due to the modification of the electric field resistance; this potential drop can be used to give the crack size using
analytical or experimentally determined relationships. Thus a calibration curve is required, which can be obtained for example by determining the DCPD output from a specimen with several known crack sizes. The temperature dependence can also be obtained by determining the DCPD output against temperature for a known crack geometry. This combination of curves can then be used to allow monitoring of crack growth in a specimen\textsuperscript{31,79}. 
Chapter 3
Experimental Procedures

3.1 Micro Pressure Tubes (MPTs):

The specimens used in the present study were all made from CANDU micro pressure tubes (MPT) made from Zr-2.5Nb alloy. Micro pressure tubes are made of the same material as full size pressure tubes and are fabricated using similar manufacturing routes as shown in Figure 4. The fabrication procedure and properties are given elsewhere. By suitable control of the processing conditions it is possible to manufacture MPTs with the same range of textures and microstructures that are seen in the full size pressure tubes used in reactors, as well as to produce textures and microstructures not seen in full size tubes. The key difference is that MPTs are much smaller in size making it easy and affordable to study the effects of processing variables. MPTs thus are useful in the study of the impact of process conditions on texture and grain size, and the relationship of these microstructural variables on mechanical response, for example creep. The MPT used in the present work is principally 64B unirradiated with the fabrication details given in Table 4; here the B-stands for the back end of the tube coming out of the extrusion during the fabrication. Table 4 also compares 64B MPT with 63B MPT which has a texture and microstructure similar to the pressure tubes used in CANDU reactors; where the full size pressure tubes are 6.3m long with an internal diameter or 103mm and a wall thickness of
4.2mm. The two tubes show different microstructure and radial hydride formation properties with similar transverse texture parameters, as summarized in Table 5\textsuperscript{34,30}.

**Table 4 Extrusion conditions of 64B and 63B MPTs**

<table>
<thead>
<tr>
<th>Tube</th>
<th>Internal Diameter (mm)</th>
<th>External Diameter (mm)</th>
<th>Quenching</th>
<th>Preheat Temperature (°C)</th>
<th>Extrusion Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>63B</td>
<td>8.34</td>
<td>13.82</td>
<td>β-quenched</td>
<td>815</td>
<td>10:1</td>
</tr>
<tr>
<td>64B</td>
<td>8.19</td>
<td>13.16</td>
<td>Slow-cooled</td>
<td>975</td>
<td>10:1</td>
</tr>
</tbody>
</table>

**Table 5 Texture and Microstructure of MPTs**

<table>
<thead>
<tr>
<th>Tube</th>
<th>Texture parameters</th>
<th>Radial hydride formation</th>
<th>Quenching microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>63B</td>
<td>(F\textsubscript{T}-0.58)</td>
<td>Resistant</td>
<td>β-quenched (fine, flat &amp; elongated grains, ~10%β)</td>
</tr>
<tr>
<td>64B</td>
<td>(F\textsubscript{T}-0.55)</td>
<td>Susceptible</td>
<td>Slow-cooled (equiaxed fine grains, ~10%β)</td>
</tr>
</tbody>
</table>
3.2 Electrolytic hydriding:

In order to put known quantities of hydrogen into the samples, an electrolytic hydriding-diffusion anneal process was developed. Electrolytic hydriding of the tubes was carried out according to the procedure mentioned in IAEA report\textsuperscript{8}. In this process a thick hydride layer is deposited using the electrolytic method and verified metallographically. The sample with a hydride layer is then annealed at the required temperature for the target hydrogen concentration; since the hydrogen concentration in solution is known as a function of temperature it is only a matter of holding the sample at this temperature for sufficient time for hydrogen to diffuse throughout the sample. An additional constraint is that for higher hydrogen concentrations, a thicker hydride layer must be deposited.

3.2.1 Electrolytic hydriding set up:

The set up that was developed for electrolytic hydriding is shown in Figure 24. The electrolytic hydriding set up consists of a bath container that can accommodate a niobium coated platinum anode mesh cylinder. The electrolyte is 0.2 molar sulphuric acid. A chemical metering pump with a single station level switch was used to pump distilled water when the distilled water in the electrolyte evaporates; thus preventing the sample from being exposed to air when the electrolyte level goes down. The bath container was set in a magnetic stirrer hot plate model Cimarec-SP131635, which is used to heat the bath to the required temperature and to keep the temperature uniform through the bath. A
constant DC power supply unit was used to apply the current for electrolytic hydriding. A current density of 2K amp/m² was determined to be the optimum for the hydriding procedure and setup used. The MPTs were spot welded to the power supply using 1mm thick Zr wires.

Figure 24 Electrolytic hydriding set up.

3.2.2 Hydriding procedure:

The micro pressure tubes were cleaned by acetone after removing the oxide layer that builds up on the surface during fabrication to ensure that a homogenous hydride layer would form. The samples were set as cathodes in the electrolytic bath. The electrolyte in the bath container was heated to a temperature of 65±5°C in the hot plate/stirrer. Once the
temperature stabilized, the cathode samples were suspended at the center of the platinum coated niobium anode mesh cylinder in the bath. Careful consideration was taken to keep the cathode samples away from contacting the anode mesh. The bath was maintained at \(65\pm5^\circ C\) during the whole electrolytic cycle to ensure the formation of a uniform hydride layer on the sample surface. A hydride layer is deposited on the pressure tube cathodes; for a target hydrogen content of 100 ppm the time spent required was 48 hours (Figure 25). The sample was then homogenized at a diffusion annealing temperature of 334\(^\circ C\) for 24 hours to ensure that the hydrogen diffused uniformly in the sample. The estimation of the homogenization time required is detailed in Appendix A.

After homogenization it is necessary to ensure that the target hydrogen content has been reached in the sample. This is done by looking at a cross section of the samples, determining that some remnant hydride layer that has not diffused in to the sample is present. At the selected TSSD temperature of 334\(^\circ C\) the maximum amount of hydrogen in solution cannot exceed 100 ppm; hence the homogenization temperature of 334\(^\circ C\) was chosen based on the hydrogen target required. When the zirconium alloy has been hydrided with a thick enough layer of hydride, the homogenous bulk hydrogen concentration in the sample is equal to the TSS at the diffusion annealing temperature. The presence of extra hydride layer on the surface after homogenization confirms that ‘extra’ hydride is present, and hence it can be assumed that the target hydrogen has been acquired. It was found that best results were obtained if the deposition and annealing
cycle was carried out twice for each sample. Carrying out two cycles of growing intermediate hydride layer thickness before diffusion annealing was found to be better than a single very thick hydride layer, since the thick hydride layer tended to fall off the tubes during the electrolytic process.

The hydride layer to be deposited on the sample for a target hydrogen of 100 ppm is about 18µm (Appendix A).

Figure 25 Hydride layer seen after electrolytic hydriding at 334°C for 24 h.
3.3 Delayed Hydride Cracking:

3.3.1 Specimen:

Arc shaped half ring segments of thickness 3 mm from the MPTs were selected as the DHC test specimen. This is the first time that DHC has been attempted on this size of sample, but it is a requirement if MPTs are to be used for DHC testing. Previous DHC testing has been on significantly larger samples. The specimens were cut using electrical discharge machining (EDM) at Twin City EDM. To obtain a sharp standardized starter notch for initiation of DHC a 0.65mm deep notch with a root radius of 15 µm was broached at Kinectrics, Mississauga, Ontario. A sharp notch was used in the present work as per the industry standards instead of pre-fatigue cracking. Figure 26 and Figure 27 gives a detailed measurement of the DHC sample. Load, P for particular stress intensity factor, \( K_I \) was then calculated from the equations given in ASTM E399\textsuperscript{82} for sharp cracks.
Figure 26 DHC Specimen with the notch tip having a root radius of 15µm.

Figure 27 EDM notch after broaching with 15 µm root radius.
3.3.2 DHC rig:

A furnace and loading apparatus was built capable of conducting simultaneous DHC testing of multiple samples, shown schematically in Figure 28. To apply a force, a stepper motor design was used, with a load cell attached to a computer to monitor the load applied. The stepper motor used in the present work is a Hayden™ brand hybrid linear actuator model no. 57K4BB-7-7001ENG. The Load cell used was Omegadyne inc. Model LC-101-500 with a load range of 0-500 lbs.
To heat the samples and loading train a laboratory fan type oven model ATS series 3610 suitable for heating up to 425°C was used. The furnace unit consists of a temperature controller ATS 900-TC16 to heat and cool the specimen at a given rate and to keep a uniform temperature across the specimen. Chromel-Alumel (K) type thermocouples were used to measure the temperature of the sample. The thermocouple was spot-welded to the sample for accuracy. The programmable temperature controller keeps the target temperature within 1°C, avoiding any under cooling in the sample.

The Direct Current Potential-Drop (DCPD) unit includes a DC power supply, model Kepco ATE-25-10 DM, able to supply ~10V DC current to the sample. For this, copper current leads, and a spot welder to attach the leads to the sample were required. The DCPD unit was connected to the sample via Zr wires of 0.25mm diameter, measuring the potential drop across the crack surface. Zr wires were used to minimize any errors in PD measurement that might arise due to contact voltages between two different metals. A Keitheley series-2701-Integra Ethernet based Digital Multimeter was used to monitor the voltages. An I/O system to the computer, MOSFET bridge switch, and a computer was used to monitor the voltages. The computer was running a LabView program to monitor and control the load, temperature and potential drop settings simultaneously.
3.3.3 Potential-drop technique:

DHC growth was monitored by the DCPD technique. A constant power supply current of 3A was found to be sufficient to measure a voltage drop across the sample but small enough not to affect the sample temperature. The sensitivity of the system was determined to be 0.005 mV; this voltage level was determined to correlate to a change in crack length of ~10 µm, as discussed below.

For the PD unit, lead wires of Zr were spot-welded to the sample crack surface within 1mm of either side of the crack. The copper current leads were crimped to platinum wires before attaching to either end of the sample by spot-welding. The samples were connected to the load chain using Zr grips with stainless steel pins of 1.5mm diameter and a small holding load of 4 lbs was applied before the test. Grips were made of Zr to avoid any corrosion products at high temperatures. The crack growth is detected by the gradual increase in potential drop once the load corresponding to the threshold stress intensity factor is reached.

\( K_I = \frac{P}{B\sqrt{W}} f \left( \frac{a}{W} \right) \) \hspace{1cm} \text{Equation 10}

Where,
\[ f \left( \frac{a}{W} \right) = \frac{\sqrt{\frac{a}{W}}}{(1 - \frac{a}{W})^{3/2}} \left[ 3.74 - 6.30 \left( \frac{a}{W} \right) + 6.32 \left( \frac{a}{W} \right)^2 - 2.43 \left( \frac{a}{W} \right)^3 \right] \]

where \( P \) is the load applied, \( a \) is the crack length; \( B \) is the thickness of the specimen; \( W \) is the width of the specimen and \( X \) is defined in Figure 26; all units in mm.

The load required to achieve specific \( K_I \) values is calculated using the equation above. It should be noted that when a broached notch, rather than a fatigue crack, is present the \( K_I \) value obtained will be an effective one, since the equation is derived based on a nominally infinitely sharp crack. The procedure to determine the threshold stress intensity factor, \( K_{IH} \) is given below.

### 3.3.4 \( K_{IH} \) experiments:

The samples were tested for \( K_{IH} \) at three different temperatures: 180, 230 and 250°C. During reactor operation the temperatures vary from \( \sim 80°C \) (during shut down) up to about 250°C at the inlet end of a fuel channel when the reactor is at power. The DHC test temperatures were chosen to simulate these conditions to study the crack initiation in Zr-2.5Nb alloy MPTs, and are typical of the temperatures studied in the literature where DHC is of most interest. Before each experiment the half ring samples were polished using fine emery paper and cleaned by an ultrasonic method to facilitate subsequent optical examination as well as spot welding. The peak temperature chosen for the entire DHC test was 320°C to obtain a maximum amount of hydrogen in solution at the test
temperature. The specimens were placed in the DHC rig and heated to the peak temperature at a rate of 1°C/min. Then the sample was kept at that temperature for an hour to dissolve most of the hydrides, and then cooled down to the test temperature at the same rate as that used during heating. After holding the samples at the test temperature for half an hour to stabilize the temperature, the load was applied. To determine the threshold stress intensity factor $K_{th}$, a load increasing mode (LIM) was used. The load was increased in steps until crack growth was seen within 24 hours of the load applied. $K_{th}$ is the maximum load at which a potential drop (PD) change occurred, indicating the start of crack growth. The load was applied with an increment in stress intensity of 0.5 MPa.m$^{1/2}$ and monitored for 24 hours every step until the potential drop changed. The thermal cycle used in the current experiments is shown in Figure 29. After the crack has grown to a predetermined PD, the load was reduced and the temperature was raised to the peak temperature and the cycle was then continued for the next test. The heat tint used here by heating to a high temperature and holding for some time before the next test helps to mark the end of the given DHC crack front as explained below. The load corresponding to the PD change is taken as the threshold stress intensity factor $K_{th}$ at that particular temperature. The threshold stress intensity factor, $K_{th}$ was determined at all three temperatures for the MPT.

Measurement of the crack length is made easy by the heat tint- method used here, i.e. heating the sample to the peak temperature and holding it for 30 minutes at a nominal holding load of 4 lbs. This results in the formation of an oxide layer on the surface. If a
heat tint is produced on a given crack, then the crack is grown further and a second heat tint is applied, such that the oxide layer will have different thicknesses. Hence the crack growth front is differentiated by these oxide layers, which are visible as different bands when seen an optical microscope. This helps in measuring the average crack length for that particular temperature / test and identifying different DHC regimes on the fracture surface of a single sample.

Figure 29. Thermal cycle used for $K_{IH}$ experiments.
3.3.5 DHC velocity (DHCV) measurements/constant displacement method:

DHCV tests were carried out at the three selected test temperatures: 180, 230, and 250°C using a constant displacement method. The same heating cycle was used for the DHC velocity measurement as was used for the KIH tests. In this case, after stabilizing at the test temperature a pre-determined load is applied on the sample and the stepper motor is deactivated by switching off. The force will drop slightly as the crack grows, and therefore the stress intensity on the sample does not go up as the crack grows as fast as would be observed under a constant load test. In the constant load method the load applied remains the same when the crack grows and the value of KI applied increases rapidly with crack extension. Once the PD reaches a predetermined value, the load on the sample is reduced. A KI of 12 MPa.m\(^{1/2}\) was chosen to study the crack growth rate in the MPT used, in agreement with much work in the literature. After stabilizing at the test temperature for 30 minutes, the load corresponding to a stress intensity of 12 MPa.m\(^{1/2}\) was applied. Once the crack grows to a predetermined value, the load is removed and a heat tint is performed. Samples 64B2 and 64B3 were DHC tested under constant load. Then the two halves of the sample were broken apart to study the fracture surface.

3.4 Metallography:

Metallographic analyses were performed to see the hydride layer formation on the surface of the MPTs after electrolytic hydriding. Optical microscopic studies were used to
examine the orientation of hydrides before DHC testing. A Transmission Electron Microscope (TEM) was used to study the microstructure of the MPTs.

After the electrolytic hydriding step, the samples were examined for the presence of hydrides using optical microscopy. Specimens cut along the circumferential-radial plane were mounted using a Buehler Simplimet 1000 automatic mounting press with a pressure of 150 psi at a temperature of 150°C. EPOMET G mounting compound was used to avoid rounding off the specimens during polishing. After the sample was mounted, grinding with the emery paper was followed up to 600 grit and then polished to a 1µm surface finish using diamond paste. This was followed by colloidal alumina attack polishing with 0.5% HF.

Samples for TEM were cut along the radial-circumferential direction normal to the axial direction and thinned down to 100 µm. Discs of 3 mm diameter were punched from the thinned samples, followed by electro-polishing in 6% perchloric acid + 94% methanol at -40°C and 20V. The thin foils were observed using a Philips CM 20 at 200 kV.

3.4.1 Fractography:

Post-fracture microstructural studies were undertaken to observe fracture surfaces and the striations indicative of DHC using optical microscopy and SEM. For this task there is little or no preparation of the sample needed compared to the polishing required for optical metallography. The two halves of the specimen were pulled apart to see the fracture surface. A JEOL 840 SEM was then used to observe the fracture surface.
**Crack length** was measured using optical microscopy with Image analysis software, an average of 9 equidistant readings on the DHC crack surface were used to determine the crack length \(a_{\text{avg}}\) on the surface. The crack length \(a_{\text{avg}}\) can then be used to confirm the initial and final \(K_I\) applied for DHC tests that were estimated from the PD signal.

**DHC velocity:** DHC crack growth rate is given by the calculated average crack length, \(a_{\text{avg}}\) (mm) divided by the time taken in seconds (\(t_{\text{DHC}}\)) for the corresponding DHC crack growth.

\[
\text{DHCV} = \frac{a_{\text{avg}} \times 10^{-3}}{t_{\text{DHC}}} \text{ (m/sec)}
\]

DHC velocity is calculated for 64B MPTs at the three test temperatures and the chosen nominal \(K_I\) of 12 MPa.m\(^{1/2}\). (Appendix B)
The presentation of results is divided into pre-cracking analysis, cracking tests and post-fracture analysis.

The pre-cracking work consisted of an evaluation of the electrolytic hydriding process and optical microscopy of the hydride morphology after hydriding of the MPT’s. Transmission Electron Microscopy (TEM) was also used to study the microstructure of the 64B micro pressure tube. Pre-cracking analysis was followed by the actual cracking tests, with data collected for the determination of the threshold stress intensity factor, $K_{\text{th}}$, and the DHC velocity tests. Post-fracture analysis of the DHC crack region provided precise measurements of the actual crack length to allow calculation of the DHC velocity. To ensure reproducibility of the test results, experiments were repeated on identical specimens for all three different temperatures tested.

### 4.1 Metallography:

The TEM micrograph obtained from the Zr-2.5Nb 64B micro pressure tube in the radial-circumferential plane is shown in Figure 30. The microstructure shows a non-uniform distribution of $\beta$-phase around the fine $\alpha$-Zr grains. The grey region shows the fine equiaxed $\alpha$-grains, while dark $\beta$ phase is shown at the $\alpha$-grain edges and corners. Figure
31 shows a TEM micrograph of the 63B tube with flattened and elongated $\alpha$-grains with $\beta$-phase at the grain boundaries. Y Li et al. previously observed the same microstructure in Zr-2.5Nb micro pressure tubes\textsuperscript{80}.

**Figure 30** TEM micrograph of the radial-circumferential section of the Zr-2.5Nb 64B MPT; $\beta$-phase indicated by arrow.
Figure 31 TEM micrograph of the radial-circumferential section of the Zr-2.5Nb 63B MPT; β-phase indicated by arrows.

4.2 Electrolytic hydriding:

The electrolytic hydriding set up was constructed based on descriptions of the AECL procedure for adding hydrogen to small sections of zirconium alloys\(^8\). The physical components of the rig and the hydriding cycle used are explained in Chapter 3. Before the start of the electrolytic process, the hydriding parameters such as the type and strength of the electrolytic bath, the temperature of the bath, the amount of current required and the hydriding time were selected. This is followed by specimen preparation to ensure the
formation of a homogenous uniform layer of hydride on the surface of the MPT section. Small sections of MPT were cut from the back end of the tube 64B. The oxide layer on the surface is removed to obtain a uniform hydride layer deposition. This was done by using abrasive papers on a standard grinding wheel. After the oxide layer was removed, the samples were cleaned in an ultrasonic bath using acetone and then cleaned in alcohol. It was noted that the clean sample needed to be immediately immersed in the electrolytic bath after this cleaning process, to avoid the potential for further oxide formation.

The hydriding procedure involves,

1. Preparation of an electrolytic bath with 0.2 molar sulphuric acid in a 2L container.

2. Preheating the electrolytic bath to the recommended 65°C in a hot-plate with a magnetic stirrer to ensure uniform temperature of the bath.

3. Placing the platinum coated Nb anode mesh in the bath.

4. Spot-welding the sample using Zr wires to conduct the current.

5. As soon as the cleaned sample is spot-welded, the sample was suspended in the solution and the electrolytic process started.

6. After hydriding for the predetermined time, the power supply was turned off and the sample was taken out of the bath and gently wiped with a damp cloth.
The target hydrogen concentration for the samples is 100 ppm. The total hydrogen content achieved in the samples is determined by the solution annealing temperature used. For the current samples the diffusion annealing temperature was 334°C which gives the maximum hydrogen that can be in solution as 100 ppm based on the dissolution solvus curves⁸ (Appendix A). To make sure the target hydrogen is achieved electrolytic hydriding was carried out in two cycles, see Section 3.2.2. This was confirmed by the fact that a hydride layer is left on the micro pressure tube surface after homogenization.

After hydriding the MPT samples were looked at under the microscope to confirm the formation of a hydride layer on the surface and distribution of hydrides in the sample. A thin sample was cut along the radial direction to observe the hydride layer formed on the surface of the tube section. The metallographic pictures are shown in a series of figures. Figure 32 shows the formation of thick hydride layer of ~10-20 µm on the surface of the MPT sample after one cycle of electrolytic hydriding. Appendix I shows the required hydride layer to be formed on the surface of the tube is about 18 µm for the target hydrogen concentration of 100 ppm. After each cycle the sample was homogenized at 334°C to diffuse hydrogen into the MPT. The cycle was repeated to attain the target hydrogen and after the second cycle of hydriding and diffusion annealing, a layer of hydride was observed on the surface. Figure 33 (a, b) shows a hydride layer of ~5-10 µm left on the surface of a micro pressure tube after the second hydriding cycle. As 334°C is determined as the diffusion anneal temperature (Appendix I) the extra hydride layer on
the surface confirms that the bulk hydrogen concentration has reached the target hydrogen concentration of 100 ppm in the sample. This is due to the fact that the maximum amount of hydrogen that can be present in solution at the diffusion annealing temperature of 334°C is 100 ppm.

Figure 34 shows the resultant hydride microstructure in the circumferential-radial direction of the tube after homogenization. The hydrides observed under the optical microscope appear to be 100-200 microns in length oriented along the circumferential direction of the tube as often observed in the CANDU pressure tubes.

Figure 32 Hydride layer formed after electrolytic hydriding for one cycle of 48 hours.
Figure 33 Hydride layer left on the surface of the sample after homogenizing.
Figure 34 Hydrides as seen in the circumferential-radial direction of the MPT.

4.3 Cracking tests:

The next step after hydriding the MPT’s was to carry out cracking tests. Cracking tests were divided into two parts: first finding the threshold stress intensity factor, $K_{IH}$, above which the crack starts growing and next to determine the DHC crack growth rate, DHCV.

4.3.1 $K_{IH}$ experiments

The tests were carried out at three different temperatures: 180, 230 and 250°C. As the threshold stress intensity factor is the load below which there is no crack growth observed, a load increasing mode approach is applied to see at what applied $K_I$ the crack
initiates from the notch. This is determined by increasing the applied load slowly and
monitoring for every 24 hrs, when there is a potential drop change, the $K_I$ corresponding
to that load is taken as $K_{IH}$. The following results present the PD versus applied load for
three different temperatures considered.

The temperature-PD profile for a sample tested at 180°C is shown in Figure 35. The
initial thermal treatment to 320°C is shown, followed by holding at 180°C. The PD
signal varies with temperature (since resistance does), but is then constant for some time.
It can be seen clearly that the PD then changes dramatically at a certain time. This occurs
when the incrementing load reaches that corresponding to the $K_{IH}$ at the test temperature.
Figure 36 shows the incremental application of load as well as the same PD graph as
shown in Figure 35. Figure 37 shows a close up of the PD change near the end of the test,
indicating the crack initiation at the load corresponding to a $K_I$ of 7.5 MPa.m$^{1/2}$. The
jump in PD after reaching the $K_I$ value of 8 MPa.m$^{1/2}$ indicates the initiation of a sudden
 crack; hence the corresponding $K_I$ is taken as the threshold stress intensity factor $K_{IH}$ for
that particular test temperature. This should be taken as $K_{IH}$, effective since initiation
occurred from the 15 µm root radius notch, rather than a fatigue/DHC crack. Note that
the crack initiates some time (approximately 400 minutes) after the load has been raised
to that particular value. Once the crack has initiated, it then appears to grow with a fairly
constant PD change as a function of time for about 100 minutes, before the test was
halted by reducing the load. Figure 38 and Figure 39 show the PD jump at the initiation
of the crack, zooming in just to the crack initiation event, for samples tested at 230 and 250°C. The behavior is somewhat different to that seen at 180°C. Here, a step-wise increase in PD with time (even at constant load) is observed, which has also been observed in the literature for DHC in Zr alloy pressure tubes\textsuperscript{84}.

**Figure 35** Temperature and PD for sample 64B4 tested at 180°C as a function of time.
Figure 36 Load applied and PD as a function of time (64B4, \( T_{test} - 180^\circ C \)).

Figure 37 Close up of load and PD at time when crack initiates. Crack growth seen at an applied load corresponding to a \( K_1 \) of 7.5 MPa.m\(^{1/2}\) (64B4 at \( T_{test} - 180^\circ C \)).
Figure 38 PD at a $K_I$ of 7.5 MPa.m$^{1/2}$ in sample 64B2, $T_{test}$ -230°C.

Figure 39 PD at a $K_I$ of 10.5 MPa.m$^{1/2}$ in sample 64B3, $T_{test}$ -250°C.
4.3.2 DHC velocity measurement results

DHC crack growth rates in the MPTs were tested at an applied load corresponding to the same $K_I$ of 12 MPa.m$^{1/2}$ for all temperatures. The tests were carried out at a constant displacement mode in all the samples except for 64B2 and 64B3, for which constant load mode was used. In constant displacement mode, as soon as the load reaches the target $K_I$, the stepper motor is switched off. In DHC, when the crack grows in size the applied $K_I$ on the sample goes up for a given applied load. If the test is carried out at constant load, the load remains constant thus increasing the applied $K_I$ rapidly as the crack grows; hence the DHC velocity could potentially become very rapid in a short time. This issue has not caused problems in testing DHC from samples cut from full size pressure tubes, but is potentially an issue with the very small samples that are available from an MPT; for an MPT the region of allowable crack growth is only ~1mm (this is the region in the sample where the stress field is reasonably uniform, any bending moments are minimised, and the ASTM equation relating $K_I$ and the applied load is valid). By switching off the motor, this effect could be reduced slightly by allowing the load to relax from that required for the initial $K_I$. Figure 40 shows the PD versus time for the 64B8 sample tested at an initial $K_I$ of 12 MPa.m$^{1/2}$ which reached a final $K_I$ of 18 MPa.m$^{1/2}$. As soon as the load reached the target $K_I$ there is a jump in PD indicating the initiation of a DHC crack. As the PD increases gradually with time the load drops with crack growth as is also seen in Figure 40. Once the load is reduced to zero at the end of the test, after growing the crack to a
required length, the PD does not go up indicating the DHC crack growth has stopped. It should be noted that while the $K_I$ has gone up during the test, if the load had instead remained constant the final $K_I$ at the final crack length would have been $\sim 26\text{MPa.m}^{1/2}$.

Figure 41 and Figure 42 show the PD versus time graphs indicating the DHC crack growth measurement at the applied $K_I$ for the samples tested at 230 and 250°C respectively.

![Figure 40 64B8 at $T_{\text{test}}-180^\circ\text{C}$ with initial $K_I$ of 12 and final $K_I$ of 18 MPa.m$^{1/2}$](image-url)
Figure 41  64B7 at $T_{test}=230^\circ$C with initial and final $K_I$ of 12 and 23 MPa.m$^{1/2}$ respectively.

Figure 42  64B5 ($T_{test}=250^\circ$C) with initial and final $K_I$ of 12 and 20 MPa.m$^{1/2}$ respectively.
4.4 Results from metallographic analysis:

Fractographic analysis was carried out by optical microscope and subsequent image analysis as well as by SEM on all the samples. Fractography studies the characteristic features left of the fracture surface and can help in measuring the crack length after DHC. Image analysis with the optical microscope was helpful in identifying the DHC crack region and measuring the crack extension. The DHC crack region was identified by the heat tint method used to oxidize the crack region. These regions, after holding at the peak temperature for some time, will show a distinct fish-scale type fracture surface called striations under the optical microscope. This striation region is indicative of the fact that step-wise delayed hydride cracking has indeed occurred, shown by the progress of the crack in the radial direction. Figure 43 shows an optical micrograph of the fracture surface of sample 64B2 tested at 230°C; the distinct blue zone with striations can be clearly seen. 64B4 sample was tested at two different applied initial $K_1$ of 8 and 12 MPa.m$^{1/2}$ at 180°C. Figure 44 shows the DHC fracture surface of the 64B4 sample; two different DHC crack zones can be observed differentiated by the heat tinting used after each test. Figure 44 shows the fracture surface for the sample 64B5 tested at 250°C showing a curving DHC crack front. An SEM micrograph of this curved region is shown clearly in Figure 46. Figure 47 shows the fracture surface at higher magnification indicating the striations.
Figure 43  DHC fracture surface 64B2 at $T_{\text{test}}=230^\circ$C showing the DHC crack zone (a) and the striations (b); arrows indicated the direction of the crack growth.

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Figure 44 64B4 sample at $T_{\text{test}}=180^\circ$C showing different DHC crack zones at two different initial $K_1$ shown in the figure.
Figure 45 64B5 sample at $T_{\text{test}}=250^\circ\text{C}$ showing the DHC fracture surface.
Figure 46 SEM micrograph showing the DHC crack region (light grey region) curving towards the edge of the sample indicating that tunneling occurred in sample 64B5 at a test temperature of 250°C.

Figure 47 SEM micrograph showing the DHC fracture surface with striations (64B5 at $T_{\text{test}}=250^\circ\text{C}$).
Chapter 5
Discussion

5.1 Analysis of the results:

The results obtained for $K_{\text{IH}}$ data on the different samples tested are shown in Table 6. The peak temperature for all the samples used was kept constant at 320°C. The various test temperatures at which the samples were tested for $K_{\text{IH}}$ are also shown in Table 6. In sample 64B3 multiple tests were carried out to identify the $K_{\text{IH}}$ values, first at 250°C and then at 230°C. The first value of $K_{\text{IH}}$ identified in this case will represent the value initiated from the broached notch, while subsequent values will be representative of DHC from a sharp crack and are therefore indicated separately in Table 6.
Table 6 $K_{IH}$ data from 64B MPT samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Peak temperature, $^\circ$C</th>
<th>Test temperature, $^\circ$C</th>
<th>$K_{IH}$, MPa.m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>64B4</td>
<td>320$^\circ$C</td>
<td>180</td>
<td>7.5</td>
</tr>
<tr>
<td>64B8</td>
<td>320$^\circ$C</td>
<td>180</td>
<td>6.5-7</td>
</tr>
<tr>
<td>64B2</td>
<td>320$^\circ$C</td>
<td>230</td>
<td>8.0</td>
</tr>
<tr>
<td>64B3</td>
<td>320$^\circ$C</td>
<td>230</td>
<td>(7.0,7.5)</td>
</tr>
<tr>
<td>64B7</td>
<td>320$^\circ$C</td>
<td>230</td>
<td>7.0-7.5</td>
</tr>
<tr>
<td>64B3</td>
<td>320$^\circ$C</td>
<td>250</td>
<td>10.5, (7.5-8.0)</td>
</tr>
<tr>
<td>64B5</td>
<td>320$^\circ$C</td>
<td>250</td>
<td>10.0</td>
</tr>
<tr>
<td>64B9</td>
<td>320$^\circ$C</td>
<td>250</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Data in closed brackets indicate the $K_{IH}$ was obtained during multiple testing on the same sample after the crack had already initiated from the broached notch (i.e. from a sharp crack).
The test results show that the threshold stress intensity factor goes up with temperature, as $K_{IH}$ at 250°C is the maximum value obtained in the current study of 10.5 MPa.m$^{1/2}$. When the $K_{IH}$ test is repeated on the same sample after initiating the crack from the notch, $K_{IH}$ came down as expected; this is discussed in detail below. $K_{IH}$ at the test temperature of 180°C shows the lowest values around 6.5-7.5 MPa.m$^{1/2}$, with $K_{IH}$ at 230°C being 7.0-8.0 MPa.m$^{1/2}$. The mean values for $K_{IH}$ are compared for the three test temperatures in Figure 48. The average threshold stress intensity factor, $K_{IH}$ values at the three temperatures are 7.0, 7.5 and 10.3 MPa.m$^{1/2}$.

![Plot of $K_{IH}$ data obtained from the notch for different $T_{test}$ (linear fit for the mean values of $K_{IH}$ is shown). Different symbols are used only for clarity.](image)

Figure 48: Plot of $K_{IH}$ data obtained from the notch for different $T_{test}$ (linear fit for the mean values of $K_{IH}$ is shown). Different symbols are used only for clarity.
5.1.1 Threshold stress intensity factor, $K_{IH}$:

$K_{IH}$ at 250°C:

The threshold stress intensity factor appears to be higher at higher temperatures where the peak temperature for all the samples is kept constant (Figure 48). Figure 49 shows the PD indicating the initiation of a crack at a load corresponding to an applied $K_t$ of 10 MPa.m$^{1/2}$. Figure 50 shows the corresponding fracture surface containing the initial crack associated with $K_{IH}$ of 10 MPa.m$^{1/2}$. $K_{IH}$ tests carried out on the same sample at this temperature (64B3) show a reduced $K_{IH}$ of 8 MPa.m$^{1/2}$, once a DHC crack has initiated (Table 6). This slight reduction in $K_{IH}$ is explained according to Y.S. Kim et al. by the difference between the stress concentrations found at the sharp tip of a DHC crack and the relatively dull tip of the broached notch. Y.S. Kim et al. found that with the same DHC crack the $K_{IH}$ decreased from 7.3 to 6.1 MPa.m$^{1/2}$ after DHC crack using load increasing mode (LIM) (Figure 51).

In all the samples tested at 250°C, the crack did not initiate just after reaching the load which would eventually correspond to the $K_{IH}$. In 64B3 the initiation of the crack occurred, as indicated by the PD increase, only after 290 min. at load, and in 64B5 sample it took 80 min. to initiate the crack. This indicates that even after reaching the threshold stress the crack did not start until the hydrides precipitated at the notch had reached the critical size for fracture.
Figure 49 64B5 at 250°C test temperature

Figure 50 Fracture surface showing the striations on 64B5, arrow indicates the initial crack during the $K_{th}$ test.
Figure 51 $K_{\text{III}}$ of the Zr-2.5Nb tube with 80 ppm H at 250°C with LIM and LDM$^{76}$.

$K_{\text{III}}$ at 230°C and 180°C:

The observed results showed no incubation time associated with the initiation of cracks at the test temperature of 230°C. The threshold stress intensity values obtained at this test temperature varies from 7-8 MPa.m$^{1/2}$ with no initial DHC pre-cracks and 7-7.5 MPa.m$^{1/2}$ after DHC pre-cracks were present in the sample.
$K_{IH}$ varied from 6.5-7.5 MPa.m$^{1/2}$ at the test temperature of 180$^\circ$C for the 64B samples used. Samples at this temperature showed the lowest $K_{IH}$ values in the temperature range tested.

Crack initiation depends on the amount of hydrogen available at the given test temperature and stress levels. By keeping the peak temperature constant at 320$^\circ$C for all the samples tested, the maximum amount of available hydrogen in solution is the same for all the samples. With an increase in the stress level at the crack tip, hydrogen flows from the bulk matrix and then precipitates when the terminal solid solubility is exceeded. The hydride grows in length until it reaches the critical hydride length and stress before fracturing. This explains why even after reaching the load corresponding to the threshold stress intensity factor, the crack does not always initiate.

The results obtained showed an increasing trend in $K_{IH}$ values; out of the three temperatures tested, samples at 180 and 230$^\circ$C show $K_{IH}$ values $\leq$ 8 MPa.m$^{1/2}$, while at 250$^\circ$C tests showed consistently higher readings for $K_{IH}$. The difference in $K_{IH}$ between samples tested at 180 and 230$^\circ$C was not as large as that between samples at 230 and 250$^\circ$C. In the past Y.S. Kim et al$^{64}$ observed a value of $\sim$8-9 MPa.m$^{1/2}$ in the radial direction of CANDU Zr-2.5Nb pressure tubes for a temperature range between 160-280$^\circ$C. The Zr-2.5Nb pressure tubes used were charged with a hydrogen concentration varying from 27-100 ppm. There was no trend with increase in temperature observed by
the authors. Kim and Kim\textsuperscript{66} have observed values for $K_{\text{IH}}$ in the range of 8-12 MPa.m$^{1/2}$ for CANDU Zr-2.5Nb pressure tubes with a circumferential texture similar to that present in the 64B MPTs used in this study.

The stress intensity for the DHC crack from the notch with 15 µm root radius can be considered an effective threshold stress intensity factor, $K_{\text{IH}}$, since the calculation for $K_I$ is based on a sharp crack. It is however a commonly measured parameter in the industry, since notches with this root radius is typical of in-service flaws. The $K_{\text{IH}}$ for the initiation of crack from a DHC crack is a ‘true’ value for DHC crack initiation. The values brackets in Table 6 are lower values than the $K_{\text{IH}}$ determined from the notch at the same test temperatures due to the sharp crack tip compared to the notch with root radius of 15 µm.

There does seem to be a slightly increasing trend in $K_{\text{IH}}$ values with an increase in temperature, observed by Shi and Puls\textsuperscript{57}. The average $K_{\text{IH}}$ data from published in the literature is \textasciitilde8.2MPa.m$^{1/2}$ according to the IAEA report. Shi and Puls theoretical and experimental data for $K_{\text{IH}}$ with temperature is shown in Figure 52. The threshold stress intensity factor increases slowly with increasing temperature and reaches \textasciitilde10 MPa.m$^{1/2}$ at 250°C. The area marked in the figure indicates the observed temperature range for the 64B MPTs tested. From Figure 52 and the discussion above it can be seen that the values reported in this thesis agree with the literature values, showing $K_{\text{IH}}$ values that increase slowly with increasing temperature and values in the range of 6.5-10 MPa.m$^{1/2}$ for the temperature range 180-250°C.
Figure 52 Comparison of theoretical and experimental data on $K_{\text{IH}}$\textsuperscript{57}; the marked area shows the temperature region and data observed in the MPTs in the current work.

5.1.2 DHC velocity measurement

Typical DHCV data obtained by the PD change is shown in Figure 53. The DHC velocity can be calculated as described in Section 3.3.5 by measuring the DHC crack length using optical microscopy and subsequent image analysis. The time for the DHC test is
calculated from the difference between the time loading started and when the load was removed after reaching a predetermined PD change. The DHC was allowed to proceed until the increase in crack length was \(\sim 1\) mm. The estimated PD change associated with this crack length change was calculated based on the previous test data, to determine an estimated crack growth with time. The DHCV data obtained for all of the samples is shown in Table 7. The initial \(K_I\) for most of the tests was kept at a value of 12 MPa.m\(^{1/2}\) with the observed final \(K_I\) increasing to about \(\sim 20\) MPa.m\(^{1/2}\). Instead of fatigue pre-cracking for DHC tests as has sometimes been carried out a sharp DHC crack was introduced in all the samples by initiating the crack by a \(K_{IH}\) test as described in the previous section before the DHCV test was started. This crack initiation usually resulted in a crack extension of 70-100 µm from the notch tip. The average DHC crack length measured by optical microscopy and crack length calculated by the area method is given in Table 7.
Figure 53 PD change with temperature for a typical DHC test (64B8, T_{test}-180\degree C)
Table 7 DHCV data:

<table>
<thead>
<tr>
<th>Sample (Peak temperature, 320°C)</th>
<th>Test temperature, °C</th>
<th>DHC crack length, ( a_{avg} ) mm</th>
<th>DHCV, ( \times 10^{-8} ) m/s</th>
<th>( K_i ), MPa.m(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>64B4 (crack 1)</td>
<td>180</td>
<td>0.378</td>
<td>2.74</td>
<td>Initial: 8, Final: 10</td>
</tr>
<tr>
<td>64B4 (crack 2)</td>
<td>180</td>
<td>0.428</td>
<td>3.11</td>
<td>Initial: 12, Final: 16</td>
</tr>
<tr>
<td>64B8</td>
<td>180</td>
<td>0.671</td>
<td>2.07</td>
<td>Initial: 12, Final: 18</td>
</tr>
<tr>
<td>64B2</td>
<td>230</td>
<td>0.50</td>
<td>8.32</td>
<td>Initial: 8, Final: 13</td>
</tr>
<tr>
<td>64B3</td>
<td>230</td>
<td>0.456</td>
<td>10.85</td>
<td>Initial: 10, Final: 13</td>
</tr>
<tr>
<td>64B7</td>
<td>230</td>
<td>0.967</td>
<td>13.45</td>
<td>Initial: 12, Final: 23</td>
</tr>
<tr>
<td>64B5</td>
<td>250</td>
<td>0.763</td>
<td>6.36</td>
<td>Initial: 12, Final: 20</td>
</tr>
<tr>
<td>64B9</td>
<td>250</td>
<td>0.703</td>
<td>10.54</td>
<td>Initial: 12, Final: 19</td>
</tr>
</tbody>
</table>

64B2 and 64B3 in constant load mode; 64B4, 64B5, 64B7, and 64B8 were done in constant displacement mode; calculation DHC velocity is given in Appendix B.
The DHCV results obtained for the 64B MPTs tested show a distinctly increasing trend with increasing temperature (Figure 54). Interestingly the DHC tests at 230°C show the highest velocity measured in the MPTs; the average DHCV measured gives $10.87 \times 10^{-8}$ m/s with a standard deviation of $2.56 \times 10^{-8}$ m/s. The tests at 250 and 180°C give an average DHC velocity of $8.45$ and $2.64 \times 10^{-8}$ m/s with standard deviations of $2.96$ and $0.53 \times 10^{-8}$ m/s, respectively. The lowest velocity was observed with the samples tested at 180°C in the temperature range tested.

![Figure 54 DHC velocities for the samples tested at different temperatures (linear fit to the mean DHCV data also shown).](image)

Figure 54 DHC velocities for the samples tested at different temperatures (linear fit to the mean DHCV data also shown).
The results obtained in the MPTs are in reasonable agreement with the DHCV tests carried out on CANDU pressure tubes in different countries via the IAEA co-ordinated research programme. The mean value of the DHC velocities observed at 250°C with a hydrogen concentration of ~58 ppm was observed to be $8.86 \times 10^{-8}$ m/s with a standard deviation of $1.07 \times 10^{-8}$ m/s. The trend of an increase in DHC velocity with an increase in temperature has also been observed, with results similar to the data shown in Figure 54. For example, Coleman and Ambler observed an Arrhenius relationship of DHC velocity with temperature in cold worked Zr-2.5Nb pressure tubes. The temperature dependence of crack velocity arises from the expression for the DHCV given by the product $D_H C_H$, where $D_H$ is the diffusion coefficient of hydrogen in $\alpha$-Zr and $C_H$ is the terminal solid solubility of hydrogen (Equation 2). With an increase in temperature the maximum amount of hydrogen in solution increases, and the speed of diffusion of H also increases, both increasing the DHC velocity at higher temperatures.
In analyzing the impact of the crack tip stress field on DHCV, it is useful to consider the analysis of Singh\textsuperscript{31}. The crack tip region is divided into three zones as shown in Figure 55, 1-process zone with stress greater than the initial yield strength ($\sigma_y$) of the material.; 2- reorientation zone with stress greater than the threshold stress ($\sigma_{th}$) for reorientation of hydrides; and 3-migration zone, where the stress is lower than $\sigma_{th}$. The schematic variation of the stress gradient in the three different zones is shown in Figure 55 (b). The diffusion equation in one dimension for hydrogen migration under a concentration, temperature and stress gradient is given by,
where, $C_r$ is the hydrogen concentration at any point at a distance $r$, $D$ is the hydrogen diffusivity in metal, $J$ is the hydrogen flux, $Q^*$ is the heat of transport of hydrogen in metal, $R$ is the gas constant, $T$ is the temperature, $\nu^*$ is the volume of transport of hydrogen in metal, $\sigma$ is the tensile or compressive stress.

The stress gradient for the driving force for the migration of hydrogen near the crack tip is provided by the stress intensity factor. The stress gradient is higher in the reorientation zone as shown in Figure 55. From the above equation it should be clear that for a given concentration and temperature there exists a critical stress gradient below which no hydrogen migration occurs. There is also a minimum stress intensity factor below which cracks do not propagate; the threshold stress intensity factor ($K_{IH}$). This states that the $K_{IH}$ provides a sufficient critical stress to,

1. start migration of hydrogen into the migration and reorientation zone
2. reorient the hydrides in the reorientation zone
3. fracture the reoriented hydrides after they grow to a critical size and
4. rupture the matrix ahead of the crack tip.

The threshold stress intensity factor is given as the maximum stress intensity factor required for any of these above four steps for DHC. In the reorientation zone near the
crack tip, the stress gradient is higher than the stress required for reorientation of hydrides. The stress required to rupture the process zone next to the crack tip depends on the size of the hydride in the reorientation zone. Thus there exists a critical size of hydride for a given process zone size, so the critical hydride size goes up with an increase in the process zone size. There exists a $K_{IH}$ which corresponds to the stress intensity factor for migration of hydrogen. With an increase in temperature the matrix strength comes down and hence the process zone size increases. This leads to an increase in the critical hydride size (given by the striation spacing) and a higher $K_{IH}$, as seen in the results obtained. At higher temperatures the amount of hydrogen available in solution goes up increasing the diffusivity of the hydrogen so the velocity of DHC is likely to go up as well.

The increase in DHCV with increase in temperature in CANDU pressure tubes is related not only to the hydrogen diffusion but also to the yield strength of the material\(^{59,70}\). CANDU Zr-2.5Nb tubes with higher yield strength and a semi-continuous $\beta$-Zr had a higher DHCV compared to the Russian RBMK Zr-2.5Nb tube with a fully discontinuous $\beta$-Zr and lower yield strength. To compare the strengths of the MPTs to the actual CANDU pressure tube materials, Vickers hardness measurements were taken on the radial-circumferential plane of the MPTs. The Vickers hardness results at an applied load of 10 kg obtained on the Zr-2.5Nb MPTs in the present work are shown in Table 8. Here the 64B MPTs are compared to the 63B tubes which are similar to the CANDU pressure
tubes microstructures. The Vickers hardness on the as manufactured pressure tubes was about 230 HV

Table 8 Vickers hardness data for MPTs

<table>
<thead>
<tr>
<th>MPT</th>
<th>Average Vickers hardness, HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>63B</td>
<td>240</td>
</tr>
<tr>
<td>64B</td>
<td>248</td>
</tr>
</tbody>
</table>

In full size pressure tubes the DHCV in the axial direction is higher than in the radial direction due to the higher diffusivity in the axial direction. Figure 56 shows the data obtained for the CANDU full size Zr-2.5Nb tubes in the axial and the radial directions; also marked are the data obtained in MPTs from the present work.
Figure 56 DHCV of the CANDU full size pressure tubes with the orientation compared to the DHC data from MPTs\textsuperscript{64}.

The in-reactor conditions, such as coolant water induced corrosion reactions and wear will have an effect on DHC for in-reactor pressure tubes. For example the continuous exposure of new Zr as the DHC crack grows, provides sites for the oxidation reaction to occur and hence may increase the flux of hydrogen locally to the crack tip and DHC site. Thus the fact that in the current work the tests were carried out in air should be considered in comparing to in-reactor data.
The memory effect of hydrides upon thermal cycling will reduce the threshold stress for hydride reorientation; this might affect the threshold stress intensity measured when carrying out multiple measurements of $K_{ih}$ on a single sample. However, it is likely that the difference between measurements from a notch compared to sharp crack is likely to be larger. Finally, it should also be noted that all the samples went through two cycles of diffusion annealing for hydrogen diffusion before the DHC test. The thermal cycles may influence the hydride thickness and also the decomposition of the $\beta$-phase which in turn will affect the DHC properties.

The Microstructure and the grain size of most CANDU pressure tubes are different to the MPT used in the current work; 63B MPT as shown in Table 4 and 5 in Chapter 3 is closer to what is seen in typical CANDU full size pressure tubes. DHC crack initiation is expected to be difficult, with higher $K_{ih}$ values, due to the flattened and elongated $\alpha$-grains. 64B MPT has fine equiaxed $\alpha$-grains with grain boundaries oriented in the radial direction making it susceptible to easy stress reorientation compared to 63B MPTs. A sample test performed on a 63B MPT specimen is shown in Appendix D. As expected the crack initiation occurred at a higher $K_i$ of ~12-15MPa.m$^{1/2}$ at a temperature of 250°C.

The model developed by Dutton et al. for DHC velocity as in Equation 2 has undergone several modifications and improvements over time; however it is still a useful first estimate. The TSS values ($C_h$ in the Equation 2) for different test temperature is calculated from the equation below,

$$TSS = C_h = A \exp\left(-\frac{Q}{RT}\right) = 1.2 \times 10^5 \exp\left(-\frac{Q}{RT}\right)$$  \hspace{1cm} \textbf{Equation 12}
Q=8550 cal/mole; R=1.987 cal/mol/K; and T is in Kelvin.

The diffusion co-efficient for hydrogen is given by,

\[ D_H = 7 \times 10^{-3} \exp\left(-\frac{Q}{RT}\right) \text{ cm}^2/\text{sec} \]  
\textbf{Equation 13}

Q = 10650 cal/mol; R=1.987 cal/mol/K; and T is in Kelvin.

From Equation 12 and 13, DHCV can be calculated using Equation 2, \( (V_{DHC} = D_H C_{H_F}) \); F is a function of hydride morphology and diffusion geometry. Here the simplified model is used to fit the experimental data obtained from the MPTs is shown in Figure 57. The DHCV predicted by the model (assuming a single optimized value for the hydride morphology factor, F) shows increasing trend with test temperature.

\[ \text{Figure 57 DHC model prediction compared to the experimental data at different test temperatures.} \]
**Striation spacing:**

Based on Equation 11, it can be seen that the driving force for the hydrogen migration is the stress gradient. DHC crack growth step includes,

1. Hydrogen migration up the tensile stress gradient in the reorientation zone

2. Precipitation of a brittle hydride in the reorientation zone when the local TSS is exceeded

3. Hydride growth in the reorientation zone until it reaches the critical size to fracture and

4. Fracture of the hydride in the reorientation zone leading to the rupture of the process zone resulting in crack growth.

The time taken by the hydride to grow to its critical size causes a delay; its subsequent fracture results in the striations observed by optical microscopy indicating the fracture has occurred by DHC. Hence the striations are a measure of critical hydride length in DHC fracture studies. The striations, when viewed under optical microscope, show two different regions: the bright grey ductile matrix and the dark hydride phase. This can also be seen clearly in Figure 47, an SEM micrograph of the DHC fracture surface. The average striation spacing data obtained at different temperatures are shown in Table 9. From the data obtained it can be seen that the first striation spacing shows an increasing trend with increasing temperature. Shek et al. explained that the decrease in striation spacing with decreasing temperature could be due to the increase in yield strength of the
material. The yield strength increases ~1 MPa for each 1K decrease in temperature for Zr-2.5Nb$^{85}$ in this temperature regime. Also the brittleness of the hydride is found to increase with decreasing temperature. Both factors contribute to why the critical hydride length and $K_{IH}$ come down with decrease in temperature. Since the fracture of the hydride at the crack tip depends on the stress level and the brittleness of the hydride, both of which comes down with temperature, this results in shorter critical hydride lengths.

The critical hydride length reduces during the DHC growth process itself as the applied $K_I$ increases with crack growth, so the striation spacing is reduced to as low as 5-6 microns in 64B5 at 250°C.

**Table 9 Striation spacing data**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test temperature, °C</th>
<th>Striation spacing, µm</th>
<th>$K_I$, MPa.m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>First</td>
<td>End</td>
</tr>
<tr>
<td>64B4</td>
<td>180</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>64B2</td>
<td>230</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>64B5, 64B9</td>
<td>250</td>
<td>24, 26</td>
<td>6</td>
</tr>
</tbody>
</table>
**Tunneling of the DHC crack front:**

The crack front observed under the microscope shows a curved region along the crack direction as seen in the fracture surfaces shown in the optical micrographs and SEM pictures. The crack was observed to grow faster in the middle of the crack front compared to the region near both the ends. This is due to tunneling of the crack front, as has also been observed in DHC of Zr-2.5Nb full size pressure tubes\textsuperscript{77}. This phenomenon can be seen in the Figure 58, where the crack at the side surface shows only a growth of \(-20\) microns, when the actual DHC crack extended up to 1 mm Figure 45.

![Figure 58](image)

**Figure 58 DHC crack extension seen on the side surface of the sample 64B5 at temperature of 250°C before opening up the sample.**
This tunneling is likely explained by the plane stress effect near the surface of the tube, where in the normal stresses near the edge of the crack become zero. When the applied \( K_I \) is low, the hydride cluster at the crack tip cannot be fractured and so no crack growth is observed. When the \( K_I \) goes up and reaches the \( K_{II} \) the first hydride cluster at the crack tip fractures and the crack extends. At the same time due to the plane stress effect near the surface, the hydrostatic stress at the surface is reduced; less hydrogen has diffused here, so no hydrides will have precipitated to fracture, leaving a ductile matrix ligament that has not fractured. When the applied \( K_I \) is high enough, the DHC crack growth extends at the middle, increasing the tunnel length but there can still be a matrix ligament left on each side of the surface that is not fractured. The plastic strain on the matrix increases with the ligament length and higher \( K_I \) and eventually the matrix ligament will start to fracture.
Chapter 6
Conclusions

The present work studied the initiation and growth of delayed hydride cracking (DHC) in arc-shaped half ring samples manufactured from micro pressure tubes (MPTs); the following conclusions can be drawn,

- Electrolytic hydriding was successfully employed to achieve the target hydrogen concentration in the MPT samples.

- A thermomechanical loading rig with Potential Drop (PD) crack growth monitoring was installed and successfully applied to DHC testing of MPT samples.

- DHC tests were performed using notched (broached) samples manufactured from MPTs. The threshold stress intensity factor ($K_{th}$) and DHC velocities measured from these samples were comparable to the data reported in the literature ($2-10 \times 10^{-8}$ m/s) that had been obtained from full size CANDU pressure tubes tested in the temperature range of 180-250°C.

- The application of the use of MPTs in DHC tests has been successfully demonstrated.
Chapter 7

Future Work

The DHC results in MPTs presented in the current work are preliminary, and there is a wide range of further developments possible.

- A feedback loop between the load cell, potential drop measurement and stepper motor should be developed, controlled within LabView. Given the calibration curve for potential drop versus crack growth that has now been obtained for this geometry of sample, it would be possible to carry out the DHC velocity measurements under a constant $K_I$ mode. This should allow for more controlled crack growth than is possible under a constant displacement mode.

- MPTs with other textures and grain sizes representing the range of microstructures that are observed in full size CANDU pressure tubes should be tested and compared to data previously reported from full size tubes. Following on from this further validation step, it will be possible to study new microstructures and textures, not previously studied, as well as to study new alloy compositions.

- Improvements can be made in the DHC rig to allow the simultaneous running of multiple samples. The furnace has been constructed with four loading sets (load cells and stepper motors), and thus at least four samples could be tested at the same time, under the same thermal profile. A single potential drop system can be used to
monitor all 4 samples relatively straightforwardly by simple switching between separate circuits on each sample. Due to the very slow growth of cracks by the DHC process, even switching every few seconds would give sufficient time resolution to allow control of the test. The furnace is large enough that more than one sample could be tested in each loading set, although tests could only be carried out under constant load or constant overall displacement in this case. Even testing 4 samples at once would greatly increase the number of samples which can be tested and hence the significance of the statistics obtained; this has been limited so far by the extensive time involved in carrying out each test.

- The bulk hydrogen concentration in the samples could be tested directly by vacuum gaseous extraction, or indirectly by differential scanning calorimetry (DSC), to confirm the target hydrogen concentration.
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Appendix A
Hydriding layer thickness, homogenization time and temperature measurements

The minimum hydride layer thickness required can be calculated from the expected target hydrogen concentration by the equation below. The equation is based on a flat sheet, but can be expected to be a reasonable guide for a cylindrical sample.

\[ T_{\text{hydride}} (\mu m) = 7.322 \times 10^{-2} \times [H] \times T \]

\(T\)-thickness of the specimen in mm,

\([H]\)-required hydrogen concentration (ppm)

<table>
<thead>
<tr>
<th>Plate Thickness (mm)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.72</td>
<td>1.45</td>
<td>2.17</td>
<td>2.89</td>
<td>3.62</td>
<td>4.34</td>
<td>5.06</td>
<td>5.79</td>
<td>6.51</td>
<td>7.23</td>
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<tr>
<td>2</td>
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<td>2.89</td>
<td>4.34</td>
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<td>7.23</td>
<td>8.68</td>
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<td>11.57</td>
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<td>5.79</td>
<td>8.68</td>
<td>11.57</td>
<td>14.46</td>
<td>17.36</td>
<td>20.25</td>
<td>23.14</td>
<td>26.04</td>
<td>28.93</td>
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<tr>
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<td>3.62</td>
<td>7.23</td>
<td>10.85</td>
<td>14.46</td>
<td>18.08</td>
<td>21.70</td>
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<td>28.93</td>
<td>32.54</td>
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<td>28.93</td>
<td>36.16</td>
<td>43.39</td>
<td>50.63</td>
<td>57.86</td>
<td>65.09</td>
<td>72.32</td>
</tr>
</tbody>
</table>

Formula: \( T_{\text{hydride}} (\mu m) = 7.232 \times 10^2 \times [H]_{Zr} \times T_{Zr}(mm) \)

\([H]_{Zr}\) = hydrogen level required

\(T_{Zr}\) = thickness of plate.

Figure 59 Calculated minimum hydride thickness results for specific target hydrogen concentration as shown in IAEA report on Zr-2.5Nb pressure tubes.\(^8\)
For 100 ppm of hydrogen and with a wall thickness of 2.49mm in 64B MPTs,
\[ T_{\text{hydride}} = 18 \, \mu m \]

When a Zr alloy with a thick enough hydride layer has been homogenized, the bulk hydrogen concentration in the sample is equal to the TSS at the diffusion annealing temperature,

\[ \text{TSS} = C = A \exp \left( -\frac{Q}{RT} \right) = 1.2 \times 10^5 \exp \left( -\frac{Q}{RT} \right) \]

\[ Q = 8550 \, \text{cal/mole}; \, R = 1.987 \, \text{cal/mol/K} \]

The homogenization temperature required to attain the target hydrogen can be calculated from the equation,

\[ T = \frac{-Q}{RT} \ln \frac{C}{A} \]

where \( T \) is in K, \( C \) is the bulk hydrogen concentration

For 100 ppm target hydrogen the homogenization temperature, \( T = 334^\circ C \).

The minimum homogenization time (t) required for the target hydrogen concentration at that particular temperature can be obtained from the equation given below, which is based on a random walk diffusion (Fick’s 1st law). The actual duration of homogenization used was 24 h to ensure uniform and complete homogenization,

\[ t = 1.5 \left( \frac{L^2}{D} \right) \]

where \( 2L \) = thickness of the sample; \( D \) = diffusivity cm\(^2\)/sec.

Diffusivity is given by,

\[ D = 7 \times 10^{-3} \exp \left( -\frac{Q}{RT} \right) \]

\[ Q = 10650 \, \text{cal/mol}; \, R = 1.987 \, \text{cal/mol/K} \]

At a homogenization temperature of 334\(^\circ\)C, \( D = 1.01 \times 10^{-6} \, \text{cm}^2/\text{sec} \)

\[ t = 1.5 \left( \frac{(2.49/2)^2}{D} \right) \]

\[ t = 6.4 \, \text{hours} \]

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Figure 60 Hydrogen terminal solid solubility (TSS) as a function of temperature. Combined data for Zr, Zircaloy-2 and Zircaloy-4\textsuperscript{16}. 

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Appendix B

DHCV calculation

DHC crack growth rate (DHCV) is given by,
\[ \text{DHCV} = \frac{a_{avg}}{t_{DHC}} \]

\(a_{avg}\)-crack length measured by Image analysis, and
\(t_{DHC}\)-time under load for DHC.

For example, at \(T_{\text{test}}\) 250°C (64B5): \(a_{avg} = 0.763\) mm, and time under load, \(t\) for 64B5 is 200 minutes,

\[ \Rightarrow \text{DHCV} = \frac{0.763 \times 10^{-3}}{200 \times 60} \text{ m/s} \]

\[ \text{DHCV} = 6.36 \times 10^{-8} \text{ m/s} \]
Appendix C

64B $K_{IH}$, DHCV and Metallography Results

$K_{IH}$ results:

![Graph showing PD at a $K_I$ of 6.5 MPa.m$^{1/2}$ in sample 64B8 $T_{test}$=180°C.]

Figure 61 PD at a $K_I$ of 6.5 MPa.m$^{1/2}$ in sample 64B8 $T_{test}$=180°C.
Figure 62 PD at a $K_1$ of 7 MPa.m$^{1/2}$ in sample 64B7 $T_{test}$-230°C.

Figure 63 PD at a $K_1$ of 10.5 MPa.m$^{1/2}$ in sample 64B9 $T_{test}$-250°C.
DHCV results:

Figure 64 64B4 at T_{test} 180^\circ C with initial and final K_{1} of 8 and 10 MPa.m^{1/2} respectively.
Figure 65 64B4 at $T_{\text{test}}=180^\circ$C with initial and final $K_I$ of 12 and 16 MPa.m$^{1/2}$ respectively.

Figure 66 64B2 at $T_{\text{test}}=230^\circ$C with initial and final $K_I$ of 8 and 13 MPa.m$^{1/2}$ respectively in constant load mode.
Figure 67 64B3 at \( T_{\text{test}} \) 230°C with initial and final \( K_1 \) of 10 and 13 MPa.m\(^{1/2} \) respectively in constant load mode.
Figure 68 64B9 at T_{test}-250^\circ C with initial and final K_t of 12 and 19 MPa.m^{1/2} respectively.
Results from metallographic analysis:

Figure 69  64B3 sample at $T_{\text{test}}$~230°C showing different DHC crack zones at two different test temperatures.
Figure 70  64B7 sample at $T_{\text{test}}$-230°C showing the DHC fracture surface.
Figure 71 64B8 sample at $T_{\text{test}}$-180$^\circ$C showing the DHC fracture surface.
Figure 72 64B9 sample at $T_{\text{test}}$-250°C showing the DHC fracture surface.
Appendix D

DHC Test on 63B sample

A sample test was run with a specimen cut from 63B MPT with a different microstructure but the same texture parameters as 64B. The test procedure for the 63B sample was the same as in the experimental section for 64B MPTs. The test temperature was 250°C. No crack growth was observed even after reaching a $K_t$ of 12 MPa.m$^{1/2}$; which is above the range of 6-11.5 MPa.m$^{1/2}$ found in the literature for CANDU pressure tubes. Then the load was decreased to a lower $K_t$ of 10 to allow the hydride to grow to a critical size and was monitored over a period of 48 hours; when no crack growth was observed, the load was then increased from 10 to 12 and then to 15 $K_t$, there was a PD jump indicating the DHC crack as soon as the load reached 15 $K_t$. This shows that 63B with flattened and elongated grains show higher $K_{IH}$ of ~12-15 MPa.m$^{1/2}$ compared to 10 for 64B MPTs.

![Figure 73 PD change at a load corresponding to a $K_t$ of 15 MPa.m$^{1/2}$](image)

Figure 73 PD change at a load corresponding to a $K_t$ of 15 MPa.m$^{1/2}$. 